# ISNOG 2016

## 20th INTERNATIONAL SYMPOSIUM ON NON-OXIDE AND NEW OPTICAL GLASSES

21-26 of August, 2016 / Nizhny Novgorod, Russia

# FINAL PROGRAM AND DIGEST

**Organized by:** G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences

**Coorganized by:** Fiber Optics Research Center of Russian Academy of Sciences

Lobachevsky State University of Nizhny Novgorod

Technopark-Mordovia

www isnog.org

| | Sunday 21st | Monday, August, 22nd | | Tuesday, August, 23rd | | Wednesday, August, 24th | Thursday, August, 25th |
|---|---|---|---|---|---|---|---|
| 8:00 – 9:00 | | Registration | | | | | |
| 9:00-9:10 | | **Opening Ceremony**<br>Lux Hall | | **Plenary Talk**<br>Business Hall | | poster Session | **Session V-2**<br>Optical Linear and Non-Linear Properties of Glasses and Fibers.<br>Business Hall |
| 9:10-9:20 | | | | | | | |
| 9:20-9:30 | | | | | | | |
| 9:30-9:40 | | | | | | | |
| 9:40-9:50 | | | | | | | |
| 9:50-10:00 | | **Plenary Talk** | | **Session I-2**<br>High-Purity Glasses, Special Glasses and Low-Loss Fibers<br>Business Hall | | | |
| 10:00 – 10:10 | | | | | | | |
| 10:10 – 10:20 | | | | | | | |
| 10:20 – 10:30 | | | | | | | |
| 10:30 – 10:40 | | | | | | | |
| 10:40 – 10:50 | | Coffee break | | | | Excursion<br>Tour to ancient Russian town Gorodets | |
| 10:50 – 11:10 | | | | Coffee break<br>and poster Session | | | Coffee break |
| 11:10 - 11:20 | | **Plenary Talk** | | | | | |
| 11:20 – 11:30 | | | | **Session I-2**<br>Business Hall | | | **Session VII**<br>Glass-Ceramics and Optical Ceramics<br>Business Hall |
| 11:30 – 11:40 | | | | | | | |
| 11:40 – 11:50 | | | | | | | |
| 11:50 – 12:00 | | | | | | | |
| 12:00 – 12:10 | | inv | | | | | |
| 12:10 – 12:20 | | | | | | | |
| 12:20 – 12:30 | | | | | | | |
| 12:30 – 12:40 | | | | | | | |
| 12:40 – 12:50 | | | | | | | |
| 12:50 – 13:00 | | | | | | | |
| 13:00 – 14:00 | | Lunch | | Lunch | | | Lunch |
| 14-00-14:10 | | Session I-1: Synthesis, Melting and<br>Processing of Glasses and Glass - Ceramics.<br>Business Hall | **Session III**<br>Modeling of Glass Structure; Glass, Surface and Interfaces; Structure and Properties.<br>Hall Standard 1 | **Session V-1**<br>Luminescent Glasses, Optical Waveguides and Glass-Ceramics for active applications.<br>Business Hall | **Session VI**<br>Optical Thin Films<br>**Session IV**<br>Phase Change Materials and Photo-Induced Effects<br>Hall Standard 1 | | **Closing Ceremony**<br>Business hall |
| 14:10 – 14:20 | | | | | | | |
| 14:20 - 14:30 | | | | | | | |
| 14:30 - 14:40 | | | | | | | |
| 14:40 - 14:50 | | | | | | | |
| 14:50 - 15:00 | | | | | | | |
| 15:00 – 15:10 | | | | | | | |
| 15:10 – 15:20 | | | | | | | |
| 15:20 – 15:30 | | | | | | | |
| 15:30 – 15:40 | | | | | | | |
| 15:40 – 15:50 | | | | | | | |
| 15:50 – 16:00 | | | | | | | |
| 16:00 – 16:10 | | Coffee break | | Coffee break<br>and poster Session | | | |
| 16:10 – 16:20 | | | | | | | |
| 16:20 – 16:30 | | | | | | | |
| 16:30 - 16:40 | | **Session I-1**<br>Business Hall | **Session VIII**<br>Glasses for Medicine, Biotechnology, Sensors, Energy applications<br>Hall Standard 1 | **Session V-1** | **Session II**<br>Glass Transition, Relaxation in Glasses and Glass-forming Liquids, Mechanical Properties. | | |
| 16:40 - 16:50 | | | | | | | |
| 16:50 - 17:00 | | | | | | | |
| 17:00 – 17:10 | | | | | | | |
| 17:10 – 17:20 | | | | | | | |
| 17:20 – 17:30 | | | | | | | |
| 17:30 – 17:40 | | | | | | | |
| 17:40 - 17:50 | | | | | | | |
| 17:50 - 18:00 | | | | | | | |
| 18:00 – 18:10 | Registration and Welcome party | | | | | | |
| 18:10 – 18:20 | | | | | | | |
| 18:30 – 18:40 | | | | | | | |
| 19:00 – 2100 | | | | | | Conference Dinner | |

# ISNOG 2016

NON-OXIDE GLASSES
NEW OPTICAL GLASSES

## 20th INTERNATIONAL SYMPOSIUM ON NON-OXIDE AND NEW OPTICAL GLASSES

21-26 of August, 2016 / Nizhny Novgorod, Russia

## Sponsors

Russian Academy of Sciences

RFBR
RUSSIAN FOUNDATION FOR BASIC RESEARCH

FORC - Photonics

Technopark-Mordovia

art photonics

ПНППК

Perm Scientific-Industrial Instrument Making Company (PNPPK)

# Welcome to ISNOG 2016, Nizhny Novgorod!

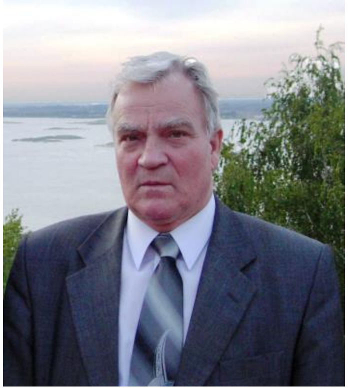
We would like to welcome all participants and guests from different countries in the world to ISNOG 2016, which will be held on August 21-26 in Nizhny Novgorod, Russia. We have great honor to organize the 20th International Symposium on Non-Oxide and New Optical Glasses (XX ISNOG), the first of which was held in Cambridge (UK) 1981, followed by Troy (the USA), Rennes (France), Monterey (the USA), Shizuoka (Japan), Monash (Australia), Clausthal-Zellerfeld (Germany), Perros-Guirec (France), Hangzhou (China), Corning (the USA), Sheffield (UK), Florianopolis (Brazil), Pardubice (Czech), Florida (the USA), Bangalore (India), Montpellier (France), Ningbo (China), Saint-Malo (France), Jeju (Republic of Korea).

Like for all previous symposia, the purpose of ISNOG-2016 is to review the recent progress, to exchange technical information and to promote R&D in non-oxide and new optical glasses. This symposium will provide a unique opportunity for researchers and scientists worldwide to gather together and discuss advancements and current trends in the related fields.

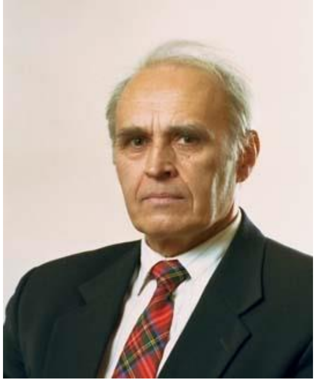
There are 110 papers accepted for presentation at ISNOG 2016, contributed by over 170 authors from 13 countries, including United Kingdom, Germany, France, Canada, Japan, Russia, Czech Republic, India, Republic of Korea, Hungary, Brazil, Slovak Republic, China, Algeria and Sweden, Belarus.

Among invited speakers we have 19 well known international scientists and experts.

Again, we extend our warmest greetings to you and hope that the jubilee ISNOG-2016 will take place in traditionally creative and friendly atmosphere.



M.F. Churbanov
Chairman
IChHPS RAS, Russia



E.M. Dianov
Co-Chairman
FORC RAS, Russia

E.V. Chuprunov
Co-Chairman
Nizhny Novgorod State University, Russia

# INTERNATIONAL ADVISORY BOARD

- **J.L. Adam (France)**
- **Aggarwal (USA)**
- **B. Aitken (USA)**
- **M. Churbanov (Chair) (Russia)**
- **S. Dai (China)**
- **H. Eckert (Germany)**
- **G. Frischat (Germany)**
- **M. Frumar (Czech Republic)**
- **J. Heo (Korea)**
- **A. Jha (UK)**
- **S. Kasap (Canada)**
- **Y. Messaddeq (Canada)**
- **M. Poulain (France)**
- **Pradel (France)**
- **K. Richardson (USA)**
- **J. Sanghera (USA)**
- **K.S. Sangunni (India)**
- **Seddon (UK)**
- **S. Tanabe (Japan)**
- **K. Tanaka (Japan)**
- **T. Wagner (Czech Republic)**
- **L. Zhang (China)**
- **X.H Zhang (France)**

# Local Organizing Committee

- **Demidov E.S.**
- **Denker B.I.**
- **Gorshkov O.N.**
- **Kozyuhin S.A.**
- **Moiseev A.N.**
- **Nishev K.N.**
- **Plotnichenko V.G.**
- **Shiryaev V.S.**
- **Sigaev V.N.**
- **Skripachev I.V.**
- **Tveryanovich Yu.S.**

## Plenary Talks

**Professor Seddon A.**, University of Nottingham, UK George Green Institute for Electromagnetics Research.

Mid-Infrared photonics: A hot topic!

**Professor Ribeiro S.**, São Paulo State University – UNESP

Down-shifting and Up-conversion to enhance the efficiency of solar cells

**Professor Dianov E.**, Fiber Optics Research Center of RAS

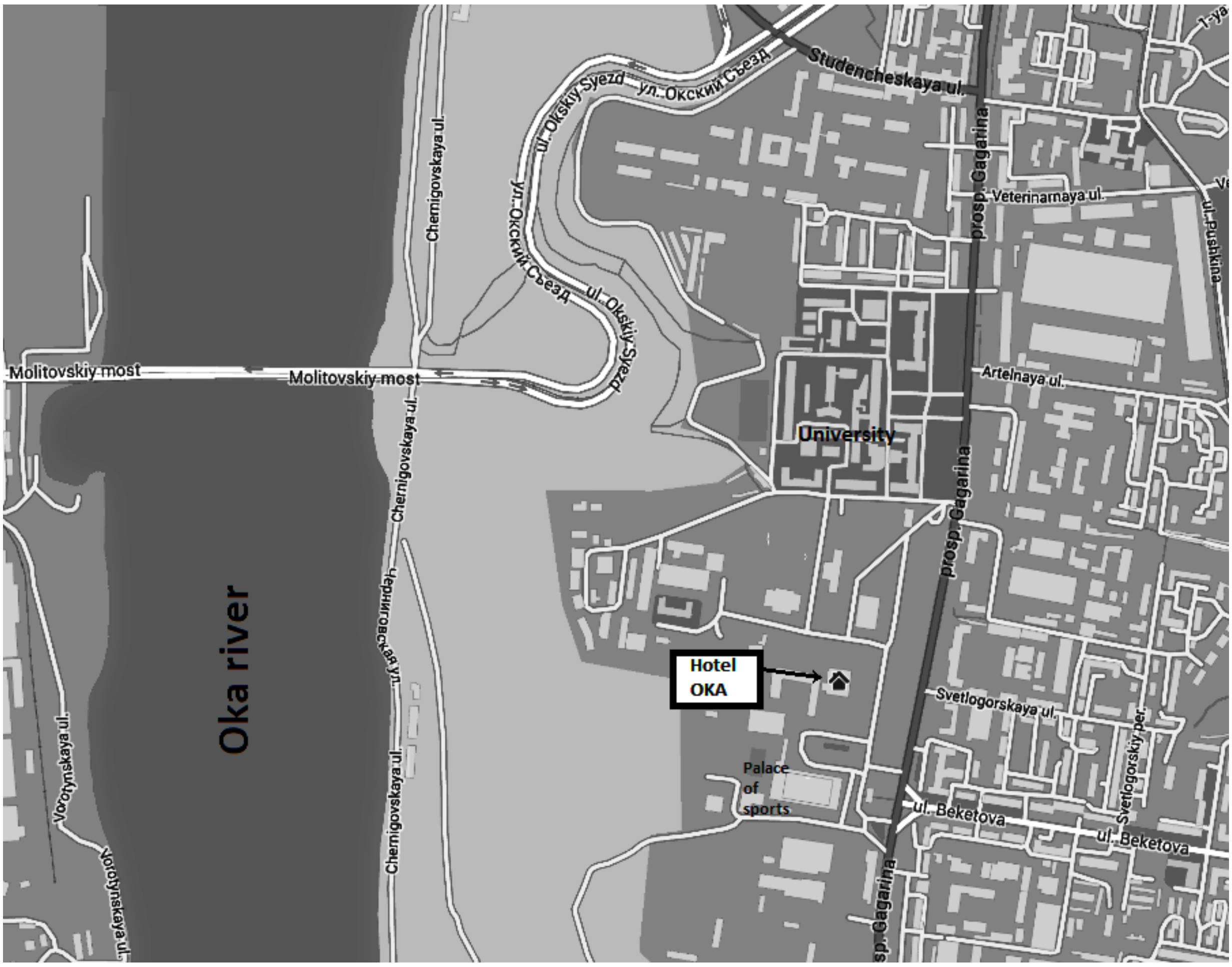
Bismuth-doped glass optical fibers: a new breakthrough in laser media

## Invited speakers

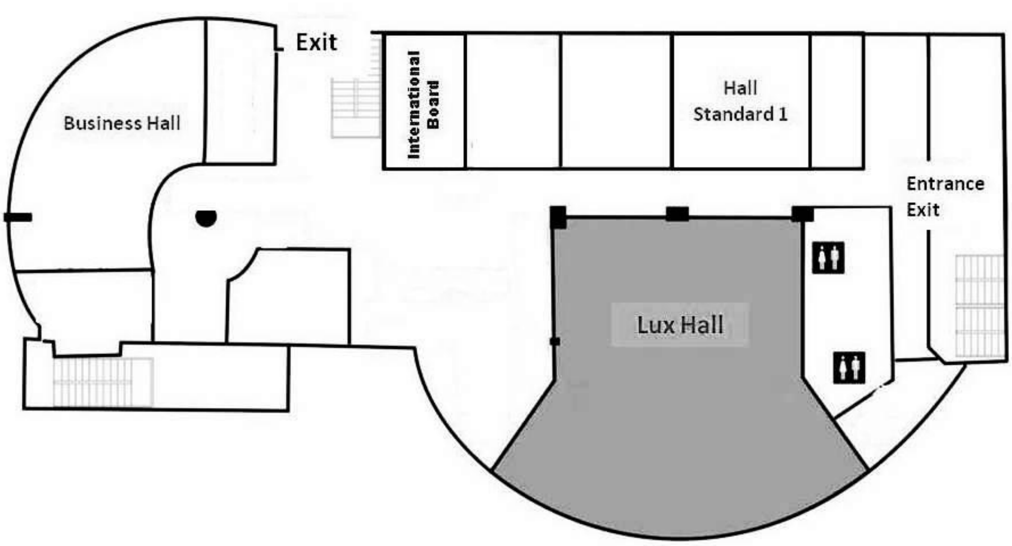
- **Nalin M.**
  Structural, thermal and optical properties of a new antimony-phosphate germanate glasses
- **Calvez L.**
  Novel ways to prepare chalcogenide glasses and non linear glass-ceramics
- **Dorofeev V.**
  High-purity tellurite glasses for fiber optics
- **Brekhovskikh M.**
- Modified fluoride ZBLAN glasses
- **Sigaev V.**
  Local modification of glass structure: from nanogratings to crystalline waveguides
- **Arbuzov V.**
  Russian neodymium phosphate glasses for the laser controlled fusion research: technology and limit properties
- **Dai S.**
  Fabrication and characterization of novel multi-material chalcogenide glass fibers and fiber tapers for Mid-infrared SC generation
- **Bufetov I**
  Hollow-core revolver optical fibers
- **Artyushenko V.**
  Mid InfraRed fiber optics – review of technologies and key applications
- **Shiryaev V.**
  Recent advances and trends in development of chalcogenide glasses for passive and active fiber optics
- **Skripachev I.**
  Towards chalcogenide glass fibers with intrinsic optical losses
- **Heo J.**
  Glasses containing chalcogenide quantum dots
- **Ledemi Y.**
  Recent progress in the development of ittrbium-doped oxyfluoride glass-ceramics for laser cooling application

- **Wágner T.**
  Chalcogenide glass films for nanoscale memories
- **Kozyukhin S.**
  Investigation of crystallization mechanism and kinetics for amorphous thin films of phase change memory materials
- **Messaddeq Y.**
  Microstructure formation in chalcogenide thin films assisted by laser

## Symposium Location



## Congress center scheme



<table>
<tr><th colspan="4">Sunday, August 21st</th></tr>
<tr><td><b>18:00-21:00</b></td><td colspan="3"><b>Registration and Welcome party</b></td></tr>
<tr><td></td><td colspan="3"></td></tr>
<tr><th colspan="4">Monday, August 22nd</th></tr>
<tr><td><b>8:00-9:00</b></td><td colspan="3"><b>Registration</b></td></tr>
<tr><td><b>9:00-9:50</b></td><td colspan="3"><b>Opening Ceremony</b><br><b>Lux Hall</b></td></tr>
<tr><td><b>9:50-10:40</b></td><td colspan="3"><b>Plenary Talk</b><br><b>Mid-Infrared Photonics: A Hot Topic!</b><br><b>Professor Seddon A.,</b> George Green Institute for Electromagnetics Research, University of Nottingham, UK</td></tr>
<tr><td><b>10:40-11:10</b></td><td colspan="3"><b>Coffee break</b></td></tr>
<tr><td><b>11:10-12:00</b></td><td colspan="3"><b>Plenary Talk</b><br><b>Down-shifting and Up-conversion to enhance the efficiency of solar cells</b><br><b>Professor Ribeiro S.,</b> São Paulo State University – UNESP, Brazil</td></tr>
<tr><td><b>12:00-12:30</b></td><td colspan="3"><b>Nalin M.</b><br><b>Structural, thermal and optical properties of a new antimony-phosphate germanate glasses</b><br><b>inv 1</b></td></tr>
<tr><td><b>12:30-13:00</b></td><td colspan="3"><b>Calvez L.</b><br><b>Novel ways to prepare chalcogenide glasses and non linear glass-ceramics</b><br><b>Inv 2</b></td></tr>
<tr><td><b>13:00-14:00</b></td><td colspan="3"><b>Lunch</b></td></tr>
<tr><td><b>Session</b></td><td><b>Session I-1:</b><br><b>Synthesis, Melting and Processing of Glasses and Glass - Ceramics.</b><br><b>Business Hall</b><br><b>Chairman: Tver’yanovich Yu.</b></td><td colspan="2"><b>Session III:</b><br><b>Modeling of Glass Structure; Glass, Surface and Interfaces; Structure and Properties.</b><br><b>Hall Standard 1</b><br><b>Chairman : Wágner T.</b></td></tr>
<tr><td><b>14:00-14:30</b></td><td><b>Dorofeev V.</b><br>High-Purity Tellurite Glasses for Fiber Optics<br><b>I-1-inv 1</b></td><td><b>14:00-14:30</b></td><td><b>Sigaev V.</b><br>Local Modification of Glass Structure: from Nanogratings to Crystalline Waveguides<br><b>III-inv 1</b></td></tr>
</table>

| | | | |
|---|---|---|---|
| **14:30-15:00** | **Brekhovskikh M.**<br>Modified Fluoride ZBLAN Glasses<br>**I-1-inv 2** | 14:30-14:50 | **Furet E.**<br>Structure and Properties of Telluride Glasses by means of Molecular Dynamics and Solid-State NMR<br>**III O-1** |
| **15:00-15:20** | **Poirier G.**<br>Optical Properties of Tantalum Germanate Glasses, Glass-ceramics and Planar Waveguides<br>**I-1 O-1** | 14:50-15:10 | **Kutyin A.**<br>Quasiparticle formulation of thermo-dynamic functions of glasses and melts<br>**III O-2** |
| | | 15:10-15:30 | **Laptash N.**<br>Bonding and Structure of Oxofluoroniobate-based Glasses: $ZnNbOF_5$–$BaF_2$ and $ZnNbOF_5$–$InF_3$–$BaF_2$ Systems<br>**III O-3** |
| **15:20-15:40** | **Sibirkin A.**<br>Chemical Processes in the Batch and in the Melt to Produce Binary and Multicomponent Tellurite-Molybdate Glasses<br>**I-1 O-2** | 15:30-15:50 | **Sen S.**<br>Structure-Property Relations in Silver Ion Conducting Homogeneous Ag-Ga-Ge-Selenide Glasses<br>**III O-4** |
| **15:40-16:00** | **Mishinov S.**<br>Adhesion mechanism of contamination of optical glassy arsenic sulfides by $SiO_2$ particles<br>**I-1 O-3** | | |
| **16:00-16:30** | **Coffee break** | | |
| **Session** | **Session I-1:**<br>**Synthesis, Melting and Processing of Glasses and Glass - Ceramics**<br>**Business Hall**<br>**Chairman: Messaddeq Y.** | **Session VIII:**<br>**Glasses for Medicine, Biotechnology, Sensors, Energy applications**<br>**Hall Standard 1**<br>**Chairman : Bufetov I.** | |
| **16:30-16-50** | **Galleani G.**<br>Fluorophosphate glass fiber for transmission in the uv<br>**I-1 O-4** | **16:30-17:00** | **Arbuzov V.**<br>Russian Neodymium Phosphate Glasses for the Laser Controlled Fusion Research: Technology and Limit Properties<br>**VIII-inv 1** |
| **16:50-17:10** | **Wang X.**<br>Research on Far-IR Suspended-core Fiber with Te-based Chalcogenide Glass<br>**I-1 O-5** | **17:00-17:20** | **Parnell H.**<br>Chalcogenide glass fibre-optics for the *in-vivo* mid-infrared optical biopsy<br>**VIII O-1** |

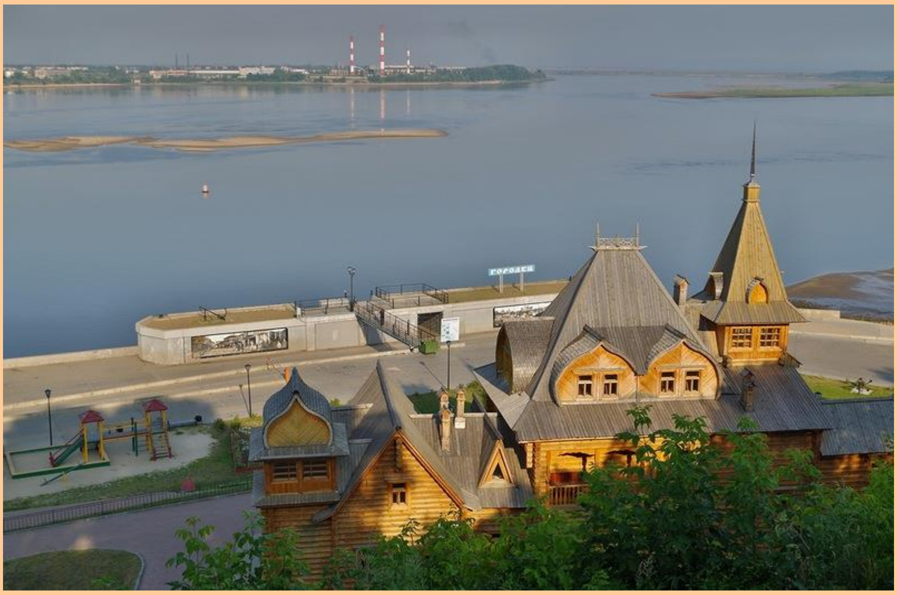
| | | | |
|---|---|---|---|
| **17:10-17:30** | **Velmuzhov A.**<br>Glasses of Ge – S – I and Ge – Se – I Systems for Infrared Fiber Optics<br>**I-1 O-6** | **17:20-17:40** | **Jayasuriya D.**<br>Fabrication of high and low numerical aperture optical fibre for sensing, mapping and imaging<br>**VIII O-2** |
| **17:30-17:50** | **Yin Q.W.**<br>The influence of PbO on spectra and thermo-optical properties of Nd$^{3+}$-doped phosphate laser glass<br>**I-1 O-7** | **17:40-18:00** | **Tver'yanovich Yu.**<br>Nano-layered solid electrolyte prepared by laser ablation<br>**VIII O-3** |
| **17:50-18:10** | **Ruan J.**<br>Broadening of NIR Emission from Bismuth Doped Germanium Glass Melting in a Controlled Reducing Atmosphere<br>**I-1 O-8** | **18:00-18:20** | **Mikhaylov A.**<br>Bipolar resistive switching in capacitor-like structures based on ionic and covalent oxide dielectrics<br>**VIII O-4** |
| | | **18:20-18:40** | **Huang F.**<br>AlF$_3$-based glasses as promising material for mid-IR solid state lasers<br>**VIII O-5** |

## Tuesday, August 23rd

| | |
|---|---|
| **Session** | **Session I-2:**<br>**High-Purity Glasses, Special Glasses and Low-Loss Fibers**<br>**Business Hall**<br>**Chairmen : Seddon A., Ribeiro S.** |
| **9:00-9:50** | **Plenary Talk**<br>**Bismuth-doped glass optical fibers: a new breakthtough in laser media**<br>**Professor Dianov E.,** Fiber Optics Research Center of RAS, Russia |
| **9:50:10:20** | **Dai S.**<br>Fabrication and characterization of novel multi-material chalcogenide glass fibers and fiber tapers for Mid-infrared SC generation<br>**I-2-inv 1** |
| **10:20-10:50** | **Bufetov I.**<br>Hollow-Core Revolver Optical Fibers<br>**I-2-inv 2** |
| **10:50-11:20** | **Coffee break and poster Session** |
| **11:20-11:50** | **Artyushenko V.**<br>Mid InfraRed Fiber Optics – Review of Technologies and Key Applications<br>**I-2-inv 3** |

| | | | |
|---|---|---|---|
| **11:50-12:20** | **Shiryaev V.**<br>Recent advances and trends in development of chalcogenide glasses for passive and active fiber optics<br>**I-2-inv 4** | | |
| **12:20-12:40** | **Skripachev I.**<br>Towards Chalcogenide Glass Fibers with Intrinsic Optical Losses<br>**I-2-inv 5** | | |
| **12:40-13:00** | **Plotnichenko V.**<br>Specifics of spectral loss measurement in IR fibers<br>**I-2 O-1** | | |
| **13:00-14:00** | **Lunch** | | |
| **Session** | **Session V-1:**<br>**Luminescent Glasses, Optical Waveguides and Glass-Ceramics for active applications**<br>**Business Hall**<br>**Chairmen : Artyushenko V., Sigaev V.** | **Session VI:**<br>**Optical Thin Films**<br>**Session IV:**<br>**Phase Change Materials and Photo-Induced Effects**<br>**Hall Standard 1**<br>**Chairmen : Arbuzov V., Kozyukhin S.** | |
| **14:00-14:30** | **Heo J.**<br>Glasses containing chalcogenide quantum dots<br>**V-1-inv 1** | **14:00-14:30** | **Wágner T.**<br>Chalcogenide glass films FOR Nanoscale memories<br>**VI-inv 1** |
| **14:30-15:00** | **Ledemi Y.**<br>Recent progress in the development of ittrbium-doped oxyfluoride glass-ceramics for laser cooling application<br>**V-1-inv 2** | **14:30-15:00** | **Kozyukhin S.**<br>Investigation of crystallization mechanism and kinetics for amorphous thin films of phase change memory materials<br>**VI-inv 2** |
| **15:00-15:20** | **Santagneli S.**<br>Photoluminescence properties of Er3+ doped phosphate tungstate glass containing Ag-nanoparticles<br>**V-1 O-1** | **15:00-15:30** | **Messaddeq Y.**<br>Microstructure Formation In Chalcogenide Thin Films Assisted By Laser<br>**VI-inv 3** |
| **15:20-15:40** | **Karaksina E.**<br>Preparation and characterization of high purity $Pr^{3+}$-doped Ga(In)-Ge-As(Sb)-Se glasses<br>**V-1 O-2** | **15:30-15:50** | **Qasmi A.**<br>Photoinduced changes of optical and structural properties in As- based thin films glassy doped with copper<br>**VI O-1** |

| | | | |
|---|---|---|---|
| **15:40-16:00** | **Zhang J.**<br>Local Environment Dependence on the Luminescence of Rare Earth Doped Chalcohalide Glasses and Glass Ceramics<br>**V-1 O-3** | **15:50-16:10** | **Shen X.**<br>Physical Properties and Crystallization Behaviours in $Ge_xTe_{1-x}$ films<br>**VI O-2** |
| **16:00-16:30** | **Coffee break and poster Session** | | |
| | **Session V-1:**<br>**Luminescent Glasses, Optical Waveguides and Glass-Ceramics for active applications**<br>**Business Hall**<br>**Chairman : Romanova E.** | **Session II:**<br>**Glass Transition, Relaxation in Glasses and Glass-forming Liquids, Mechanical Properties**<br>**Hall Standard 1**<br>**Chairman : Wen Lei** | |
| **16:30-16:50** | **Tang Z.**<br>Studies of various praseodymium additives doped chalcogenide Se-based fibres<br>**V-1 O-4** | **16:30-16:50** | **Brandova D.**<br>Crystallization and relaxation behavior of Ge11Ga11Te78 infrared glass<br>**II-O-1** |
| **16:50-17:10** | **Zhang P.**<br>Fabrication and characterization of $Ge_{20}As_{20}Se_{15}Te_{45}$ chalcogenide glass for photonic crystal by nanoimprint lithography<br>**V-1 O-5** | **16:50-17:10** | **Fraenkl M.**<br>Study of ionic properties by electrochemical impedance spectroscopy<br>and radioactive tracer diffusion<br>**II-O-2** |
| **17:10-17:30** | **Bentouila O.**<br>Spectroscopic analysis of $Tm^{3+}/Yb^{+3}/Ho^{+3}$ tri-doped fluorophosphates glasses<br>**V-1 O-6** | **17:10-17:30** | **Koštál P.**<br>Viscous Behavior of Chalcogenide Materials<br>**II-O-3** |
| **17:30-17:50** | **Koltashev V.**<br>Spectral Properties of $Er^{3+}$-doped High-Purity Tellurite Glasses<br>**V-1 O-7** | **17:30-17:50** | **Maslennikova I.**<br>Nanocrystallization of RE – doped Tellurite Glasses<br>**II-O-4** |
| **17:50-18:10** | **Kharakhordin A.**<br>Visible and near-infrared luminescence of Pb-active centers in silica glass<br>**V-1 O-8** | **17:50-18:10** | **Pynenkov A.A.**<br>The effect of crystallization on the luminescent properties of bismuth-doped barium gallium germanate glasses<br>**II-O-5** |
| **18:10-18:30** | **Ermakov R.**<br>The Study of the State of Bismuth Ions in Bi-doped GeSx (1<x<2) and Ge-As- S Glasses<br>**V-1 O-9** | | |
| | | | |

| Wednesday, August 24th | |
|---|---|
| **9:00-10:40** | **Poster Session** |
| **10:40-17:30** | **Excursion**<br>**Tour to ancient Russian town Gorodets**<br> |
| **19:00-21:00** | **Conference Dinner: "Royal" restaurant of OKA Grand Hotel** |

| Thursday, August 25th | |
|---|---|
| **Session** | **Session V-2.**<br>**Optical Linear and Non-Linear Properties of Glasses and Fibers.**<br>**Business Hall**<br>**Chairmen : Shiryaev V., Dai S.** |
| **9:00-9:20** | **Chen F.**<br>Linear and nonlinear optical properties of chalcogenide glasses within Ge-Sn-Se system<br>**V-2 O-1** |

| | |
|---|---|
| **9:20-9:40** | **Guo H.T.**<br>Study on the magneto-optical properties of $Ga_2S_3$-$GeS_2$- based chalcohalide glasses<br>**V-2 O-2** |
| **9:40-10:00** | **Romanova E.**<br>Accurate Measurement of the Nonlinear Optical Constants of Chalcogenide Glasses<br>**V-2 O-3** |
| **10:00-10:20** | **Sukhanov M.**<br>Optical and Thermal Properties of Monoisotopic Glasses on the Basis of Arsenic Sulfide,<br>Germanium Sulfide and Arsenic Selenide<br>**V-2 O-4** |
| **10:20-10:50** | **Manzani D.**<br>A portable luminescent thermometer based on green up-conversion emission of $Er^{3+}/Yb^{3+}$ co-doped tellurite glass<br>**V-2 O-5** |
| **10:50-11:20** | **Coffee break** |
| **Session** | **Session VII.**<br>**Glass-Ceramics and Optical Ceramics**<br>**Business Hall**<br>**Chairman : Calvez L.** |
| **11:20-11:40** | **Dymshits O.**<br>Synthesis, Structure and Optical Properties of Transparent Glass-Ceramics with Nanocrystals of Rare-Earth Niobates<br>**VII O-1** |
| **11:40-12:00** | **Novikova A.**<br>Effect of LiF Sintering Aid on the Properties of $MgAl_2O_4$ Ceramics.<br>**VII O-2** |
| **12:00-12:20** | **Timofeeva N.**<br>Fabrication of Fe2+:ZnSe Polycrystalline Samples with Different Geometry of Doping and Investigation of Generation Characteristics of Synthesized Materials<br>**VII O-3** |
| **12:20-12:40** | **Qiao X.**<br>Luminescent Glass-ceramics Containing Fluoride, Aluminate and Borate Subphases for WLED Application<br>**VII O-4** |
| **13:00-14:00** | **Lunch** |
| **14:00-15:00** | **Closing Ceremony**<br>**Business Hall** |

# Poster Session
# Wednesday, August, 24th, 9h00 – 10h40

**P1** **Preparation of tellurite-molybdate glasses containing of lanthanum oxide from precipitated batch**
Fedotova I.G.

**P2** **Preparation of the $TeO_2$ – $WO_3$ glasses by using of the batches precipitated from aqueous solutions**
Gavrin S.A.

**P3** **Thermal and crystallization properties of fluorozirconate-phosphate glasses doped with rare earths**
Goncharuk V.K.

**P4** **Peculiarities of structure, crystallization and luminescence in the $TeO_2$-$PbO\bullet P_2O_5$-$PbF_2$:$EuF_3$ glasses**
Ignatieva L.N.

**P5** **Synthesis and study of new In-containing oxyfluoroniobate glasses.**
Savchenko N.

**P6** **Fluorozirconate and fluorohafnate glasses, doped with europium**
Zhidkova I.

**P7** **The use of the ICP-AES method to determine matrix components and impurity elements in the As-S, As-Se chalcogenide glass systems**
Fadeeva D.

**P8** **Optical, thermal and crystallization properties of high-purity $TeO_2$-$ZnO$-$La_2O_3$-$Na_2O$ glasses**
Motorin S.

**P9** **Methodology to evaluate the stability of crystallization tellurite glasses by DSC methods**
Balueva K.

**P10** **Removing the defective surface layer by magnetorheological treatment**
Kolpashchikov V.

**P11** **Is the term “Polyamorphism” correct for noncrystalline substance?**
Minaev V.

**P12** **Structural characterization and electrical conductivities of highly Ion-conducting glasses and glass ceramics in the system**
Santagneli S. H.

**P13** **Effect of silver and sodium ions on optical properties and structure $TeO_2$-$WO_3$-$La_2O_3$ glass**
Stepanov B.

**P14** **Isothermal and laser crystallization of amorphous thin films of PCM materials: comparative analysis of the two mechanisms**
Lazarenko P.

**P15** **Excitation induced NIR emission analysis in $Pr^{3+}$ single and $Pr^{3+}$, $Yb^{3+}$ co-doped TZYN glasses for optical amplifiers**
Dagupati R.

**P16** **Photoluminescence and thermal lens spectroscopic investigations of highly efficient fluorophosphates glasses doped with $Nd^{3+}$ and $Er^{3+}$**
Gonçalves T. S.

**P17** **Luminescent lead tungsten fluorophosphate glasses and glass-ceramics**
Poirier G.

**P18** **Superposition spectra and interionic energy migration in fluorophosphate:$Ho^{3+}/Er^{3+}$ glass**
He D.B.

**P19** **Up-conversion detection of 1.908 micron radiation of Tm: YLF in the glass composition $TeO_2$-$PbF_2$-$Ho_2O_3$-$Yb_2O_3$**
Budruev A.

**P20** **Study of magnetooptic properties of high-purity tellurium dioxide based glasses**
Yakovlev A.

**P21** **Thermal and optical properties of niobium phosphate glasses and glass-ceramics**
Poirier G.

**P22** **NMR spectroscopy of the fluoride glasses in the $BiF_3$–Rb(Cs)F–$ZrF_4$ systems**
Kavun V.

**P23** **Investigation of heterophase inclusions as a source of optical losses in high-purity chalcogenide and tellurite glasses for fiber optics**
Ketkova L.A.

**P24** **A study of glasses in the $TeO_2$ -$P_2O_5$PbO-$PbF_2$-$MF_3$(M-Er, Eu, Nd) system by light nonelastic scattering method**
Marchenko Yu.

**P25** **Nonlinear optical properties of high-purity tellurite glasses**
Smayev M.P.

**P26** **Glass formation region and optical properties of $TeO_2$-$MoO_3$-$Bi_2O_3$ system**
Zamyatin O.A.

**P27** **Optical absorption of *d*-elements in the tellurite-molybdate glasses**
Zamyatin O.A.

**P28** **Electrical, dielectric, and optical properties of PbO-$Ga_2O_3$-$Bi_2O_3$ glasses**
Labaš V.

**P29** **Planar waveguides based on tungsten-tellurite glass**
Gorshkov O.

**P30** **Effect of visible light on Ag doped GST thin films**
Singh P.

**P31** **Hot pressing of transparent ceramics of $Tb_2O_3$-$Y_2O_3$ solid solutions**
Permin D.

**P32** **Effect of CoO Addition on the Structure and Optical Properties of Transparent Glass-Ceramics based on ZnO and $Zn_2SiO_4$ nanocrystals**
Shemchuk D.

**P33** **Evanescent Wave Analysis of a Multimode Chalcogenide Fiber Embedded into a Crude Oil**
Korsakova S.

**P34** **Whispering Gallery Modes of Optical Microresonators Made of Chalcogenide Glass**
Zhivotkov D.

**P35** **Chalcogenide fused fiber couplers development and characterization**
Benderov O.

**P36** **On the Possibility of Mid-IR Supercontinuum Generation in Dispersion Engineered Chalcogenide Fibers with All-Fiber Femtosecond Pump Source**
Anashkina E.

**P37** **Fractal structure of polycrystalline zinc selenide surface defects**
Kolesnikov A.N.

# ISNOG 2016

Monday, August, 22nd

***Lux Hall***

# Plenary session

# Plenary lectures

**Professor Angela B. Seddon**

Mid-Infrared Photonics: A Hot Topic!

University of Nottingham, UK George Green Institute for Electromagnetics Research, Mid-Infrared Photonics Group,
E-mail: angela.seddon@nottingham.ac.uk

Professor Angela B. Seddon leads the Mid-Infrared Photonics Group at The University of Nottingham, UK, with world-class facilities for fabricating mid-infrared fibreoptic devices. Her aim is to create a new paradigm in portable, real-time mid-infrared medical molecular sensing and imaging for early, fast and reliable medical diagnosis and precise removal of cancers during surgery. She is elected author of 240 publications and five book chapters. She is Fellow of the Royal Society of Chemistry, Fellow of the Society of Glass Technology and Fellow of SPIE.

## Mid-infrared photonics: A hot topic!

A.B. Seddon

This Plenary Talk will address recent advances towards portable fibre-optic biomedical, and chemical, mid-infrared molecular sensing and imaging.

The mid-infrared (MIR) spans 3 to 25 μm wavelength region. It encompasses the molecular fingerprints of numerous gases, liquids and solids. In this spectral range, molecular species exhibit fundamental vibrational absorption bands with large extinction coefficients, hence MIR spectroscopy potentially provides extremely sensitive molecular analysis. To date, only weak blackbody broadband sources have been commonly available, so the source/analyte/detector have had to be in close proximity to complete the optical circuit. Alternatively, samples must be brought to a bright synchrotron MIR broadband source.

We wish to establish a new paradigm in portable, real-time MIR molecular sensing and imaging to open up the MIR spectral region for more general use. This new paradigm will be enabled through focused development of fibre devices and systems which are robust, functionally designed, safe, compact and cost effective and which are based on active and passive MIR optical fibres.

We set a record in demonstrating extreme broad-band supercontinuum (SC) generated light: 1.4-13.3 μm, in a specially engineered, high numerical aperture MIR optical fibre [1]. This was the first experimental demonstration truly to reveal the potential of MIR fibres to emit across the MIR molecular ”fingerprint spectral region” and a key first step towards bright, portable, broadband MIR sources for potential applications in real-time chemical sensing, and imaging, and *in vivo* biomedical sensing and imaging [2].

Rare-earth-ion (RE-)-doped fibre lasers have excellent beam quality, can be pulsed, are compact and are integratable with fibre-optics, but have not yet been demonstrated at ≥ 3.9 μm wavelength. MIR quantum cascade lasers lack beam quality and the ability to be pulsed. MIR optical parametric oscillator lasers are not compact and MIR gas lasers are rather unreliable. MIR RE-fibre-lasers are now needed with emission beyond 3.9 μm to pump fibre MIR SC for portable, compact all-fibre MIR SC laser sources. We have demonstrated [3] small-core MIR RE-fibre with emission in the 4-5 μm wavelength region and long RE excited-state lifetimes. The long lifetimes confirm that neither RE clustering, nor glass devitrification, has occurred during the intricate thermal processing to make MIR RE-fibre and that there is potential for gain and lasing.

MIR RE-fibre lasers have promise as discrete MIR sensors in their own right. Potential applications include: coherent MIR imaging and MIR OCT (optical coherent tomography), ship-to-ship, free-space communications and aircraft counter-measures. MIR RE-fibre lasers should enable well-controlled laser cutting/patterning of soft materials, analogous to the maturing field of high-power near-infrared fibre lasers for cutting/welding of hard materials. In medicine, new wavelengths for laser surgery of human tissue will lead to more diverse and better matter/light interactions through resonance with protein/lipid absorption at newly available MIR wavelengths.

Supported in part by the European Commission through the Framework Seven (FP7) project MINERVA: MId- to NEaR infrared spectroscopy for improVed medical diAgnostics (317803; www.minerva-project.eu)

1. CR Petersen, U Møller, I Kubat, B Zhou, S Dupont, J Ramsay, TM Benson, S Sujecki, N Abdel-Moneim, Z Tang, D Furniss, AB Seddon and O Bang, Nat. Photon.Journal name: NatueNat. Volume: 8. Pages: 830–834 (2014). Article selected for Nat. Photon.Journal name: NatueNat *News&Views* Gr Steinmeyer and JS Skibina 8 814-815 (2014) Entering the mid-infrared.
2. AB Seddon, Int. J. Appl. Glass Sci 2 [3] 177-191 (2011).
3. Z Tang, D Furniss, M Fay, H Sakr, L Sójka, N Neate, N Weston, S Sujecki, TM Benson and AB Seddon, Opt. Mat. Exp. 5 (4) 870-886 (2015).

**Professor Sidney J. L. Ribeiro**

Down-shifting and Up-conversion to enhance the efficiency of solar cells

Institute of Chemistry of the São Paulo State University (UNESP),Araraquara-SP, Brazil.
E-mail: sidney@iq.unesp.br

Sidney J. L. Ribeiro Full Professor of Inorganic Chemistry at the Institute of Chemistry of the São Paulo State University (UNESP),Araraquara-SP, Brazil.

On-going research projects deal with natural polymers (bacterial cellulose, silk fibroin), organic-inorganic hybrids, waveguides (optical fibers and thin films), porous materials and luminescent markers for biomedicine.

International board of the Journal of Sol-Gel Science and Technology and Journal of Non-Crystalline Solids.

ISI WebOfScience- Ribeiro SJL; ResearchID- E-9864-2012; Citations (google scholar)- Sidney J.L. Ribeiro

# Down-shifting and up-conversion to enhance the efficiency of solar cells

S.J.L. Ribeiro[1,4], E. Pecoraro[1], T.C. Silva[1], G. Galleani[1], D.Manzani[1], S.F.H. Correia[2], P. P. Lima[2],
P.S. André[2], R.A.S. Ferreira[2], L.D. Carlos[2]
[1]Institute of Chemistry- São Paulo State University (UNESP), CP 355 Araraquara-SP, 14801-970 Brazil
[2]Dept. of Physics and CICECO- Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal
[3]Dept. of Electric and Computer Engineering and Instituto de Telecomunicações, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisbon, Portugal
sidney@iq.unesp.br

Increasingly interest is observed in the utilization of lanthanide based materials in solar energy conversion. Concerning Si cells a good part of the UV-VIS and of the IR solar spectrum is lost either as heat in the case of the UV-VIS or simply not absorbed in the case of IR [1]. Two approaches will be addressed in this presentation: i) Fluoride Glasses in energy upconversion and ii) Plastic Optical Fibers (POFs) for downshifting in Luminescent Solar Concentrators (LSCs). i) Fluoroindate glasses are well known as good hosts for optically active lanthanide ions due to their relatively low phonon energies. The consequently low non-radiative rates observed for lanthanide excited states allow several different energy transfer processes involved in down-conversion down-shifting and up-conversion schemes which can be very efficient in these glass hosts.. We have been studying lanthanide ions containing fluorindate glasses aiming the possible enhancement of efficiency in energy conversion of Si photocells [2]. $Er^{3+}$-$Yb^{3+}$ ions are considered in up-conversion where IR light (≈1.5 μm) is converted in visible light and of around 1000 nm. ii) Plastic optical fibers and hollow tubes have been considered as LSC. The active layers used to coat the bulk fibers or fill the hollow-core ones are Rhodamine 6G- or $Eu^{3+}$ doped organic-inorganic hybrids. Bulk-coated LSC's presented maximum conversion efficiency ($\eta_{opt}$) and concentration factor (*F*) of 0.6 % and 6.5 respectively. Concerning hollow-core LSCs the optimized device displays $\eta_{opt}$=72.4 % and *F*= 12.3 [3].

Brazilian Agencies FAPESP, CAPES and CNPq are acknowledged for financial support.

1. S.F.H. Correia, V. Zéa-Bermudez, S.J.L.Ribeiro, P.S.André, R.A.S. Ferreira, L.D. Carlos, J. Mater. Chem.A, 2014, 2, 5587
2. L.J. Borrero-González, G. Galleani, D. Manzani, L.A.O.Nunes, S.J.L.Ribeiro, Opt.Mater. 35(2013)2085-2089.
3. S.F.H. Correia, P.P. Lima, E. Pecoraro, S.J.L. Ribeiro, P.S. Andre, R.A.S. Ferreira, L.D. Carlos, Prog. Photovolt. Res. Appl. (2016) DOI: 10.1002/pip.2772

**Prof. Evgeny M. Dianov**

Bismuth-doped glass optical fibers: a new breakthrough in laser media

Fiber Optics Research Center of the Russian Academy of Sciences

Prof. EVGENY M.DIANOV is Scientific Director of the Fiber Optics Research Center of the Russian Academy of Sciences.

He graduated from Moscow State University in 1960 and began his scientific career in the P.N.Lebedev Physical Institute of the USSR Academy of Sciences (1960-1983), then worked in the General Physics Institute (1983-2006) and in the Fiber Optics Research Center of RAS (2006- present). He received the Ph.D. degree in Physical and Quantum Electronics in 1966 and the Doctor of Science degree in Physics in 1974.

In 1994 Prof. Dianov became a Full Member of the Russian Academy of Sciences.

His research interests include fiber optics, laser physics and nonlinear optics and he has published more than 700 scientific papers and patents.

He received the State Prize of the Soviet Union for “Neodymium Glass Lasers” in 1974 and the State Prize of Russia for “Infrared Fibers” in 1998.

Prof. Dianov is a Member of IEEE, ACerS, MRS, a Fellow of OSA.

# Bismuth-doped glass optical fibers: a new breakthrough in laser media

E.M. Dianov
Fiber Optics Research Center of the Russian Academy of Sciences, Vavilova St. 38, 119333 Moscow, Russia

Promising active media for the creation of lasers and optical amplifiers in the near infrared (NIR) region, bismuth-doped (Bi-doped) optical fibers span a spectral range of 800-1800 nm. This range includes the spectral regions 1250-1500 and 1600-1800 nm, where efficient rare-earth fiber lasers are absent. The presentation will review recent results on the technology of Bi-doped fibers, luminescence properties of various Bi-doped fibers, the nature of Bi-related NIR emitting centers and the development of efficient Bi-doped fiber lasers (BDFL) and optical amplifiers (BDFA) covering the spectral region 1150-1800.

inv 1

# Structural, thermal and optical properties of a new antimony-phosphate germanate glasses

Murilo Montesso[1], Danilo Manzani[2], Sidney J. L. Ribeiro[2], José P. Donoso[3], Claudio J. Magon[3], Igor D'Anciães A. Silva[3], Raman Kashyap[4], Marcelo Nalin[1,2*]
[1]Chemistry Department, São Carlos Federal University (UFSCar) – São Carlos – SP – Brazil
[2]Institute of Chemistry, São Paulo State University (UNESP) – Araraquara – SP – Brazil
[3] Physics Institute of São Carlos, University of São Paulo – USP, São Carlos, SP
[4] Department Eng. Physics, Polytechnique Montreal, Montreal, Canada
mnalin@iq.unesp.br

In this work we present the production and characterization of a new binary glass system based on $(100\text{-}x)GeO_2\text{-}xSbPO_4$, where $0 \le x \le 70$ mol %. Structural, thermal and optical properties were investigated as a function of the $GeO_2$ content. The results were supported by thermal analysis (DSC), Raman spectroscopy, UV-visible absorption, near-infrared transmittance, and M-lines technique. Glass transition temperatures ($T_g$) remains unchanged at around 400 ºC regardless the concentration of $GeO_2$, indicating a competitive behavior between $GeO_4$ and $PO_4$ units as responsible for the structure connectivity. On the other hand, the thermal stability parameter against crystallization ($\Delta T = T_x - T_g$) linearly increases as a function of $GeO_2$ content reaching 400 °C for the glass with 90 mol % of $GeO_2$. Raman spectroscopy was used to evaluate the glass structural changes as a function of the $GeO_2$ concentration. A stretching band around 420 $cm^{-1}$ was assigned to the symmetric stretching mode of Ge-O-Ge linkages in six member rings - six $GeO_4$ units. UV-visible absorption curves show that the increases of the $GeO_2$ content shifts the absorption edges of the glasses to higher energies. Infrared curves show the multiphonon cut-off at 2500 $cm^{-1}$, which is limited by the absorption of the second-harmonic vibration of phosphate units and by OH absorption at 2800 $cm^{-1}$. By using M-lines technique, a decrease of the linear refractive indices from 1.75 to 1.67 was observed as a function of $GeO_2$ content. The glasses were doped with $Er^{3+}/Yb^{3+}$ ions and the luminescent properties were studied. Visible up-conversion emissions at red and green regions, as well as the infrared emission at 1550 nm were observed for the glass samples under excitation at 980 nm and three different mechanisms are proposed. Finally, planar waveguides were produced by femtosecond micromachining technique using the doped glass samples. Passive and active properties were studied and a attenuation loss of 1.5 dB/cm was obtained.

inv 2

# Novel ways to prepare chalcogenide glasses and non linear glass-ceramics

L. Calvez[1], B. Xue[1], E. Petracovschi[1], M. Hubert[1*], G. Delaizir[2], X.H. Zhang[1]
[1]Equipe Verres et Céramiques, UMR 6226 Institut des Sciences Chimiques
de Rennes, Campus de Beaulieu, Avenue du Général de Gaulle, 35042, Rennes, France
[2]Laboratoire Sciences des Procédés Céramiques et Traitements de Surface (SPCTS, ENSCI),
Centre Européen de la Céramique, 12 rue Atlantis, 87068 Limoges, France
[*] Now at Celsian Glass and solar, Eindhoven, Netherlands
laurent.calvez@univ-rennes1.fr

Chalcogenide glasses are widely used for infrared applications. The presence of oxygen during their synthesis process leads to the presence of detrimental absorption bands on the transmission spectra. To avoid this phenomenon, these glasses are synthesized using expensive and single use silica tubes sealed under vacuum. The low thermal conductivity of silica also limits the quenching rate, and thus the size of the samples produced. In this study, we present a new synthesis way to make chalcogenide glasses and glass-ceramics without the use of silica tubes. An amorphous powder of the $80GeSe_2$-$20Ga_2Se_3$ glass is produced by mechanical milling of the raw starting elements (Ge, Ga, Se) and is then sintered using Spark Plasma Sintering (SPS) technique. Bulk glasses and glass-ceramics with higher dimensions and transparent in the infrared region were produced [1]. This process paves the way of a novel approach for the production of chalcogenide glasses and glass-ceramics for infrared applications at a lower cost. We have also demonstrated the possibility to apply this technique for various glass compositions such as Te-As-Se, Ge-Sb-Se, Ge-Ga-Te…

Moreover, it is well known that thermal treatment is regarded as a useful way to generate permanent second harmonic generation (SHG) property in chalcogenide glass for example. The presence of nano-particles with high non-linearity susceptibility in glassy matrix contributes directly to the SHG phenomenon. Here, we propose to use this new way of synthesis to make hybrid glass-ceramics by sintering the $Ge_{20}Sb_{12}S_{68}$ glassy powder doped with CdS nano-particles which possesses SHG property. This way can overcome the limitation of the thermal treatment method for preparing glass-ceramics where an uncontrollable crystallization takes place leading to surface-crystallization [2]. Glassy powder and CdS nano-particles were thoroughly mixed and sintered into disc by hot-pressing which presented a pretty low transmission in the mid-IR (30 % around 5 μm) and a relatively high transmission of 60 % at 10.6 μm [3]. Signals of Second-harmonic generation were observed in these samples. This novel method could be an interesting approach to synthesize materials with 'à la carte' properties.

1. M. Hubert, G. Delaizir, J. Monnier, C. Godart., H.L Ma, X.H Zhang, L.Calvez. An innovative approach to develop highly performant chalcogenide glasses and glass-ceramics transparent in the infrared range. //Optic Express, vol.19 (23), 2011
2. B. Xue, L. Calvez, V. Nazabal, X.H. Zhang, G. Delaizir, G. Martinelli, Y. Quiquempois. Mechanical milling and SPS used to obtain GeS2-βGeS2 infrared glass-ceramic. // Journal of Non Cryst. Sol., Volume 377, 240–244, 2013
3. B. Xue, B. Fan, X.H. Zhang, Y. Quiquempois, G Martinelli, L. Calvez. Second-harmonic generation in chalcogenide glass-ceramic doped with CdS nanocrystals. // Material Letters, 132 (1), 2014

# ISNOG 2016

Monday, August, $22^{nd}$

## *Business Hall*

# Session I-1

**Session I-1: Synthesis, Melting and Processing of Glasses and Glass–Ceramics**

I-1-inv 1

# High-purity tellurite glasses for fiber optics

Dorofeev V.V.
G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences,
Tropinina st. 49, 603950 Nizhny Novgorod, Russia
e-mail: dorofeev@ihps.nnov.ru

Tellurium dioxide based glasses containing oxides of tungsten, zinc, molybdenum, bismuth, alkali metals and rare earth elements are promising material for fiber optics devices for infrared region.

They are characterized by a high transparency in the near and mid-IR, highly nonlinear optical properties and excellent rare earth oxides solubility.

Possibility of producing of optical fibers with low loss up to 3-3.5 μm [1], the efficient luminescence of REE ions [2] and high nonlinear optical properties [3] have been demonstrated. The application of tellurite glasses is currently limited to high optical loss in routine samples related primarily to the presence of 3d-transition metals and hydroxyl groups impurities.

This work is devoted to the study tellurite glasses in terms of the importance of the optically active impurities removal for use in fiber optics of near and mid-IR ranges.

Tellurium dioxide based glasses were produced by melting the oxides in crucibles of gold or platinum inside sealed a silica chamber in the atmosphere of purified oxygen. The oxides, made by original techniques [4, 5], as well as commercially produced oxides were used for glass synthesis. The zinc-tellurite and tungstate-tellurite glasses compositions with the addition of modifying components of bismuth, lanthanum, sodium oxides stable to crystallization were developed.

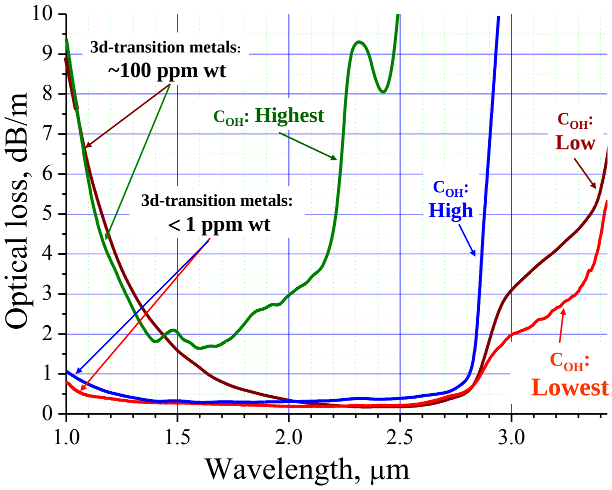


Fig. 1 Loss in the fibers of $TeO_2$-$WO_3$-$La_2O_3$-$Bi_2O_3$ glasses with different content of 3d-transition metals and OH-groups impurities
Core 50 μm / Cladding 150 μm

The total content of 3d-transition metals did not exceed 1-2 ppm and the hydroxyl groups absorption at maximum of the band around ~3 μm was as low as $n \cdot 10^{-3}$ cm$^{-1}$ in the best glass samples [6]. The glasses with a higher content of impurities have been also prepared for the comparative analysis of target properties. Preforms and optical fibers were produced from the tellurite glasses and investigations of the optical fibers total losses dependence on the impurities content of the initial glasses were carried out (Fig. 1). It is found that the 3d-transition metals impurities determine the level of fiber loss preferably up to ~1.5 μm and have no effect on the loss in the wavelength range further 2 μm. The main source of optical loss in the 2-5 μm region is hydroxyl groups impurity, and for wavelengths above 3.5 μm multiphonon absorption is added. Optical loss in the record optical fiber of the glass with the hydroxyl groups absorption of 0,001 cm$^{-1}$ is 0.3 dB/m at 2.5 μm, 0.5 dB/m at 2.8 μm and 2 dB/m at 3 μm.

Achievement a low concentration of limiting impurities in the glasses allowed to investigate the luminescence properties of promising for use in the mid-IR REE in areas hidden in the samples with insufficient purity by hydroxyl groups broad bands. The influence of the hydroxyl groups content on the luminescence intensities and decay times was demonstrated.

The study was partly supported by the Russian Foundation for Basic Research (15-43-02185, 15-03-08324).

1. V. Dorofeev, A. Moiseev, I. Kraev et al. "Tungstate-tellurite glass fibers for spectral region up to 3 µm," in *Advanced Photonics Congress*, OSA Technical Digest (online), paper JM5A.3, (2012).
2. A. F. Kosolapov, V. Dorofeev et al., "Er-doped Tungstate-Tellurite Glasses and Fibers," in *Advanced Photonics*, paper JM5A.10, (2014)
3. M.Yu. Koptev, E.A. Anashkina, A.V. Andrianov, V.V. Dorofeev, A.F. Kosolapov, S.V. Muravyev, and A.V. Kim, Widely tunable mid-infrared fiber laser source based on soliton self-frequency shift in microstructured tellurite fiber, Optics Letters Vol. 40, No. 17, 4094 (2015)
4. A.N. Moiseev, A.V. Chilyasov, V.V. Dorofeev et al., "Method for purifying tellurium dioxide," Patent RF 2301197, Bull. 17 (2007).
5. A.N. Moiseev, A.V. Chilyasov, V.V. Dorofeev, I.A. Kraev, "Method of obtaining high-purity tungsten oxide (VI)," Patent RF 2341461, Bull. 35 (2008).
6. V.V. Dorofeev, A.N. Moiseev, M.F. Churbanov, G.E. Snopatin, A.V., Chilyasov, I.A. Kraev, A.S. Lobanov, T.V. Kotereva, L.A. Ketkova, A.A. Pushkin, V.V. Gerasimenko, V.G. Plotnichenko, A.F. Kosolapov, E.M. Dianov, "High purity $TeO_2$-$WO_3$-($La_2O_3$, $Bi_2O_3$) glasses for fiber-optics," Opt. Mater. 33, 1911–1915 (2011).

I-1-inv 2

# Modified fluoride ZBLAN glasses

M. Brekhovskikh[1], L. Moiseeva[2]
[1]N.S.Kurnakov Institute of General and Inorganic Chemistry RAS, Russia
[2]A.M.Prokhorov Institute of General PhysicsRAS, Russia
mbrekh@igic.ras.ru

Fluoride glasses remain to be an attractive material for thirty years in shorter optical devices with application lying in the visible and mid IR spectral range due to their low phonon energy (~500-600 cm$^{-1}$). In this review, the information on glass-forming fluoride systems is presented, and the main methods for synthesizing glasses on the basis of fluorides of the metals of Groups I–IV, their physicochemical properties, techniques for producing fibers and areas of application, and the techniques for purifying them from undesired impurities are discussed. Modern materials science studies in the area of fluoride glasses are aimed at searching for glasses activated with rare-earth elements (REEs) with a broad IR transmission range and high optical homogeneity with the purpose of creating efficient active optical media in a wide spectral range, as well as converters of IR radiation into the visible range for enhancing the efficiency of solar cells and exciting photocatalysts. Our previous results demonstrated that fluorochlorohafnate glasses had a broader IR transmission window and lower relaxation losses compared to ZBLAN. To reduce the losses caused by multi-phonon relaxation the fluorozirconate glass composition was modified by substitution of $Zr^{4+}$ for $Hf^{4+}$ and $F^-$ was replaced by "heavier" $Cl^-$ and $Br^-$ by partial substitution $BaF_2$ for $BaCl_2$ and $BaBr_2$ respectively. Glass formation with no visible signs of crystallization took place in the fluoride–chloride system at Cl/F ratios under 1/8 and in the fluoride–bromide system at Br/F ratios under 1/15.

The analysis of the influence of impurities on the optical transparency, crystallization, and phase purity of the glasses is presented. The methods for the deep purification of the initial substances for preparing fluoride glasses with the minimum content of impurities are considered. Original procedures for synthesizing fluorides of elements and glasses free from oxygen-containing impurities are created on the basis of physicochemical studies of the interactions of fluorinating agents with the components of fluoride glasses. The development of ultrapurification processes for the preparation of fluoride glasses with the minimum possible impurity concentration is a challenging problem. The main difficulty in developing the technology of fluorides as key components of optical materials is related to the ultrapurification step, which is complicated by the high reactivity of fluorides for construction materials, their hygroscopicity, and their tendency toward pyrohydrolysis.

We have developed general methodological approaches and apparatus for the preparation of fluoride and fluorochloride glasses in chemically active media (fluorine, xenon difluoride, chlorine trifluoride, bromine trifluoride, and carbon tetrachloride), which ensure a decrease in oxygen concentration in the glasses by two orders of magnitude (down to $10^{-3}$ wt %) relative to the oxygen concentration in the starting fluorides ($10^{-1}$ wt %).

The publication was supported by the Federal Agency of Scientific Organizations within the State Assignment on Fundamental Research to the Kurnakov Institute of General and Inorganic Chemistry and the Russian Foundation for Basic Researches RFBR grant No. 15-03-02507

I-1-O-1

# Optical properties of tantalum germanate glasses, glass-ceramics and planar waveguides

C.R. Cunha[1], F.C. Cassanjes[1], G. Poirier[1], R.R. Gonçalves[2] and S.J.L Ribeiro[3]
[1] Institute of Science and Technology, Federal University of Alfenas, Poços de Caldas-MG, Brazil
[2] Department of Chemistry, University of São Paulo (USP), Ribeirão Preto-SP, Brazil
[3] Department of Inorganic Chemistry, São Paulo State University (UNESP), Araraquara-SP-Brazil
Corresponding author: gaelpoirier@gmail.com

Germanate glasses containing increasing contents of $Ta_2O_5$ from 0 % to 20 mol % were prepared by melting at high temperatures and quenching. Glass samples containing 15 and 20 % of $Ta_2O_5$ exhibit preferential orthorhombic $Ta_2O_5$ precipitation under heating. Three sets of glass samples were also doped with $Eu^{3+}$, $Er^{3+}/Yb^{3+}$ and $Tm/Yb^{3+}$ respectively. A detailed crystallization study performed by DSC allowed to determine the best nucleation and growth temperatures for a controlled $Ta_2O_5$ crystallization and transparent glass-ceramics. $Eu^{3+}$ spectroscopy pointed out a progressive increase of the crystallinity and the lifetimes suggest an increasing refractive index around the $Eu^{3+}$ ions with longer heat-treatment times, suggesting a richer $Ta_2O_5$ environment around the rare earth ions. $Er^{3+}$ luminescence in the near infrared in the $Er^{3+}/Yb^{3+}$ codoped samples also exhibits great changes in the emission behavior around 1,5 μm regarding the $Ta_2O_5$ content as well as heat-treatment time in the most $Ta_2O_5$ concentrated samples. An increase in the emission bandwith has been observed both in glass samples with increasing $Ta_2O_5$ contents as well as in glass-ceramic samples with increasing heat-treatment times, suggesting a higher tantalum oxide environment around $Er^{3+}$ ions and possible migration in the tantalum oxide crystalline phase. Progressive decrease of radiative lifetimes also support this hypothesis. Upconversion mechanisms also exhibit dependence of the composition and heat-treatment time on the final emission behavior. Emission measurements on $Tm^{3+}/Yb^{3+}$ glass samples exhibit a strong emission around 1650 nm and a strong dependency of the $Ta_2O_5$ content and heat-treatment time realted with $Ta_2O_5$ precipitation. Finally, planar waveguides were prepared from these doped glass samples by $Na^+/Ag^+$ ion exchange and characterized with respect to their refractive index, guiding behavior and luminescent properties.

I-1-O-2

# Chemical processes in the batch and in the melt to produce binary and multicomponent tellurite-molybdate glasses

A.A. Sibirkin[1,2], O.A. Zamyatin[1,2]
[1]National Research Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, Russia
[2]G.G.Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, Nizhny Novgorod, Russia
asibirkin@rambler.ru

Traditionally tellurite glasses are prepared by melting of a mixture of binary oxides (batch) taken in a preset ratio and quenching of the melt produced. The optical properties of the manufactured glasses are determined primarily by the nature and the oxidation state of oxide-forming elements - macro-components, dopants and impurities, as well as of glass microhomogeneity. These features are derived from the corresponding characteristics of the batches, their melting conditions, including the nature of the crucible material and gaseous environment around the melt, and the melt quenching mode. In these processes an important role belongs to the chemical reactions between the mixture components, their directions and rates. These peculiarities were studied thoroughly for optical silicate glasses. The chemical changes of the batch initial components to produce tellurite glasses have not been researched in details.

This report presents the results of research on the preparation of tellurite-molybdate glasses originated of batches which differ each other in the manner of manufacturing and in the chemical form of tellurium, molybdenum, bismuth, lanthanum and other elements. The followed substances were tested as the batch materials: 1) the precipitates isolated from the solutions of the elements compounds; 2) the mixtures of inorganic acids and their salts which are capable to decompose into binary oxides if taken in the individual state; 3) the mixture of complex oxides of elements. The chemical processes affecting the optical properties of the glass prepared which take place in the courses of batch preparation from the aqueous solution, of the thermal treatment of the solid batch, and of batch melting, are described.

The advantage of the first method is the use of the finely dispersed mixture containing particles sized from tens down to few nanometers. This feature reduces the duration of the homogenizing fusion which contributes to decrease in melt contamination with container material. The compounds of elements in the high oxidation state ($Te^{+6}$ in telluric acid and $N^{+5}$ in nitrates) included in the second type of batch provide the condensed phase with the oxidant at each stage of the process. This circumstance hinders the process of reduction of $Mo^{+6}$ atoms which is responsible for the decrease in the glass optical transparency in the visible and near infrared spectral ranges. The third kind of batch is composed of the complex oxides which possess a lower melting point as compared with that for the corresponding binary oxides. This property affords a possibility of preparation of glasses of better optical quality with the high content of refractory oxide.

The use of the batch composed of the chemically reactive components allows to manufacture tellurite-molybdate glasses of high optical transparency in the short-wave range.

I-1-O-3

# Adhesion mechanism of contamination of optical glassy arsenic sulfides by $SiO_2$ particles

Mishinov S.V., Churbanov M.F., Shiryaev V.S., Ketkova L.A., Suchkov A.I.
G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, 49 Tropinin str., 603950 Nizhny Novgorod, Russia
E-mail: ser.mishinov@yandex.ru

The practice of production of chalcogenide glasses shows their high adhesion to the silica glass used as the construction material of equipment in most cases [1]. It can lead to the contamination of surface layers of chalcogenide glass samples by nano- and microsized silica particles [2]. During the subsequent operation of the glass, for example, for drawing optical fibers, the particles contaminate the melt causing the additional optical losses and a decrease in mechanical strength.

The aim of this work was to investigate the adhesion mechanism of contamination of optical glassy arsenic sulfides by silica-glass particles. The investigation of adhesion strength of the boundary of (As-S)-$SiO_2$ solid phases was carried out by the steady detachment method. The presence of heterogeneous impurity particles on the surface and in the volume of the chalcogenide ingot was found by optical microscopy, electron microscopy and laser ultramicroscopy. The chemical composition of inclusions was determined by an energy-dispersive X-ray microanalysis.

The influence of the composition of chalcogenide glasses, the temperature and time conditions of the adhesion contact formation on the adhesion strength of (As-S)-$SiO_2$ solid phase boundary was studied. The adhesion strength was demonstrated to increase with the content of sulfur in the glass matrix. It was found the presence of millimeter-sized silica particles (Fig. 1) on the surface of chalcogenide ingot after testing under conditions, when the adhesion strength of the (As-S)-$SiO_2$ solid phase boundary exceeded the limit strength of silica glass (≈10 MPa).

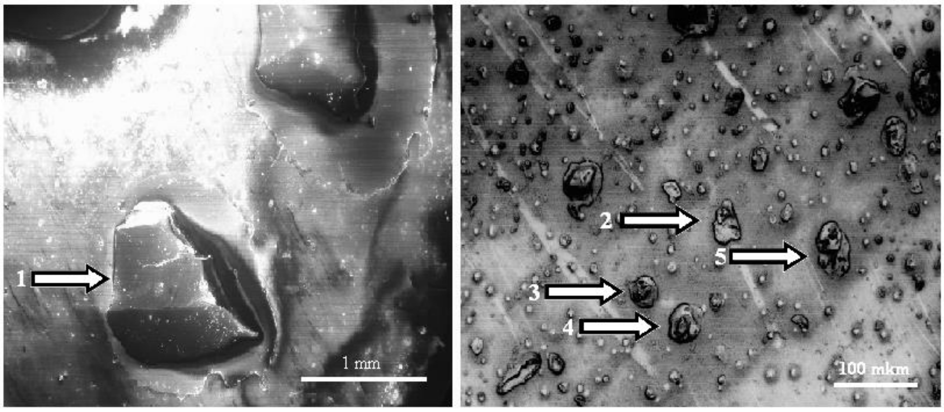


Figure 1. The micrograph of the surface of the $As_{35}S_{65}$ glass after the contact with silica glass at the temperature of 360 °C (1, 2, 3, 4, 5 - silica particles)

There are two possible mechanisms of formation of impurity heterogeneous particles. The first mechanism is the separation of protruding surface defects of silica glass because of the radial and longitudinal shrinkage of chalcogenide sample during the process of glass cooling. This mechanism is quite probable in the case, when the used silica-glass ampoule has initial high roughness. The second mechanism of contamination can be associated with peeling of $SiO_2$ particles due to the presence of surface cracking that can occur during the high temperature baking of silica glassware. It should be noted, that two mechanisms of formation of the inclusions may occur at the same time and complement each other. Preparation of the arsenic sulfide glass samples with minimum content of $SiO_2$ particles is associated with the optimization of temperature and time conditions of synthesis and annealing processes, as well as with the development of technological procedures aimed for reducing the inner surface roughness of silica glassware.

This work was supported by the Russian Science Foundation (Russia, Grant No. 15-12-20040).

1. V.S. Shiryaev, S.V. Mishinov, M.F. Churbanov, J. Non-Cryst. Solids, 408 (2015) 71–75.
2. S.V. Mishinov, M.F. Churbanov, A.N. Gorokhov, et.al., Inorganic Materials, 52 (2016) (to be published)

## I-1-O-4

# Fluorophosphate glass fiber for transmission in the UV

G. Galleani[1,2], Y. Ledemi[2], S. Morency[2], Y. Messaddeq[1,2]
[1]Institute of Chemistry – Sao Paulo State University – UNESP, Araraquara, Sao Paulo, Brazil
[2]Centre d´Optique, Photonique et Laser – Laval University, Quebec, Canada
gugalleani@yahoo.com.br

Novel fiber materials transmitting in the deep ultraviolet (below 300 nm) and vacuum ultraviolet (below 200 nm) are highly desirable for specific applications like in agriculture for elemental sensing (phosphorus and sulfur with atomic absorption lines at 177 and 181 nm, respectively) and for excimer lasers radiation delivery in microlithography. To this end, fluorophosphate vitreous materials appear as excellent candidates thanks to their large glass-forming ability and transmission windows that can be extended to the deep-UV (down to ~160 nm) when their content of impurities are kept ultra-low [1]. They may thus offer an excellent alternative to UV-grade silica fibers that sustain immediate damage during the UV light propagation [2]. Here, we report on the development of highly-pure fluorophosphate step-index optical fibers. Efforts were dedicated on achieving glass preforms with high optical quality for fiber drawing. Step-index optical fiber with numerical aperture of 0.15 was fabricated and the optical losses in the UV region of the fluorophosphate fiber were investigated. The potential of this material to be used as deep-UV transmitting optical fiber will be discussed. Efforts were dedicated on the glass purification and the preparation of high optical quality preforms for fiber drawing. The potential of using these new fibers in deep-UV practical applications will be discussed.

1. Ehrt, D.; Seeber, W.; Glass for high performance optics and laser technology. Journal of Non-Crystalline Solids., v. 129, p. 19, 1991.
2. J. Vydra, G. F. Schoetz, Improved all-silica fibers for deep-UV applications, SPIE Proceedings, v. 3596, p. 165, 1999.

## I-1-O-5

# Research on far-IR suspended-core fiber with Te-based chalcogenide glass

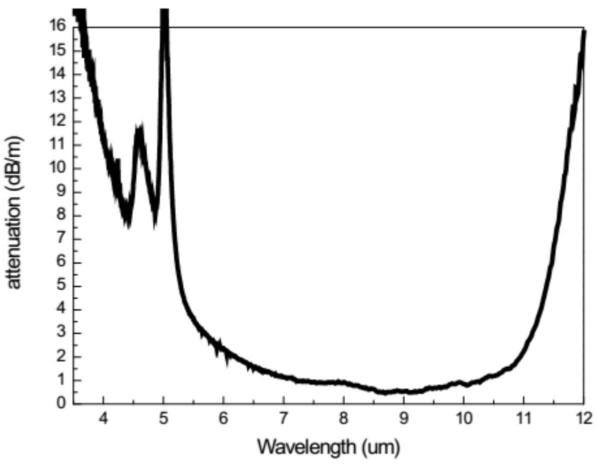
Xunsi Wang[1,2], Zheming Zhao[1,2,3], Shuo Liu[1,2], Zhanghao Pan[1,2], Shi-xun Dai[1,2], Qiu-hua Nie[1,2]
[1]Laboratory of Infrared Material and Devices, Advanced Technology Research Institute, Ningbo University, Ningbo 315211, China
[2]Key Laboratory of Photoelectric Materials and Devices of Zhejiang Province, Ningbo 315211, China
[3]Nanhu College, Jiaxing University, Jiaxing 314001, China

With the development of infrared optics, low-loss, large waveguide materials are required. Especially, low-loss Te-based optical glass fiber development for far-infrared application has grown to be a focus, which shows the highest value of nonlinearity among glasses. Here, Te-based far-infrared chalcogenide (Ge-As-Se-

Te, GAST) glasses and specialized fiber have been prepared and investigated. Firstly, specialized structure show helps to enhance the nonlinearity, such as suspended-core structured fibers with AsS or As-Se glass were manufactured [1-4], however, the high phonon energies of these glasses lead to their transparence were limited not longer than 6-9 μm. In contrast, tellurium glasses have largest nonlinearity in the glass host, and their lower phonon energies mean that their transparence wavelength can easily cover the far-infrared optical windows [5-7]. However, strong metallic character of Te leads to a greater tendency towards crystallization. Fortunately, some low-loss fibers can be obtained using some stable chalcogenide glasses with some specialized Ge-As-Se-Te (GAST) glass compositions [8]. The refractive index of Te-enriched part of the GAST glasses can be varied from 3.2 to 3.4, here ~15 % content of Se results in far greater stability toward crystallization [9, 10].

Here, some GAST glasses were prepared by traditional vacuum melt-quenching and vapor distillation method. Structure and physical properties of GAST glass system were studied with XRD and DIL. Optical spectra of GAST glass system were obtained by spectrophotometer and infrared spectrometer. Main purification processes with different oxygen-getters (Mg & Al) were disclosed.

Then, low-loss GAST fiber with structures of single index and Suspended-core fibers were prepared by a novel extrusion method, the losses of the index fiber were 0.46 dB/m at 8.7 μm and 1.31 dB/m at 10.6 μm, with base loss under 1 dB/m from 7.2 to 10.3 μm, just shown as Fig. 1. The fiber attenuation was measured by the cut-back method. The results show that, the fiber attenuation can be decreased effectively by the ways of reasonable purification and novel extruded-processing. At last, we chose $Ge_{20}As_{20}Se_{15}Te_{45}$ glass and a novel extrusion technology to fabricate a suspended-core fiber. The glass rods were previously fabricated and purified as before. To reach subwavelength core dimensions, the fibers are made by processes of three steps, just shown as Fig. 2(a1, a2, a3). Thanks to the novel extrusion method, the glass nature and tailored fibers geometry can be protected perfectly. Fig. 2 (b1, b2) shows that the structures of suspended-core are well identical in the preform and the fiber. To our best knowledge, it may be the first far-IR suspended-core fiber based on telluride glass.



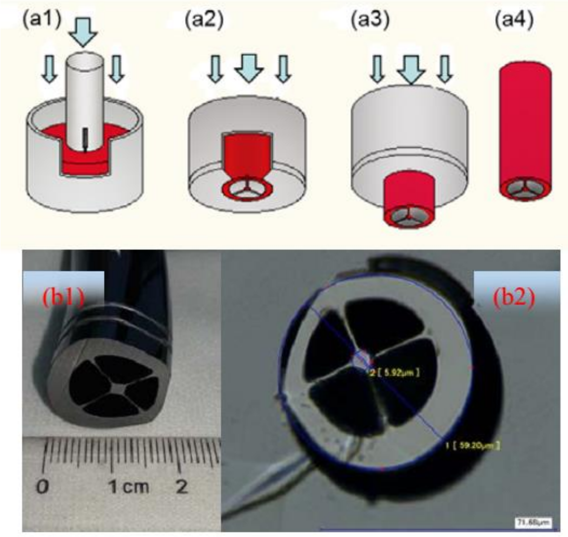


Fig.1 Attenuation of GAST fiber (core Ge20As20Se15Te45/ cladding Ge20As20Se17Te43)

Fig.2 (a) Schematic diagram of novel preform extrusion processes; Cross-sections of preform (b1) and suspended-core fiber (b2).

1. J. M. Harbold, F. Ilday, F. W. Wise, J. S. Sanghera, V. Q. Nguyen, L. B. Shaw, and I. D. Aggarwal, Highly nonlinear As-S-Se glasses for all-optical switching, Optics Letters, 27(2002)119-121.
2. P. Houizot, F. Smektala, V. Couderc, J. Troles, and L. Grossard, Selenide glass single mode optical fiber for nonlinear optics, Optical Materials, 29(2007)651-656.

3. G. Boudebs, F. Sanchez, J. Troles, and F. Smektala, Nonlinear optical properties of chalcogenide glasses: comparison between Mach–Zehnder interferometry and Z-scan techniques, Optics Communications, 199(2001)425-433.
4. S. Sanghera, I. D. Aggarwal, L. B. Shaw, C. M. Florea, P. Pureza, V. Q. Nguyen, and F. Kung, Nonlinear properties of chalcogenide glass fibers, Journal of Optoelectronics and Advanced Materials, 8(2006)2148-2155.
5. A.A. Wilhelm, C. Boussard-Plédel, Q. Coulombier, J. Lucas, Development of Far-Infrared Transmitting Te Based Glasses Suitable for Carbon Dioxide Detection and Space Optics, Advanced Materials, 19(2007)3796-3800.
6. S. Danto, P. Houizot, C. Boussard-Pledel, X.-H. Zhang, F. Smektala and J. Lucas, A Family of Far-Infrared-Transmitting Glasses in the Ga–Ge–Te System for Space Applications, Advanced Functional Materials, 16(2006)1847-1852.
7. Z. Yang and P. Lucas, Tellurium-Based Far-Infrared Transmitting Glasses, Journal of the American Ceramic Society, 92(2009)2920-2923.
8. J.S. Sanghera, V.Q. Nguyen, P.C. Pureza, F.H. Kung, R. Miklos, and I.D. Aggrawal, Fabrication of Low-Loss IR-Transmitting Ge30As10Se30Te30 Glass Fibers, Journal of Lightwave Technology, 12(1994)737-741.
9. V.K. Tikhomirov, D. Furniss , A.B. Seddon, J.A. Savage, P.D. Mason, D.A. Orchard, K.L. Lewis, Glass formation in the Te-enriched part of the quaternary Ge-As-Se-Te system and its implication for midinfrared optical fibers, Infrared Physics & Technology 45(2004)115-123.
10. Z. Yang, T. Luo, S. Jiang, J. Geng, P. Lucas, Single-mode low-loss optical fibers for long-wave infrared transmission, Optics Letters, 35(2010)3360-3362.

I-1-O-6

# Glasses of Ge – S – I and Ge – Se – I systems for infrared fiber optics

A.P. Vel'muzhov
G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences,
Nizhny Novgorod, Russia
velmuzhov.ichps@mail.ru

The glasses of Ge–S–I and Ge–Se–I systems are considered to be the promising materials for fabrication of optical fiber amplifiers and lasers. They are characterized by high transparency in the near and middle IR-range, by great ability to dissolve the rare-earth elements, and by high quantum efficiency of luminescence [1–3]. The goal of the work is to develop the techniques for preparation of glasses with low content of optically active impurities, investigation of the properties of glasses and determination of the compositions most suitable for drawing the optical fibers with low optical losses.

The present work represents the approaches to preparation of special-purity of Ge–S–I and Ge–Se–I systems providing the decrease in the contaminating effect of apparatus material due to decrease in temperature and in duration of the synthesis of glass-forming melt. These approaches are based on melting of the products of thermal decomposition of vitreous $Ge_2S_3I_2$, $Ge_2Se_3I_2$ and on the use of germanium (II) sulfide, germanium (IV) iodide and $Ge_{40}S_{60}$ alloy as the sources of germanium. The samples of glasses with the content of hydrogen impurity in the form of bonds S–H and Se–H $(2–5)\cdot 10^{-6}$ mas %, of silicon $(1-4)\cdot 10^{-5}$ mas %, of metals $<5\cdot 10^{-5}$ mas % are prepared which is by 1–2 orders of magnitude lower than in the glasses of these systems prepared by the traditional method of melting of simple special-purity substances.

Thermal, optical properties and stability to crystallization of $(100–y)GeS_2 – yGeI_4$ ($y$ = 3.8–12.2), $[GeS_x]_{90}I_{10}$ and $Ga_5[GeS_x]_{85}I_{10}$ ($x$ = 1.35, 1.5, 1.7, 2.0, 2.3, 2.45, 2.6), $[GeS_{1.5}]_{100-z}I_z$ ($z$ = 0, 1, 3, 5, 8), $[GeSe_4]_{100-x}I_x$ ($x$ = 0, 1, 3, 5, 8, 10) glass compositions were investigated. It was found that in $[GeS_x]_{90}I_{10}$ system the glass transition temperature, the band gap energy and the tendency to crystallization of glasses non-monotonically depend on their composition passing through the maximum value at $x$ = 2.0. In other investigated systems the properties of glasses monotonically change with increase of iodine and germanium (IV) iodide. The glasses of $85.8GeS_2 – 14.2GeI_4$, $[GeS_{1.5}]_{90}I_{10}$, $[GeS_{2.6}]_{90}I_{10}$, $[GeS_{1.5}]_{92}I_8$ and

$[GeSe_4]_{95}I_5$ composition are mostly suited for drawing the optical fibers by crucible method with respect to their common properties. It is for the first time that optical fibers were drawn from these glasses and their optical losses were measured. The minimum optical losses were 2.7 dB/m at 5.1 μm wavelength in $85.8GeS_2 – 14.2GeI_4$ glass and 1.7 dB/m at 5.5 μm in $[GeSe_4]_{95}I_5$ glass. The main reasons of optical losses in optical fibers were found and the ways to their further reduction were proposed.

This work was supported by the Russian Science Foundation (Russia, Grant No. 15-12-20040).

1. M. Zhu, X. Wang, C. Jiang, H. Xu, Q. Nie, P. Zhang, S. Dai, X. Shen, T. Xu, G. Tao, X. Zhang, Freely adjusted properties in Ge–S based chalcogenide glasses with iodine incorporation, Infrared Physics & Technology 69 (2015) 118–122.
2. V. Krasteva, D. Machewirth, G.H Sigel, $Pr^{3+}$-doped Ge–S–I glasses as candidate materials for 1.3 μm optical fiber amplifiers, Journal of Non-Crystalline Solids 213&214 (1997) 304–310.
3. A.P. Velmuzhov, A.A. Sibirkin, V.S. Shiryaev, M.F. Churbanov, A.I. Suchkov, A.M. Potapov, R.M. Shaposhnikov, V.G. Plotnichenko, V.V. Koltashev, A.D. Plekhovich, Preparation of Ge – Sb – Se – I glass system via volatile iodides, Journal of Non-Crystalline Solids 405 (2014) 100–103.

---

I-1-O-7

# The influence of PbO on spectra and thermo-optical properties of $Nd^{3+}$-doped phosphate laser glass

Q.W. Yin, L. Wen, D.B. He*
Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics, CAS, Shanghai, 201800, China
*Corresponding author: hdb798123@163.com

$Nd^{3+}$-doped phosphate glasses are widely used as host material in high energy laser device for its high energy storage ability. However, the poor thermal-mechanical properties of phosphate glasses limits its wide application in the high average power systems with some repetition rate. So it is important to improve the thermal-optical properties such as thermal optical coefficient and photoelastic coefficient to decrease the thermal distortion of laser glass by adjusting the compositions of glass.

Although the addition of PbO is benefit for improving photoelastic constants (PEC) of phosphate glasses, which has large polarizability[1],but the influence of PbO on the spectra of $Nd^{3+}$ ions in phosphate glass is seldom studied. In this paper, the $P_2O_5$-$K_2O$–$Al_2O_3$–(20-x)BaO-xPbO-$Nd_2O_3$ ($x$=0,3,6 mol) glass system has been melted and studied.

Optical properties of $Nd^{3+}$-doped phosphate glasses have been studied on the basis of the Judd–Ofelt theory. Emission cross section of $Nd^{3+}$ of three samples at 1.053 μm are $4.29\times10^{-20}$, $4.34\times10^{-20}$, $4.42\times10^{-20}$ cm$^2$, respectively, which shows that the replacement of BaO by PbO can improve the laser gain of $Nd^{3+}$-doped laser glass. The thermo-optic coefficient ($ds/dt$) of three samples are $-1.49\times10^{-6}$, $-1.65\times10^{-6}$, $-1.64\times10^{-6}$°C$^{-1}$, respectively, reveal that the replacement of BaO by PbO may have little influence on the thermo-optic coefficient of glass. The thermal expansion coefficient of three glass samples are respectively at $133.77\times10^{-6}$ to $134.47\times10^{-6}$°C$^{-1}$, which shows the little influence on the thermal properties.

Results shows that the replacement of BaO by PbO in phosphate glass can improve the laser and thermal-optical properties of laser glass.

1. Jaemin CHA, Mizuyo KAWANO, Journal of the Ceramic Society of Japan, **116** 1100-1103 (2008).

I-1-O-8

# Broadening of NIR emission from bismuth doped germanium glass melting in a controlled reducing atmosphere

C.-Z. Liu, J. Ruan*, J.-J. Han, and X.-J. Zhao
State Key Laboratory of Silicate Materials for Architectures (Wuhan University of Technology),
122 Luoshi Road, Wuhan 430070, China PR
Corresponding Author: jian_ruan@whut.edu.cn

Bi-doped glass with ultra-broadband near-infrared (NIR) emission is one of promising candidates for broadband fiber amplifier and tunable lasers in the wavelength region from 1000 nm to 1600 nm, covering both of the second and the third communication windows. In this study, bismuth doped germanium glasses are prepared by conventional melting-quenching method with a controlled reducing atmosphere for glass melting by using $Si_3N_4$ and BN additives. Broadening of NIR emission by the rising of efficient near infrared emission around 1460 nm~1500 nm was observed in the obtained glass samples, which show a characteristic broadband absorption band around 500 nm. The ratio of the emission around 1460 nm~1500 nm to the one around 1150 nm was studied as a factor of bismuth ion doping concentration, alkaline and alkaline earth ions species, and reducing additive content. Efficient emission around 1460 nm~1500 nm was only obtained in the samples doping with low bismuth concentration. Its origination was supposed to be bismuth clusters related. The reducing atmosphere controlled by $Si_3N_4$ and BN additives was found to be necessary for the formation of above mentioned bismuth-related centers, and it could be an efficient approach for fabricating bismuth-doped multi-component glass and fiber preform.

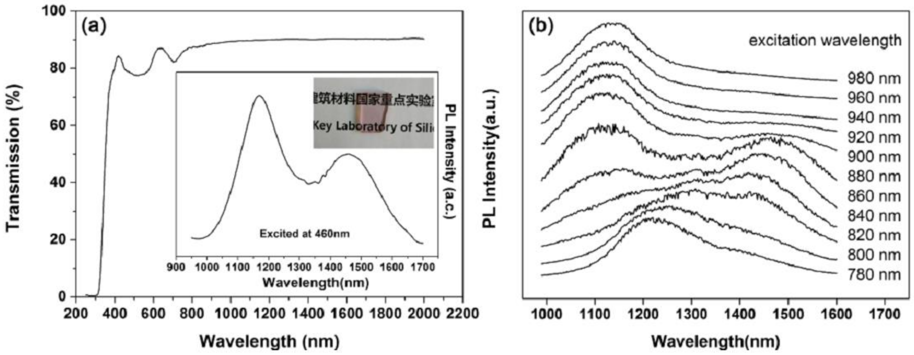


Figure 1 (a) Transmission spectrum of a glass sample with a thickness of ~2.2 mm, the inset shows its photograph and emission spectrum under excitation at 460 nm; (b) its NIR emission spectra under different excitation wavelengths.

Fig. 1(a) shows a glass sample with transmission around 90 % in the NIR wavelength region. Efficient emission consisted with two band were observed from it when excited at 460nm. FWHM of the emission band around 1470 nm reached 250 nm, which could cover the gap between the second window and the third window in optical communication.

Fig. 1(b) shows its excitation wavelength-dependent NIR emission. Three types of Bi-related active centers could be confirmed, which will be great helpful for fully understand the luminescent mechanism of Bi-doped glass and fibre.

1. E.M. Dianov. Bismuth-doped optical fibers: a new active medium for NIR lasers and amplifiers. SPIE LASE. International Society for Optics and Photonics, 2013:86010H-86010H-10.
2. M.Y. Peng, J.R. Qiu, D.P. Chen, et al. Bismuth- and aluminum-codoped germanium oxide glasses for super-broadband optical amplification. Optics Letters, 2004, 29(17):1998-2000.

# ISNOG 2016

## Tuesday, August, 23rd

## *Business Hall*

## Session I-2

**Session I-2: High-Purity Glasses, Special Glasses and Low-Loss Fibers**

I-2-inv 1

## Fabrication and characterization of novel multi-material chalcogenide glass fibers and fiber tapers for Mid-infrared SC generation

Shixun Dai*, Xunsi Wang, Peiqing Zhang, Yanan Sun, Hongya Ou, Baohua Luo
Laboratory of Infrared Material and Devices, Advanced Technology Research Institute, Ningbo University, Ningbo, 315211, China
*Corresponding email:daishixun@nbu.edu.cn

Chalcogenide glass fibers are excellent candidates for broadband supercontinuum (SC) generation due to their excellent MIR transparency and high third-order nonlinearity. In this work, we reports on the fabrication and characterization of two kinds of multi-material chalcogenide fiber with high numerical apertures (NAs). We fabricated multi-material $As_2Se_3$-$As_2S_3$ and $Ge_{15}Sb_{25}Se_{60}$-$Ge_{15}Sb_{20}Se_{65}$ chalcogenide fiber preforms via the modified one-step co-extrusion and rod-in-tube process, respectively. The preforms were drawn into multi- and single-mode fibers with high NAs (1.45 and 1.0), whose core/cladding diameters were 11/246 and 63/507 μm, respectively. The minimum loss of the single-mode $As_2Se_3$-$As_2S_3$fiber is about 5.2 dB/m at 5.8 μm. We experimentally demonstrated the SC generation in a 15-cm-long multi-material $As_2Se_3$-$As_2S_3$ chalcogenide taper with 1.9 μm core diameter and the ZDW was shifted to 3.3 μm. When pumping the taper with 100 fs short pulses at 3.4 μm, a 20 dB spectral of the generated SC spans from 1.5 μm to longer than 4.8 μm. By pumping a 20-cm-long $Ge_{15}Sb_{25}Se_{60}$-$Ge_{15}Sb_{20}Se_{65}$ fiber using 100 fs pulses at 5.0 μm, SC spanning from ~3.8 to ~8.6 μm with a dynamic range of ±20 dB was generated. In addition, $Ge_{15}Sb_{20}Se_{65}$ bare glass fiber with a diameter of 500 μm was fabricated, and then tapered with different tapering parameters through a modified resistance heating experimental platform with an aim to elucidate the effect of the tapering temperature, taping speed and taper length on the formation of the tapering structure and their performance.

I-2-inv 2

## Hollow-core revolver optical fibers

I.A. Bufetov, A.F. Kosolapov, A.D. Pryamikov
Fiber Optics Research Center, Russian Academy of Sciences, 38 Vavilov Street, 119333 Moscow, Russia;
iabuf@fo.gpi.ru

The optical properties and applications of low-loss revolver hollow-core optical fibers based on different glasses are reviewed.

Hollow-core glass fibers opened up new possibilities in the development of fiber optics [1]. The lowest optical loss so far (1.2 dB km$^{-1}$) is offered by so-called hollow-core photonic crystal fibers (HCPCFs), whose guidance properties are ensured by the photonic bandgap of a microstructured fiber cladding [2]. Another mechanism capable of ensuring guidance properties of a hollow core takes advantage of antiresonant reflection (similar to reflection from a Fabry–Perot interferometer; see e.g. a review by Poletti [3]). To confine light in hollow-core anti-resonant fibers (HC-ARFs), their core is surrounded by glass membranes identical in thickness, which is chosen such that interference of rays reflected from different membrane surfaces leads to a considerable increase in reflectivity for back-reflected light. As a result, the optical loss in the fiber decreases. The HC-ARFs differ from the HCPCFs in that a larger transmission bandwidth is possible, in combination with somewhat higher optical losses. The lowest optical loss in the HC-ARFs reported to date is 24 dB km$^{-1}$ at a core diameter Dc = 94 um [4]. Note that the optical loss in the HC-ARFs is inversely proportional to the third, or higher, power of Dc [3], so lower losses are much easier to achieve at larger core diameters.

A special place among the HC-ARFs is held by hollow-core revolver fibers with a reflective cladding formed by a single ring of capillaries (Fig.1).

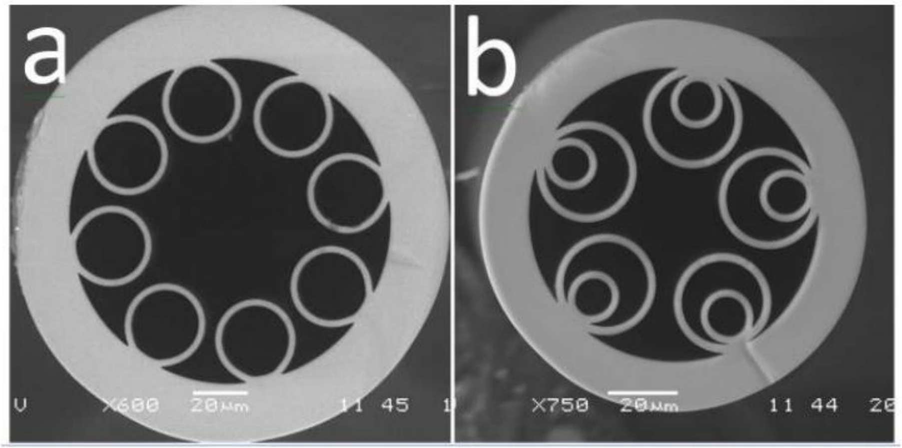


Fig.1. The cross section images of revolver fibers (RF): a) RF with single nontouching capillaries in the cladding [7]; b) RF with double nested capillaries [8].

Such a fiber design was first proposed in 2011 by Pryamikov et al. [5], who viewed it as a hollow-core fiber with a negative curvature of the core–cladding interface. Subsequently, this term was also applied to fibers with a hypocycloid-shaped core boundary [6] and with reflective cladding elements differing significantly in shape from circular capillaries [4]. The shape of such elements resembles a stylized image of an ice cream cone. Gladyshev et al. [7] proposed a particular name for hollow-core fibers with a reflective cladding in the form of a single ring of circular capillaries: hollow-core revolver fibers (HCRFs). Such fibers have a simple design, with a low fraction of light propagating in the fiber material (compared to that propagating through the hollow core) and insignificant dispersion in their transmission windows. The lowest optical loss obtained to date in the revolver fibers is at a level of 100 dB km$^{-1}$. Efficient Raman generation has been demonstrated in an HCRF on the 1.06 → 1.9 um vibrational transition of molecular hydrogen [7]. HCRF have been fabricated not only from v-SiO$_2$, but also from chalcogenide [9] and soft [10] glasses and even from PMMA [11]. Authors thank RFBR for support (grant #14-29-07176).

1. Russell P.St.J. Science, 299, 358 (2003).
2. Roberts P.J., Couny F., Sabert H., et al. Opt. Express, 13, 236 (2005).
3. Poletti F. Opt. Express, 22, 23807 (2014).
4. Yu F., Wadsworth W.J., Knight J.C. Opt. Express, 20, 11153 (2012).
5. Pryamikov A.D., Biriukov A.S., Kosolapov A.F., et al. Opt. Express, 19, 1441 (2011).
6. Wang Y.Y., Wheeler N.V., Couny F., et al. Opt. Lett., 36, 669 (2011).
7. Gladyshev A.V., Kolyadin A.N., Kosolapov A.F., et al. Quantum Electron., 45, 807 (2015).
8. A.F. Kosolapov, G.K. Alagashev, A.N. Kolyadin, et al. Quantum Electron., 46, 267 (2016).
9. Kosolapov A.F., Pryamikov A.D., Biriukov A.S. et al. Opt. Express, 19, 25723 (2011).
10. Cubillas A.M., Jiang X., Euser T.G. et al. Proc. of SPIE, 9157, 91573N (2014).
11. Setti V., Vincetti L., Argyros A. Opt. Express, 21, 3388 (2013).

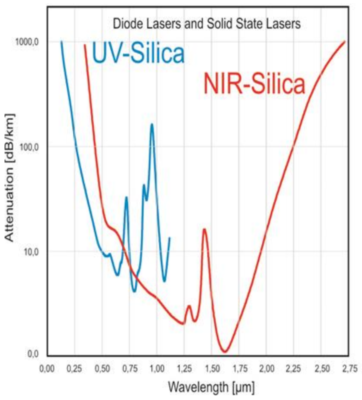
I-2-inv 3

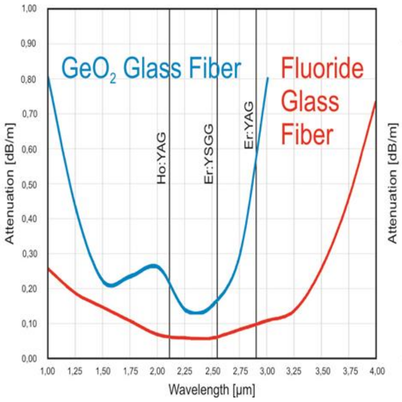
# Mid infrared fiber optics – review of technologies and key applications

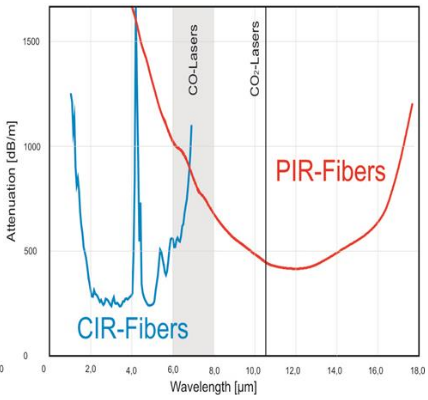
Viacheslav Artyushenko
art photonics GmbH, Rudower Chaussee 46, 12489 Berlin, Germany

Well known fused silica fibers possess by high transmission in a broad spectral range from 180nm up to 2.2 µm and can be used for Near-InfraRed (NIR-) spectroscopy or for delivery of power for Diode, Nd- or Ho-lasers. As their transmission is limited for a longer wavelengths by fundamental multi-phonon absorption wing – the large family of IR-materials was investigated to develop fibers for Mid InfraRed (MIR) range, i.e. for 2-16 µm range.

Strong demand for various applications in spectroscopy, laser power delivery, pyrometry sensing and IR-imaging in “finger-print” Mid IR-range 2-16 µm has initiated >30 years ago an intensive development of new types of IR-glass fibers, Hollow Waveguides and Polycrystalline IR-fibers (PIR-fibers) extruded from Silver Halide solid solutions. Progress in technology for all these key groups of Mid IR-fiber optics will be reviewed for comparison.







The 2nd part of review will cover key areas of applications for IR-glass and polycrystalline fiber optics vs Hollow Waveguides, including comparison of their pragmatic exploitation parameters when they are assembled as:

1) Laser cables for power delivery of IR-lasers like Er:YAG; CO- & CO2-laser, etc.;

2) Spectroscopy probes used for reaction/ process monitoring in lab/ industry and for biomedical diagnostics;

3) IR-endoscopes or bundles to enable non-contact temperature monitoring and flexible IR-imaging.

Finally, the most advanced laser, spectroscopy and sensing IR-fiber systems will be reviewed with the analysis of new development trends and estimation of the growing market needs.

I-2-inv 4

# Recent advances and trends in development of chalcogenide glasses for passive and active fiber optics

Vladimir Shiryaev
G.G.Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences,
49 Tropinin Str., 603950 Nizhny Novgorod, Russia
E-mail: shiryaev@ihps.nnov.ru

Chalcogenide glasses due to their optical and physico-chemical properties are promising materials for the production of optical fibers for the near and mid-infrared range. There are a lot of chalcogenide glasses based on sulfides, selenides and tellurides of arsenic, germanium and other elements used or developed for various functional passive and active applications, such as a transfer of mid-IR radiation, IR monitoring, low-temperature pyrometry, analytical remote spectroscopy, IR fiber lasers and amplifiers, high-speed switches, supercontinuum generators, etc.

The glasses for mid-IR fiber optics must have a wide spectral range of transparency, low content of limiting impurities, good stability against crystallization and good mechanical strength. The additional requirements to active glasses include the high value of nonlinear refractive index, low coefficient of two-photon absorption and intensive photoluminescence in the mid-IR range.

Development of chalcogenide glasses for IR fiber optics can be carried out in the following directions: 1) production of chalcogenide glasses with ultra-low content of impurities and optical fibers with low optical losses; 2) fabrication of solid-core microstructured fibers (to obtain controlled dispersion, endleely single-mode operation, supercontinuum geteration, and soliton propagation); 3) production of hollow-core microstructured fibers for IR radiation power delivery and sensors; 4) preparation of fibers with a wide range of transparency - from 1 to 25 μm (based on Te-rich glasses); 5) preparation of luminescent glasses doped with activators for creation of new pump sources, amplifiers and sensor devices; 6) use of high non-linearity of glasses for creation of generators of supercontinuum and nonlinear devices operating in the mid-infrared.

The report gives the current status on preparation and investigation of chalcogenide glasses and fibers and ways to improve their optical properties and functional characteristics. The methods for preparation of high-purity As-Se, Ge-As-S, As-Se-Te, As-S-Se, Ge-Sb-Se, and Ge-As-Se-Te glasses, including the samples doped with rare earth elements, have been developed [1, 2]. To synthesize the high-purity glass samples, the multi-stage technique based on the chemical distillation purification of glass and components, as well as the chemical vapor transport reaction technique to purify and to load the individual Ga or In metals in the glass matrix have been developed. The optical transmittance of the produced glasses, their structure, physico-chemical, optical linear and non-linear properties and the content of limiting impurities were determined. Glass compositions with low tendency to crystallization were established. The prepared glass samples have a record low content of limiting impurities: oxygen - <0.1 ppm wt, carbon - <0.5 ppm wt, hydrogen - <0.02 ppm wt, silicon - <0.1 ppm wt, transition metals - <0.05 ppm wt. Using the "rod-in-tube" and “double crucible” drawing methods, the multimode and single-mode optical fibers were prepared; their optical and mechanical properties were investigated. The minimum optical losses in multimode As-Se-Te glass fiber were 150 dB/km at a wavelength of 6.6 μm, and ones in As-Se glass fiber were <50 dB/km at 2.7 μm. Minimum optical losses in Pr(3+)-doped Ge-As-Ga-Se glass fiber were <1 dB/m at pumping wavelengths and in the spectral range of 5.8-6.5 μm. The prepared doped glasses and fibers exhibit an intensive photoluminescence in the spectral ranges of 1.3-2.5 and 3.5-5.5 μm [3].

Up-to-date level of optical, mechanical and emission characteristics of chalcogenide glass fibers are sufficient for their use in various passive and active devices for mid-IR transmitting and generation.

This work was supported by the Russian Science Foundation (Russia, Grant No. 16-13-10251).

1. Shiryaev V.S., Churbanov M.F. J. Non-Crystalline Solids, 377 (2013) 225.
2. Shiryaev V.S., Churbanov M.F., et.al., Optical Materials, 4820 (15) 222.
3. Karaksina E.V., Shiryaev V.S., Kotereva T.V., Churbanov M.F., J. Luminescence, 170 (2016) 37

I-2-inv 5

# Towards chalcogenide glass fibers with intrinsic optical losses

M.F. Churbanov, I.V.Skripachev, G.E.Snopatin, V.G. Plotnichenko
Institute of Chemistry of High Purity Substances of RAS
49, Tropinina Str., 603950, GSP-75, Nizhny Novgorod, Russia,
e-mail: churbanov@ihps.nnov.ru

The first report on optical fibers from chalcogenide glasses refers to 1965 [1]. The optical fibers from $As_2S_3$ with length of 30 cm and with core diameter of 5- 200 μm at ~10 % transmission in the range of 1.5÷6.5 μm were used to fabricate the irregular bundle for transmission of optical image. High transparency in the middle IR-range is the property determining various functional applications of chalcogenide optical fibers. Fabrication of chalcogenide optical fibers with optical losses equal or close to intrinsic losses is one of the main directions of development conducted for 50 years.

The intrinsic optical losses comprise the contributions from different constituents of interaction of radiation with optical medium. These are the electron and multi-phonon absorption, free-carrier charge absorption, scattering on fluctuations of density and concentration of components [2-4]. Calculation of losses with different physical models gives the values lying in sufficiently broad range (from hundredth parts up to the units of dB/km) for the same glass. The exact value of intrinsic optical losses is important for practice and for comparison of conformity of theoretical and actual structure of glasses.

Extrinsic, excessive losses are due to absorption of radiation by impurities, by scattering on optical inhomogeneities in glass and on the defects of waveguide structure of optical fiber. The lowest losses, attained up to the present time in multi-mode optical fibers for the majority of chalcogenide glasses, are in the range of 40-100 dB/km [4-6]. There is a difference by 10-100 times between the theoretical and attained losses. They are relatively close in optical fibers from $As_2S_3$: 0.06-5 dB/km [2, 4] and 12 dB/km, respectively. At the present time the length of samples of optical fibers from $As_2S_3$, used to measure the losses, is 150-200 m.

The level of excessive optical losses is determined by the content of impurities in the initial substances, by the contamination effect of apparatus material and environment in the process of fabrication of glasses and optical fibers, by crystallization and microliquation of glasses, by perfection of technology for preparation of glasses and optical fibers. A relative contribution and nature of manifestation of these factors are specific to each type of glass and optical fiber. The general tasks are the invrease in chemical and phase purity of glasses. The further development of the physical and chemical fundamentals of all stages of the used processes is required which provide the fabrication of glasses with the content of limiting impurities of 0.1-1 ppb wt. and of heterophase micro-impurities of 0.1–10 cm$^3$. The report gives the approaches developed for solution of these tasks in view of the nature of each glass as well as new results on preparation of more pure chalcogenide glasses and optical fibers with low optical losses.

1. N.S.Kapany, R.J.Simms, Infrared Physics, 1965, v.5, pp 69-80.
2. E.M.Dianov, M.Yu.Petrov, V.K.Sysoyev, V.G.Plotnichenko, Kvantovaya Electronika (Rus Journal), 1982, v.9, №4, pp 798-800.

3. M.E.Lines, J.Appl.Phys., 1984, v.55, №11, p.4058.
4. G.E.Snopatin, V.S.Shiryaev, V.G.Plotnichenko, e.a. Inorganic Materials, 2009, v.45, №13, pp. 1439-1460.
5. V.S.Shiryaev, M.F.Churbanov, G.E.Snopatin, F.Chenard, Optical Materials, 2015, v.48, pp. 222-225.
6. Z.Tang, V.S.Shiryaev, D.Furmiss, e.a., Optical Materials Express, 2015, 5(8), 1722-1737.

I-2 O-1

# Specifics of spectral loss measurment in IR fibers

Plotnichenko V.G.[1], Sokolov V.O.[1], Kryukova E.B.[1], Snopatin G.E.[2], Skripachev I.V.[2], Churbanov M.F.[2]
[1]Fiber Optics Research Center of the Russian Academy of Sciences, Vavilova St. 38, 119333 Moscow, Russia, e-mail: victor@fo.gpi.ru
[2]G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, Tropinina st. 49, 603950 Nizhny Novgorod, Russia

Main error sources and their contribution to the total error of measuring the optical loss spectrum by cut-back method in the middle IR range (2-20 μm) for multimode optical fibers made from materials with a high (2 to 4) refractive index value are analyzed.

It is shown that in case of insufficient fiber length, a neglect of the refractive index values leads to a systematic overestimation of the measured optical losses: the higher the refractive index of fiber core material, the greater is an overestimation. In measurements the greatest contribution to the total error is typically introduced by a preparation quality of fiber ends and by the signal-to-noise ratio after the initial fiber piece.

The dependence of the experimental setup parameters (i.e. spectral dependence of signal-to-noise ratio and surface quality of the ends), as well as the optical fiber lengths used in measurements, on the determination accuracy of fiber losses is analyzed for optical fibers from chalcogenide glasses, as an example. Figure presents the dependence of the optical loss ratio $\alpha_0/\alpha$, calculated with taking into account the refractive index values α of the core material and without $\alpha_0$, on the optical fiber loss at different ratios of initial/final fiber lengths (2/1, 10/1 and 100/1). It is shown that the ratio $\alpha_0/\alpha$ grows with increasing the refractive index of the fiber core material.

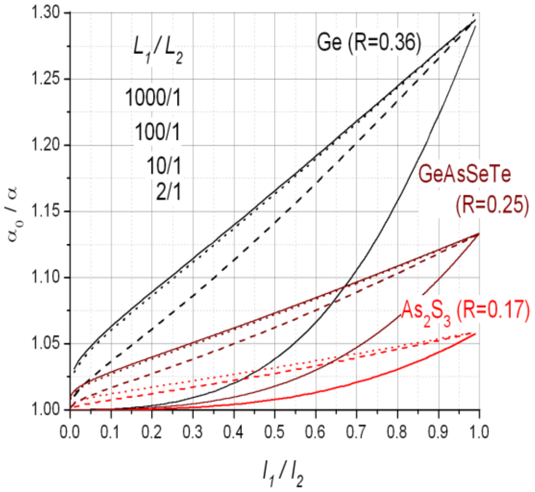


Figure. The ratio of calculated optical losses when accounting for single $\alpha_0$ and multiple α reflections at the optical fiber ends made from crystalline Ge ($n$ = 4), and chalcogenide GeSeTe ($n$ = 3) and $As_2S_3$ ($n$ = 2.4) glasses from measured $I_1/I_2$ ratio of the signal intensities after the initial and cut optical fiber pieces.

This work was supported by Russian Science Foundation (RSF), grant № 15-12-20040

# ISNOG 2016

## Tuesday, August, 23rd

## *Hall Standard 1*

## Session II

**Session II: Glass Transition, Relaxation in Glasses and Glass-forming Liquids, Mechanical Properties**

II-O-1

# Crystallization and relaxation behavior of $Ge_{11}Ga_{11}Te_{78}$ infrared glass

D. Brandová, R. Svoboda, J. Málek
Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic
E-mail of the corresponding author: daniela.brandova@student.upce.cz

The non – isothermal crystallization kinetics and structural relaxation kinetics of $Ge_{11}Ga_{11}Te_{78}$ infrared glass were studied by differential scanning calorimetry (DSC) and by thermomechanical analysis (TMA). This is first study of thermal behavior of Ge – Ga – Te chalcogenide material performed in such detail. The complexity of crystallization process evinced and was treated by deconvolution procedure using Fraser – Suzuki (FS) function. [1] The apparent activation energy of crystallization E for each set of DSC and TMA curves were estimated by the Kissinger [2] and Kissinger – Akahira – Sunose equations. [3] In case of DSC curves the values of maximum of crystallization peak $T_p$ were used, while for the evaluation of crystallization activation energies from the TMA measurements the extrapolated initial crystallization temperatures $T_{ic}$ were used. The comparison of the evaluated activation energies for DSC and TMA data shows the similar trend and confirms the fact that the viscous flow during glass softening is ceased by the initial surface formation of Te crystallites. In addition, direct comparison of the DSC and TMA data reveals that only a narrow temperature window exists between the start of the glass softening and first formation of Te crystallites – this confirms the reported [4] difficulties regarding commercial applicability of Ge-Ga-Te glasses.

In the second step of kinetic analysis the appropriate kinetic model was chosen. The studied chalcogenide glass exhibited two overlapping crystallization peaks. The initial crystallization process was described using the nucleation – growth Johnson – Mehl – Avrami [5] kinetic model and corresponds to the surface precipitation of tellurium. The following crystallization process was described by autocatalytic Sestak – Berggren [6] model and corresponds to the growth of GeTe and $Ga_2Te_5$ crystalline phases. The suitability of the pre – selected models was confirmed by additional testing of various different models. Based on the XRD data, the first crystallization peak corresponds to the formation of hexagonal Te (P3121) and the second crystallization peak corresponds to the formation of hexagonal $Ga_2Te_5$ (P3m1) and rhomboedral GeTe (R3m).

The structural relaxation kinetics was described in terms of Tool – Narayanaswamy – Moynihan model and operates in region of glass transition. The DSC measurements worked with constant – ratio (CR) and constant – heating rate (CHR) cycles. The TMA relaxation experiments were then based on the simple dependence of $T_g$ on cooling rate $q^-$; this type of TMA structural relaxation measurements was recently used to study relaxation behavior in several other chalcogenide glasses [7]. The both methods exhibited similar activation energies.

This work has been supported by the Czech Science Foundation under project No. 16-10562S and by the SGS_2016_014.

1. Perejón A, Sánchéz-Jiménez PE, Criado JM, Pérez-Maqueda LA. Kinetic analysis of complex solid-state reactions – a new deconvolution procedure. J Phys Chem B 2011;115:1780-91.
2. H.E. Kissinger. Anal.Chem. 29 (1957) 1702.
3. M.J. Starink, Thermochim. Acta 404 (2003) 163.
4. S. Danto, P. Houizot, C. Boussard-Pledel, X. H. Zhang, F. Smektala, J. Lucas, Adv. Funct. Mater. 16 (2006) 1847.
5. Avrami M. Kinetics of phase change I – General theory. J Chem Phys. 1939;7:1103–12.
6. Šesták J. Thermophysical Properties of Solids, Their Measurements and Theoretical Analysis. Elsevier: Amsterdam; 1984.
7. R. Svoboda, D. Brandová, J. Málek, J. Non-Cryst. Sol. 432 (2016) 493.

II-O-2

# Study of ionic properties by electrochemical impedance spectroscopy and radioactive tracer diffusion

M. Fraenkl[1], K. Shimakawa[2], Jan M. Macak[3], T. Wágner[1,3]
[1]Department of General and Inorganic Chemistry, University of Pardubice,
Studentská 573, Pardubice 532 10, Czech Republic
[2]Joint Laboratory of Solid State Chemistry of Inst. of Macromolecular Chem. of the AS CR, v.v i., Prague and University of Pardubice, Studentska 95, 532 10 Pardubice, Czech Republic.
[3]Center of Materials and Nanotechnologies, Faculty of Chemical Technology, University of Pardubice, Legii sq. 565, 53210 Pardubice, Czech Republic

Solid-state ion conductors are an important class of materials. These materials attract considerable interest due to their potential applications in the field of electrolytes in batteries and fuel cells, gas sensors, etc [1, 2].

Electrochemical impedance spectroscopy (EIS) is powerful method for understanding dynamics of ionic transport. For analysis of impedance spectra we use model based on Dyre's random walk theory [3-6]. Directly obtained information are hopping times of mobile ions. Diffusion coefficient is calculated.

Radioactive tracer diffusion is macroscopic method which provide us diffusion coefficient [7].

Case example is chalcogenide glass $GeSb_2S_5$ doped with Ag. The study shows, how helpful this approach can be to understand ionic transport mechanism.

The authors thank to project KONTAKT II (CR-USA) LH14059 for financial support.

1. S. Horike, D. Umeyama, and S. Kitagawa, Accounts Chem. Res. 46, (2013) 2376.
2. R. J. Klein, S. Zhang, S. Dou, B. H. Jones, R. H. Colby, and J. Runt, J. Chem. Phys. 124, (2006) 144903.
3. S. Stehlik, K. Shimakawa, T. Wagner and M. Frumar, J. Phys. D: Appl. Phys. 45 (2012) 205304.
4. D. S. Patil, K. Shimakawa, V. Zima, J. Macak, and T. Wagner, J. Appl.Phys. 113 (2013) 143705.
5. D. S. Patil, K. Shimakawa, V. Zima, and T. Wagner, J. Appl. Physics 115 (2014) 143707.
6. J. C. Dyre, J. Appl. Phys. 64 (1988) 2456.
7. E. Bychkov, Solid State Ionics 136–137 (2000) 1111–1118.

II-O-3

# Viscous behavior of chalcogenide materials

P. Koštál[1], T. Hofírek[2], J. Málek[2]
[1]Department of Inorganic Technology, University of Pardubice, Doubravice 41, Pardubice 532 10,
Czech Republic,
[2]Department of Physical Chemistry, University of Pardubice, Studentská 573, Pardubice 532 10,
Czech Republic
e-mail: petr.kostal@upce.cz

Chalcogenide glasses are interesting materials which have been widely studied since 1960s. Their properties designate them as suitable materials for various interesting applications, e.g. optical lenses and fibers, image-sensors, rewritable memory discs or non-volatile PCRAM memory devices [1, 2]. Knowledge of viscous behaviors of amorphous materials is very important. This basic physical property is essential for technology and production of glassy materials. Viscosity is also directly connected with structural relaxation of glass and with crystal growth in undercooled melt. Structural relaxation is very slow rearrangement of thermodynamically unstable glass toward equilibrium and it is in fact very slow flow of material and hence it is influenced by viscosity. Cold crystallization process is influenced by diffusion which is determined also by viscosity. This crystallization process which takes place in undercooled melt region also strongly influences the flow of this undercooled melt in low viscosity region. Growing crystals cause that viscosity is immeasurable in this region. The interpolation of viscosity data, measured above (higher region of undercooled melt and glass) and under (melt) this immeasurable region, is then necessary for determination of viscosity. The appropriate viscosity theory is necessary for this interpolation [3].

We have studied viscous behavior of different chalcogenide materials in our laboratory more than fifteen years [4]. We have used penetration, parallel-plate and rotating bob methods for these studies. Penetration method is based on measuring of penetration depth or rate of indenter which is pushed into sample by constant force. The penetration method can be used to measure viscosity in the range of $10^7$ - $10^{13}$ Pa.s. We have used hemispherical [5] and cylindrical [6, 7] shapes of indenter. Parallel-plate method [7] is based on measuring of time dependence of height of sample which is squeezed between two parallel plates. This method can be used to measure viscosity in the range of $10^4$ - $10^{10}$ Pa.s. In the case of rotating bob method the stainless steel bob is immersed into measured liquid and makes rotating motion with constant angular velocity. The moment of force produced by viscosity of liquid is measured by use of torsion spring.

We also made a broad literature research which was focused on chalcogenide materials and measuring methods of their viscosity. Knowledge of all published data combined with our measurements allows us to make several interesting comparisons, e.g. correlations of viscosity glass transition temperatures $T_{12}$ or kinetic fragilities.

This work was supported by the Czech Science Foundation under project No. 16-10562S and by IGA University of Pardubice under the research project SGS_2016_014.

1. G.S. Murugan, Photonic Glasses and Glass-Ceramics, (2010).
2. J. L. Adam, X. Zhang, Chalcogenide glasses, Prepartion, properties and application, (2014).
3. M. I. Ojovan, Phys. Chem. Glasses-B, 53 (2012) 143-150.
4. J. Malek, Thermochim. Acta, 311 (1998) 183-198.
5. R. W. Douglas, W.L. Armstrong, E.J. P., H. D., Glass Technol., 6 (1965) 52-55.
6. S.V. Nemilov, G.T. Petrovskii, J. Appl. Chem.-USSR+, 36 (1963) 222-225.
7. F. Q. Yang, J.C.M. Li, J. Non-Cryst. Solids, 212 (1997) 126-135.
8. G. J. Dienes, H. F. Klemm, J Appl, Phys,, 17 (1946) 458-471.

II-O-4

# Nanocrystallization of RE–doped tellurite glasses

V.K. Goncharuk[1,2], V.Ya. Kavun[1], V.E. Silant’ev[1], A.A. Mamaev[1], P.A. Starodubtsev[2], I.G. Maslennikova[1]
[1] Institute of Chemistry, FEB RAS, Vladivostok, Russia
[2] Pacific S.O. Makarov Higher Naval School, Vladivostok, Russia
masl@ich.dvo.ru

At present there is an increasing interest to the tellurite glasses due to a possibility to use them in the optical data recording and communication systems [1]. The tellurite glasses have the highest linear and nonlinear refractive indexes among the oxide glasses and possess high transparency in the range from near UV to IR (0.35 – 6 μm). They combine chemical stability, mechanical strength, high resistance to corrosion and atmospheric moisture. The high solubility of rare-earth (RE) metals and relatively low phonon energy make it possible to develop lasers based on the tellurite glasses [2].

Nonocrystallization of the (100-x-y)$TeO_2$-xPbO·$P_2O_5$-y$PbF_2$ : z$MF_3$ (M= Er, Eu, Nd; x=42.5-30, y=5-30 and z=0.5 mol. %; for $ErF_3$ z=0.5-3.0 mol. %) glasses were investigated. It has been found that doping rare-earth (III) fluorides promoted nucleation in the bulk glasses. The sizes of generated particles were about 2–5 nanometers and their shapes were close to spherical (Fig. 1). The growth rate of crystallites depended on the rare earth fluoride dopes and lead fluoride content. $MF_3$ plays the role of nucleation agent in glasses. Increasing of the $ErF_3$ doped results in the growing amount of nucleation centers, whereas increasing of the $PbF_2$ content results in growing particle dimensions. Glass forming rate also effects the particle size. XRD data confirmed amorphous structures of the glass samples. According to luminescence data increasing the $PbF_2$ and rare-earth(III) fluorides concentrations led to rise luminescence intensity of both neodymium(III) and erbium(III) in the IR range and europium(III) in the visible range. Increasing of luminescence intensity evidences that crystallite structures appear in glass bulk and rare-earth ions segregate into crystallite particles.

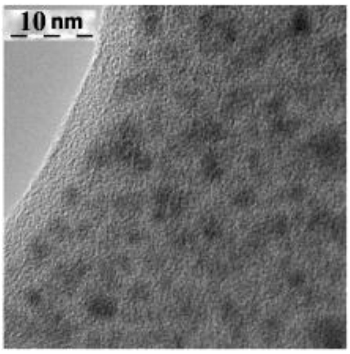


Figure 1. TEM image of the 40$TeO_2$-30PbO $P_2O_5$-30$PbF_2$ : 0.5$ErF_3$ glass.

The heat treatment of the glasses contained of 5–10 mol. % of $PbF_2$ during 1–3 hours at temperature of about $T_x$ promotes the glass ceramic formation, where the crystalline phase is $Pb_2P_2O_7$. Samples remained transparent up to 2 hours of heat treatment. After 3 hours they became opaque. Heat treatment of the investigated glasses at suitable conditions enables to produce transparent glass ceramics.

1. A. Jha, B. Richards, G. Jose, et al., Review on structural, thermal, optical and spectroscopic properties of tellurium oxide based glasses for fibre optic and waveguide applications, Int. Mater. Rev., 57 (2012) 357−382.
2. S. Zhao, X. Wang, D. Fang, et al., Spectroscopic properties and thermal stability of $Er^{3+}$-doped tungsten-tellurite glass for waveguide amplifier application, J. Alloys Compd., 427 (2006) 243–246.

II-O-5

# The effect of crystallization on the luminescent properties of bismuth-doped barium gallium germanate glasses

Pynenkov A.A.[1], Nishchev K.N.[1], Kyashkin V.M.[1], Firstov S.V.[2]
[1]N.P.Ogarev Mordovia State University, Saransk
[2]Fiber Optics Research Center of the Russian Academy of Sciences, Moscow
alekspyn@yandex.ru

The optical materials doped with bismuth are promising active media for wideband optical amplifiers and lasers operating in the near infrared wavelength range [1]. That is why the investigation of this type of active media is of great interest.

In this summary we report the results of a comparative study of the luminescent properties of Bi-doped barium gallium germanate glasses and glass-ceramics of the sa me chemical composition.

The investigated glasses with compositions of 14BaO – 2 $Ga_2O_3$ – (84-$x$) $GeO_2$ – $x$$Bi_2O_3$ ($x$=0-5) were fabricated by the conventional melting-quenching method. The glasses were synthesized in air atmosphere. The glass-ceramics were obtained from the sintered glass samples by high-temperature annealing process with different treatment times. In this case, the annealing temperature was ~650 $^{o}$C close to the crystallization temperature of the glass. The parameters of crystalline phase formed in glasses were analyzed by X-ray diffractometer Empyrean (PANanalytical). The luminescence spectra were recorded using a spectrofluorimeter FLSP920 (Edinburgh Instruments).

Fig. 1 shows the luminescence spectra of glass and grass-ceramic excited at the wavelength of 450 nm. Two bands peaked at ~820 nm and ~1270 nm are characteristic for Bi-doped glasses. A single broad luminescence band with maximum near 850 nm was detected in the glass-ceramics. It should be noted that luminescence intensity in the range of ~820-850 nm substantially raised with increase of the crystalline phase whereas the intensity of the band at 1270 nm region decreased. We suggest that this effect is probably caused by a structural modification of local environment of a Bi ion emitting in near IR region. Taking into account the structural glass-ceramic parameters identified by means of X-ray analysis, the model of the crystalline phase structure containing Bi ions was developed.

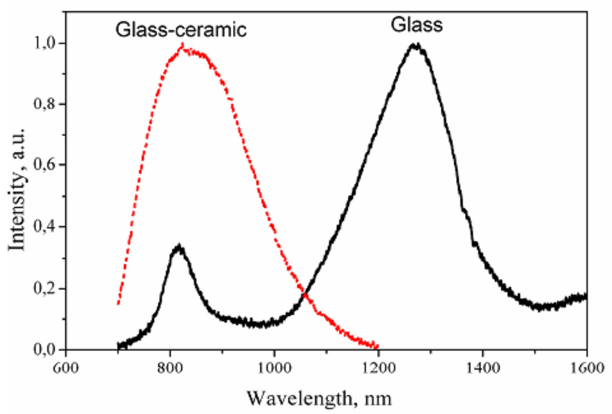


Fig.1. Luminescence spectra of glass and glass-ceramic at the excitation λ=450 nm.

1. I. A. Bufetov, M. A. Melkumov, S. V. Firstov, K. E. Riumkin, A. V. Shubin, V. F. Khopin, A. N. Guryanov, and E. M. Dianov, “Bi-Doped Optical Fibers and Fiber Lasers,” IEEE J Sel. Top. Quant. 20(5), 0903815 (2014).

# ISNOG 2016

Monday, August, 22nd

***Hall Standard 1***

# Session III

**Session III: Modeling of Glass Structure; Glass,**

**Surface and Interfaces; Structure and Properties**

III-inv 1

# Local modification of glass structure: from nanogratings to crystalline waveguides

V.N. Sigaev[1], S.V. Lotarev[1], S.S. Fedotov[1], A.S. Lipatyev[1], T.O. Lipatyeva[1], P.G. Kazansky[1,2]
[1]International Center of Laser Technology, D. Mendeleyev University of Chemical Technology, Miusskaya Sq., Moscow 125047, Russia
[2]Optoelectronics Research Centre, University of Southampton, Southampton SO17 1BJ, United Kingdom
vlad.sigaev@gmail.com

Depending on conditions of femtosecond (FS) laser beam exposure, the glass structure can be modified in the micron and submicron scale by significantly different ways forming amorphous ranges with changed refractive index, birefringent microdomains (nanogratings), glass-ceramic or fully crystalline fragments of different architecture (waveguides, splitters, gratings, etc.).

Studies of nanogratings have been concentrated mainly on silica glass so far, while information about features of interaction of FS beam with multicomponent glasses is very limited. Laser writing of amorphous waveguides in glasses was demonstrated scores of times whereas there is the only article reporting the waveguide properties of crystalline lines written in the bulk of a glass [1]. In general, research in this area is at an early stage.

In this work, using a FS ytterbium laser TETA (wavelength 1030 nm, pulse duration 290 fs, pulse energy up to 0.1 mJ, pulse repetition frequency up to 100 kHz) and PHAROS laser (wavelength 1030 nm, pulse duration of 280 fs to 10 ps, pulse energy up to 0.2 mJ, pulse repetition frequency up to 500 kHz) the study of a wide variety of oxide glasses was carried out and conditions of formation of nanogratings and their thermal stability were described.

Literature data on the formation of nanogratings in silica glass, glassy germanium dioxide and industrial borosilicate glasses were compared and the possibility of modifying the structure of glasses in alkali silicate, borosilicate and borate systems by the FS laser radiation was examined with the aim to clarify conditions for the formation of birefringent gratings.

Correlations between the degree of connectivity of the glass-forming network and the FS laser beam parameters that forms nanogratings were established. The formation of nanogratings with a detectable phase shift in multicomponent glasses is found to require much more FS pulses as compared to silica glass. This is obviously due to prolonged redistribution of mobile cations inside the nanogratings.

Studies of glass crystallization under FS laser radiation have been carried out mainly for glass compositions exactly corresponding to that of the growing crystal. Higher stability of the FS laser crystallization of glasses is shown to achieve for glass compositions deviating from the composition of the growing crystals. It was demonstrated for lanthanum borogermanate (LBG) glasses crystallizing with formation of ferroelectric stillwellite-like phase $LaBGeO_5$. These glasses are characterized by lower crystallization ability and can be obtained with a high degree of optical homogeneity facilitating formation of more uniform crystalline channel by FS laser beam. Method of local crystallization of glasses consisting in the formation of the seed crystal by a stationary FS laser beam with a uniformly increasing pulse energy was proposed specifically for glasses with low crystallization ability.

Applying FS laser beam with elliptical cross-section of the waist enables writing $LaBGeO_5$ crystalline waveguides of very small thickness (up to 1.5 $\mu$m) in the bulk of LBG glasses. Optical losses of crystalline and amorphous multimode waveguides in the bulk of LBG glasses prepared by us were not more than 1.6 and 0.95 dB/cm at the wavelength of 633 nm, respectively.

Taking into account promising pyroelectric properties of $LaBGeO_5$ crystals, arrays of polycrystalline channels penetrating the LBG glass plate were fabricated by FS laser beam.

The work was financially supported by Ministry of Education and Science of Russia (grant 14.Z50.31.0009) and Russian Foundation of Basic Research (grants 14-03-00931, 16-03-00541 and 16-33-01050).

1. Stone A. et al. Scientific reports, 2015, 5, 10391.

III-O-1

# Structure and properties of telluride glasses by means of molecular dynamics and solid-state NMR

L. Bouëssel du Bourg[1], L. Le Pollès[1], C. Roiland[2], M. Deschamps[3], B. Bureau[2], T. Bataille[1], C. Gonçalves[2], V. Nazabal[2], C. Pickard[4], E. Furet[1]
[1]Institut des Sciences Chimiques de Rennes - UMR 6226 - Ecole Nationale Supérieure de Chimie de Rennes - 11, allée de Beaulieu, 35708 Rennes Cedex 7, France
[2]Institut des Sciences Chimiques de Rennes - UMR 6226 - Université de Rennes 1 - av. du Général Leclerc, 35042 Rennes Cedex, France
[3]CEMHTI - CNRS UPR 3079 - 1D av. de la Recherche Scientifique, 45071 Orléans Cedex 2, France
[4]TCM Group, Cavendish Laboratory, 19 JJ Thomson Avenue, Cambridge, CB3 0HE UK
eric.furet@ensc-rennes.fr

Chalcogenide glasses have been extensively studied over the past decades due to the wide spectrum of physical properties exhibited (high linear and non-linear refraction indices, reversible amorphous-to-crystal transitions, thermoelectric properties,…) [1]. Among them, they possess large infrared transparency windows that extend far beyond the two atmospheric bands (3-5 μm & 8-12 μm – Fig. 1) and cover the vibrational signatures of most molecules. Such features have paved the way to various photonic-related applications, such has remote sensing/*in vivo* investigations by *fiber evanescent wave spectroscopy* or low cost thermal imaging.

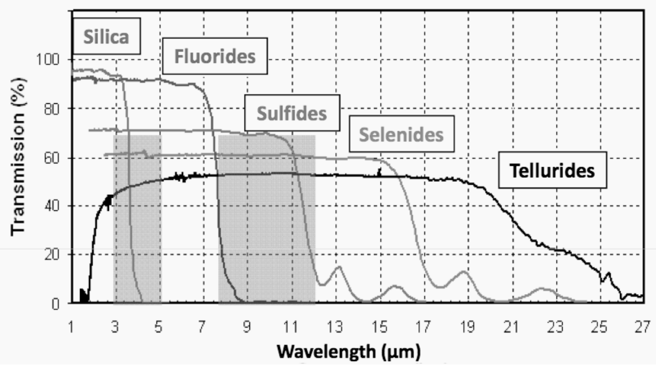


Figure 1. Typical transmittance spectra of silica, fluorides and chalcogenides bulk glasses. The atmospheric transparency windows are depicted by colored orange boxes

The subset of tellurium materials are known to exhibit the largest transparency windows. For example, the prototypical $GeTe_4$ glass transmits beyond 20 μm [2]. On the other hand, their synthesis is complicated, because they are prone to demixing and devitrification processes. Addition of selenium helps to reduce these difficulties, while simultaneously preserving the large IR transparency window of the $GeTe_4$ parent composition. In order to rationalize the impact of Se in these glasses, solid-state NMR is a helpful tool, being sensible to local order. However, $^{77}$Se, $^{73}$Ge and $^{125}$Te isotopes are challenging nuclei due to both their low gyromagnetic coefficients ($|\gamma| < 10^6$ rad.s$^{-1}$.T$^{-1}$) and natural abundances (< 8 %), as well as the strong quadripolar coupling in the case of $^{73}$Ge.

In this context, we wish to present results of recent investigations that we have carried out on Ge-Te and Ge-Te-Se glasses, by combining solid-state NMR measurements and NMR parameters calculations on *in silico* samples produced by molecular dynamics simulations [3].

This work is funded by the French National Research Agency (ANR), project ANR-14-CE07-0013

1. X. H. Zhang, B. Bureau, P. Lucas, C. Boussard-Pledel, J. Lucas, Chemistry European Journal 2008, 14, 432.
2. B. Bureau, S. Danto, H. L. Ma, C. Boussard-Plédel, X. H. Zhang, J. Lucas, Solid State Sciences 2008, 10, 427.
3. L. Bouëssel du Bourg, C. Roiland, L. Le Pollès, M. Deschamps, C. Boussard-Plédel, B. Bureau, C. J. Pickard, E. Furet, Physical Chemistry Chemical Physics 2015, 17, 29020.

III-O-2

# Quasiparticle formulation of thermodynamic functions of glasses and melts

A.M. Kutyin[1,2]
[1]Lobachevsky State University, pr. Gagarina 23, Nizhny Novgorod, 603950 Russia
[2]Devyatykh Institute of Chemistry of High_Purity Substances, Russian Academy of Sciences,
Tropinina str., 49, Nizhny Novgorod, 603950 Russia
e_mail: kutyin@ihps.nnov.ru

On the one hand, the fluid is generated by the *NPT*-ensemble with three-dimensional pseudopotential interaction determines the elementary excitations (quasi-particles), which correspond to the so-called hole notions of fluid. On the other hand, vacancy model Schottky and Frenkel is calculated according to a statistical formula for the number of vacancies Bose and Fermi, after their union in parastatistics determine the quasiparticle corresponding extended quasicrystalline notions of fluid. Thus, parameters are mathematically simpler and more flexible in the practical application of the phenomenological theory, while approaches are similar in structure, can be decrypted by means of a statistical method of self-consistent, single-particle description of a system of interacting particles.

The set of generated by parastatistics thermodynamic functions for a system of the *m* interacting nodes (collective degrees of freedom) on a structural (formular) unit of matter is as follows:

$$G^\circ(T) - (H^\circ(0) - T\,S^\circ(0)) = -\,m\cdot RT\cdot\mathbf{ln}\,\frac{1+b}{1+b_p}, \quad H^\circ(T) - H^\circ(0) = -\,m\cdot RT\cdot g^{*\prime}\cdot\overline{n}\,, \tag{1}$$

$$C_p^\circ(T) = m\cdot R\cdot[(g^{*\prime})^2(b\cdot(1+b) - (p+1)^2 b_p\cdot(1+b_p)) - (g^{*\prime} + g^{*\prime\prime})\cdot\overline{n}\,], \tag{2}$$

$$b = 1/(\mathbf{exp}(g^*) - 1),\ \ b_p = 1/(\mathbf{exp}((p+1)g^*) - 1),\ \ \overline{n} = b - (p+1)b_p, \tag{3}$$

Critical" change of the parameter of the internal dimension at the glass transition temperature $T_g$

$$d = d_0\,/\,(1 - (T\,/\,T_g)^{\,t}),\ \text{при}\ T \le T_g;\ d = \infty\ \text{при}\ T > T_g$$

transforms the reduced Gibbs activation energy $g^*$ from the form corresponding to the glassy state $g^* = d\ \ln(1 + g_l^*/\,d)$ in the form $g_l^* = h^*/\,T - s^*$, which corresponds to the liquid, including the supercooled liquid state. In addition to the caloric functions (1)–(3) model defines the heat capacity leap $\Delta_{gl\to l}C_P$ at devitrification and the parameters, which characterize of the enthalpy and entropy redundancy of glass ($\Delta_{gl/l}H(0) = mRT_g\,\overline{n}\ g^{*2}t/(2d_0)$ and $\Delta_{gl/l}S(0) = \Delta_{gl/l}H(0)/T_g$,) Contribution of $m_e$ optical and quasi local modes in the thermodynamic functions, as is customary, are submit Einstein's equations:

$$G_e(T) = -\, m_e R\, \theta \ln(1+b_e), \qquad H_e(T) = m_e R{\cdot}\theta\, b_e, \qquad C_{Pe}\,(T) = m_e R\,(\theta/T)^2 b_e(1+b_e), \quad (4)$$

where $b_e = 1/(\exp(\theta(1/T - \alpha^*)) - 1)$, $\theta$ – Einstein temperature, parameter $\alpha^*$ is interconnected with the anharmonicity constant.

The set of thermodynamic functions of the model besides submitted caloric include functions related to the thermal equation of state for fluid and glass, which determines the dependence of the molar volume $V = V_0 + \Delta V_{l/g} + \Sigma\Delta V_e$ of temperature and pressure. Volume changes recorded after the close-packing volume ($V_0$), are determined by Einstein's and collective modes as derivatives $\Delta V = (\partial G/\partial P)_T$ from the corresponding expressions (1) and (4).

The phenomenological theory was used for co-processing calorimetric and volumetric data of a number of inorganic glasses and melts. Secured by this theory a contraction mapping of physicochemical properties of the substances to the set of structural and energy parameters of similarity - basis of the completion of missing experimental data and develop forecasting techniques of properties of multicomponent, glass-forming systems for modern technologies of Optical Materials.

III-O-3

# Bonding and structure of oxofluoroniobate-based glasses: $ZnNbOF_5$–$BaF_2$ and $ZnNbOF_5$–$InF_3$–$BaF_2$ systems

N. Laptash, I. Maslennikova, A. Slobodyuk
Institute of Chemistry, Far Eastern Branch of Russian Academy of Sciences, Vladivostok, Russia
laptash@ich.dvo.ru

Oxide fluoride glasses have been researched as host materials for optically active ions because they have comparatively low phonon energies that correspond to oxide glasses, and high chemical and mechanical stabilities related to fluoride glasses. Although oxide and fluoride ions have similar ionic radii, the ratio of oxide and fluoride ions in the glass must alter the coordination structure that affects the elements' functionality because of their different valences. The fluorine/oxygen substitution influences glass formation and structure, namely, network connectivity. It was assumed [1] that a vitreous network in the $NbO_2F$–$BaF_2$ system was built from the association of Nb(O, F)$_6$ polyhedra, the connectivity of which depended on the O/F and (O,F)/Nb ratios. Recently, we have shown that a glass network in the $K_2NbOF_5$–$MF_3$ (M = Al, In) systems was built from the chains of corner-sharing octahedra through –Nb–F(O)–M– and –Nb–F–Nb– bridges, and no bridging –Nb–O–Nb– species were present [2]. Nevertheless, it is still believed that the network of oxofluoroniobate glasses based on $NbO_2F$, $CuNbOF_5$, or $MnNbOF_5$ is built from niobium polyhedra linked through oxygen bridges [3]. This assumption is based on the infrared (IR) spectra of these glasses containing a rather intensive and broad band at 600–800 cm$^{-1}$, which is virtually absent in their Raman spectra. We observe similar picture in the case of glass-forming systems $ZnNbOF_5$–$BaF_2$ and $ZnNbOF_5$–$InF_3$–$BaF_2$ (see Figure), investigated by vibrational (infrared and Raman) and solid state NMR spectroscopy. Nature of the discussed band is connected with high ionic mobility of $NbOF_5^{2-}$. Probably, its fast reorientations result in equalization of Nb–O and Nb–F distances and the emergence of synchronous Nb–O and Nb–F stretches reflected as the infrared band at 712 cm$^{-1}$ (Fig.) and not observed in the Raman spectrum.

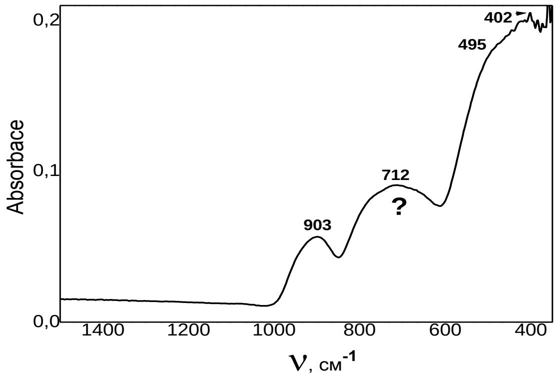


Fig. Infrared spectrum of the $50ZnNbOF_5$–$50BaF_2$ glass.

1. Z.C.K. Bouchaour,, M Poulain, M. Belhadji, I. Hager, , R. El Mallawany, New oxyfluoroniobate glasses, J. Non-Cryst. Solids, 351 (2005) 818–825.
2. N.M. Laptash, I.G. Maslennikova, A.B. Slobodyuk, V.Ya. Kavun, V.K. Goncharuk, Bonding and structure of oxofluoroniobate-based glasses, Inorg. Chem. 52 (2013) 5722–5728.
3. S. A. Polyshchuk, L. N. Ignatieva, N. N. Savchenko, and Yu. V. Marchenko, Glass Formation in Niobium Fluoride Systems, Russ. J. Inorg. Chem. 60 (2015) 1044–1051.

## III-O-4

# Structure-property relations in silver ion conducting homogeneous Ag-Ga-Ge-selenide glasses

M. Marple, D.C. Kaseman, S. Kim, S. Sen
Dept. of Materials Science & Engineering, University of California at Davis, Davis, CA 95616, USA
Email of corresponding author: sbsen@ucdavis.edu

Fast ion conducting glasses are of key interest for their potential applications in energy conversion/storage, memory, display and sensor technologies. However, the best contenders in this class of materials suffer from the lack of thermodynamic stability against phase separation, devitrification and moisture attack. We report the finding of glass-forming chalcogenide alloys in the system Ag-Ga-Ge-Se characterized by modified random networks that overcome these debilitating problems and at the same time display superionic silver conduction at ambient temperature. Homogeneous glasses in this system are synthesized and their structure is characterized using Raman and one- and two-dimensional $^{77}$Se, $^{71}$Ga and $^{69}$Ga nuclear magnetic resonance (NMR) spectroscopy. The structure of these glasses consists predominantly of a charge-compensated network of corner-sharing (Ga/Ge)$Se_{4/2}$ tetrahedra where the negatively charged $GaSe_{4/2}$ tetrahedra are charge balanced by the Ag cations. The deficiency in Se required to satisfy the tetrahedral coordination of Ga in glasses with $Ag_2Se:Ga_2Se_3 < 1$ is accommodated by the formation of homopolar Ge-Ge bonds. Progressive addition of $Ag_2Se$ efficiently removes Ge-Ge bonding such that their concentration essentially goes to zero at the chemical threshold $Ag_2Se:Ga_2Se_3 = 1$. Further addition of $Ag_2Se$ beyond this threshold (i.e., $Ag_2Se:Ga_2Se_3 > 1$) results in the modification of the Ga,Ge-Se tetrahedral network via depolymerization and formation of non-bridging Se atoms. Therefore, the compositional evolution of the structure of these glasses displays the characteristics of both the isoelectronic alkali/alkaline-earth aluminosilicate glasses and the purely covalent, continuously alloyed chalcogenide networks. Such composition-dependent structural evolution is shown to be consistent with the corresponding variation in glass transition temperature and molar volume and to provide a fundamental understanding of the potential energy landscape for silver ion transport in these materials.

# ISNOG 2016

## Tuesday, August, 23rd

## *Hall Standard 1*

## Session IV, Session VI

**Session IV: Phase Change Materials and Photo-Induced Effects**

**Session VI: Optical Thin Films**

### VI-inv 1

# Chalcogenide glass films for nanoscale memories

Tomáš Wágner, Bo Zhang, Silvie Valkova, Max Fraenkl, Miloš Krbal, Miloslav Frumar, G. Chen*
Department of General and Inorganic Chemistry, Faculty of Chemical Technology, and Centre for Materials Science, University of Pardubice, Cs. Legion's Sq. 565, Pardubice 532 10, Czech Republic.
*Department of Physics & Astronomy, Athens, USA

A range of material systems exist in which nanoscale ionic transport and redox reactions provide the essential for switching as platform for reconfigurable electronic devices and biological like computing. One class relies on mobile cations, which are easily created by electrochemical oxidation of the corresponding electrode metal, transported in the insulating layer, and reduced at the inert counter electrode. These devices are termed electrochemical metallization memories (EMC) or conductive bridge random access memories [1]. The material candidates for electrolytes in such devides have been recently studied. They are amorphous chalcogenides [2, 3] and also oxides ($SiO_2$, $WO_3$, $TiO_2$ and others [1]) containing metal elements (Ag, Cu) or their compounds ($Ag_2S$, CuS) and gaining some portion of ionic conductivity and becoming mixed ionic-electronic conductors [3-10].

The aim of this work is to present our current results on syntesis and resistive switching of chalcogenide based nanowire array cells and planparalel cells.

The authors thanks to project KONTAKT II (CR-USA) LH14059 for financial support.

1. W. Lu, D. S. Jeong, M. Kozicki, R. Waser, MRS Bulletin, 37 (2012) 124.
2. M. Frumar and T. Wagner, Curr. Opinion Solid St. Mat. Sci. **7** (2003) 117.
3. M. Frumar, B. Frumarova, T. Wágner, Amorphous and Glassy Semiconducting Chalcogenides. In: Bhattacharya P, Fornari R, and Kamimura H, (eds.), Comprehensive Semiconductor Science and Technology, volume 4, pp. 206–261 (2011) Amsterdam, Elsevier.
4. Š. Stehlík, J. Kolář, M. Bartoš, Mil.Vlček, M. Frumar, V. Zima, T. Wágner, Sol. State Ionics 181, (2010) 1625.
5. J. Kolář, T. Wágner, V. Zima, Š. Stehlík, B. Frumarová, L. Beneš, Mil. Vlček, M. Frumar, J. Non-Cryst. Solids, 357 (2011) 2223.
6. I. Kaban, P. Jóvári, T. Wágner, M. Bartoš, M. Frumar, B. Beuneu, W. Hoyer, N. Mattern, J., Eckert, J. Non-Cryst. Solids, 357 (2011) 3430.
7. Š. Stehlik, K. Shimakawa, T. Wágner, M. Frumar, J. Phys. D: Appl. Phys. 45 (2012) 205304.
8. J. Kolář,J. Macák, K. Terabe, T. Wágner, J. Mater. Chem. C 2 (2014) 349-355.
9. B.Zhang, M. Fraenkl, J. M. Macak, T. Wágner, Mater. Lett., 163 (2016) 4-7.
10. J. Akola, B. Beuneu, R. O. Jones, P. Jovari, I. Kaban, J. Kolář, I.Voleska, T. Wágner, J. Phys. - Cond. Matt., 27 (2015) 485304.

---

### VI-inv 2

# Investigation of crystallization mechanism and kinetics for amorphous thin films of phase change memory materials

A. Sherchenkov[1], S. Kozyukhin[2,3], A. Babich[1], P. Lazarenko[1]
[1]National Research University of Electronic Technology, Zelenograd, Russia
[2]KurnakovInstitute of General and Inorganic Chemistry, RAS, Moscow, Russia
[3] National Research Tomsk State University, Tomsk, Russia
E-mail: sergkoz@igic.ras.ru

Phase change memory (PCM) devices are actively developed now. However, in order phase change memories become widespread devices the data processing time must be sufficiently decreased. For this purpose increasing of crystallization rate for PCM materials is required, which strongly motivates investigation of the crystallization mechanism and kinetics. Due to the number of specific properties chalcogenide compound $Ge_2Sb_2Te_5$ (GST225) is considered to be one of the most promising PCM materials. So, the aim of this work was investigation of the thermal properties, mechanism and kinetics of crystallization for GST225 thin films.

GST225 thin films were prepared by thermal evaporation of synthesized material. XRD study (D8 ADVANCE Bruker and Rigaku Smart Lab.) showed that the synthesized materials had a trigonal structure, but as-deposited thin films were amorphous. According to the Rutherford Backscattering Spectroscopy (RBS) and Energy Dispersive X-Ray Analysis (EDXRA) composition of the films was close to that of the synthesized material. Differential scanning calorimetry (DSC-50, Shimadzu) revealed a number of heat effects for as-deposited films. Exothermic peak in the range of 130-190 °C is due to the crystallization of amorphous phase. For the investigation of crystallization mechanism and kinetics of GST225 thin films joint use of the model-free Ozawa-Flynn-Wall and model-fitting Coates-Redfern methods [1] was proposed. For this purpose DSC measurements were carried out at 8 different heating rates in the range of 5 – 90 °C/min. Joint application of these methods allowed to estimate effective activation energies and pre-exponential factors as functions of conversion, and establish reaction (crystallization) model.

It was found that effective activation energy gradually decreases with the increase of conversion, which indicates that crystallization of GST225 films is a complex process consisting of at least two stages. For crystallization process the most obvious stages are nucleation and crystal growth. According to the results crystallization process most adequately can be described by the second and third order reactions, which are characteristic for spontaneous nucleation with further growth without overlapping. These assumptions allowed us to determine activation energies of nucleation and crystalline growth.

According to atomic force microscope (SolverPro, NT-MDT) as-deposited films have island-like structure, however mean height of the islands does not exceed 1 nm. Crystallization of the thin film at 150 °C is accompanied by the increase of mean height nearly on the order of magnitude. We suppose that island-like structure promote nucleation from the film surface.

Determined kinetic triplet (effective activation energy, pre-exponential factor and reaction model) for GST225 films allowed us to estimate possible data processing and storage times of the PCM cell. It was found that GST225 thin film can provide the data processing time of the phase change memory cell about nanoseconds which is comparable with that of the random access memory.

Thus, in this study thermal properties, mechanism and kinetics of crystallization for GST225 films were investigated, and the model of amorphous thin film crystallization was proposed. Obtained kinetic parameters for GST225 films allowed predicting data processing and storage times of the PCM cell. It was found that GST225 thin film can provide the data processing time of the PCM cell comparable with that of the random access memory.

This study was supported by Ministry of Education and Science of RF (project ID: RFMEFI57514X0096).

1. Sherchenkov A, Kozyukhin S, Babich A 2014 J. Therm. Anal. Calorim. 117(3) 1509.

VI-inv 3

# Microstructure formation in chalcogenide thin films assisted by laser

A. Douaud, S. H. Messaddeq, Y. Messaddeq
Centre d'Optique, Photonique et Laser (COPL), Université Laval, Québec, G1V 0A6, Canada
Younes.Messaddeq@copl.ulaval.ca

The spontaneous formation of self-assembled and/or self-organized patterns is a fundamental and technologically significant. This process is achieved by exploiting dewetting and phase separation in thin films and can be thermally or laser induced. Although dewetting has been observed widely in a variety of materials [1] e.g., polymers [2], organic semiconductors [3] and metals [4], less attention has been paid regarding glassy thin films.

The present study focuses on laser-induced dewetting of As-based chalcogenide thin films in view of the interesting optical properties like photo-induced anisotropy, photodarkening, phase change etc [5]. The glassy system Ag-As-S is explored to obtain dewetted pattern by controlling the amount of sulphur and silver, respectively. The difficulty in producing silver-rich chalcogenide glasses resides in the fact that they have a large tendency to phase separation [6]. Preparation of those glasses by melt-quenching is therefore limited to a narrow glassy domain of composition [7], with a small amount of silver. To enlarge the glassy formation domain, we used co-evaporation as an alternative method which allows that the two constituents (As-S and Ag) are evaporated separately but simultaneously onto the same substrate by current induced heating and e-beam.

On this respect, understanding the parameters involved in the laser dewetting (such as time, power, film thickness, etc.) of As-S-Ag thin films will help to predict, control and manipulate to obtain ordered nanostructures.

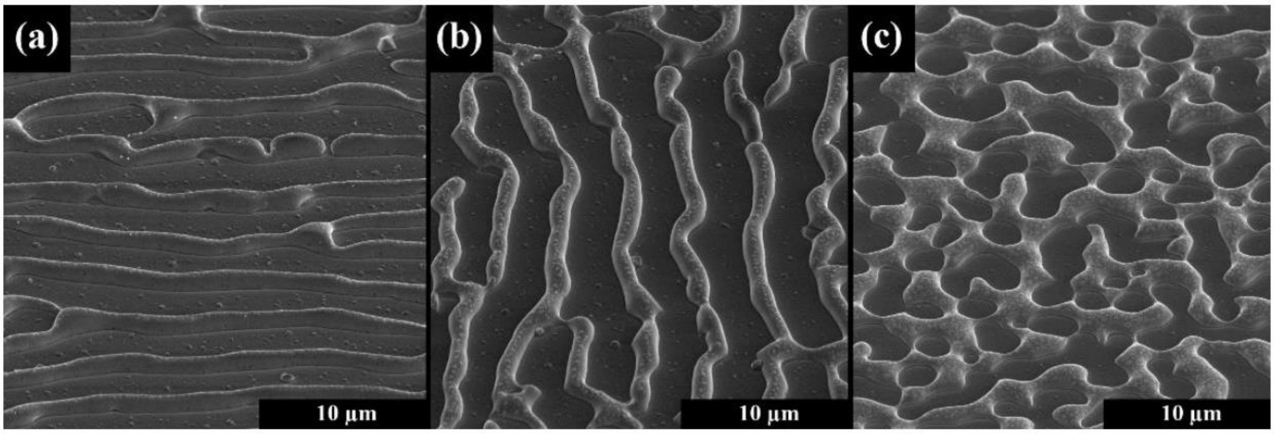


Figure 1 – Examples of laser-induced dewetting of a thin film (thickness = 600 nm) depending on the polarization of the laser: (a) vertical, (b) horizontal, and (c) circular.

1. Gentili D., Foschi G., Valle F., Cavallini M. & Biscarini F., Applications of dewetting in micro and nanotechnology, Chemical Society Reviews, 41 (2012) 4430–4443.
2. Leopoldes J. & Damman P., From a two-dimensional chemical pattern to a three-dimensional topology through selective inversion of a liquid-liquid bilayer, Nature Materials 5 (2006) 957–961.
3. Giri G., Park S., Vosgueritchian M., Shulaker M. M. & Bao Z., High-mobility, aligned crystalline domains of TIPS-pentacene with metastable polymorphs through lateral confinement of crystal growth, Advances Materials 26 (2014) 487–493.
4. Breitling A. and Goll D., Hard magnetic FePt thin films and nanopatterns, Journal of Magnetism and Magnetic Materials, 320 (2008) 1449–1456.
5. Zakery A. and Elliott S. R., Optical properties and applications of chalcogenide glasses: a review, Journal of Non-Crystalline Solids, 333 (2003) 1-12.

6. Stehlik S., Kolar J., Frumar M., Wagner T., Phase separation in chalcogenide glasses: The system AgAsSSe, International Journal of Applied Glass Science, 2 (2011) 301-307.
7. Kawaguchi T. and Maruno S., Photoinduced surface deposition of metallic silver in Ag-As-S glasses, Journal of Applied Physics, 77 (1995) 668.

VI O-1

# Photoinduced changes of optical and structural properties in As-based thin films glassy doped with copper

A. Qasmi[1], S.H. Messaddeq[1], M. El Amaroui[1], and Younès Messaddeq[1,2]
[1]Center for Optics, Photonics and Lasers, Laval University, 2375 rue de la Terrasse, Quebec City, QC, G1V 0A6,Canada
[2]Instituto de Química, UNESP, Araraquara, C.P. 355, CEP 14801970,Araraquara, SP, Brazil
Corresponding author email: sandra.messaddeq@copl.ulaval.ca

It is well known that one of the photoinduced changes in As-based chalcogenide materials by exposure to near-bandgap light result in the red shift of the absorption edge i.e. photodarkening (PD). However since the observation of Liu et al. [1] showing that the presence of 1 % Cu in bulk $As_2S_3$, eliminates the PD, there remains a lack of detailed study concerning the influence of different experimental conditions on the composition, structure, optical properties of As-based glassy doped with copper. Accordingly, in the present work we have investigated the effect of copper on the photoinduced phenomena of chalcogenide glassy system $Cu_{10}(As_{20}S_{80})_{90}$.

Photoinduced changes of the optical and structural properties of the films were studied after films exposure to different band-gap illumination (5, 2.5, 2.4, 1.55 eV) and time exposure (0-90 min). The optical absorption edge measured for the film $90(As_{20}S_{80})$-10Cu thin films above and near the bandgap show that the red shift of the gap by above bandgap photon illumination is considerable higher ($\Delta E$g = 0.9 eV) than $\Delta E$g induced by near bandgap illumination ($\Delta E$g =0.14 eV). The morphology of the surface after exposure was examined using a scanning electron microscopy (SEM). The chemical compositions measured using an energy dispersive analyzer (EDX) indicate an increase of the oxygen atoms into the exposed area. Raman spectra of the illuminated samples provide an evidence of the light-induced structural changes: a decrease in $AsS_{3/2}$ pyramidal units formation of Cu-S bonds. The formation of copper arsenosulphide ($Cu_3AsS_4$) and CuO was also confirmed as the power density of exposure increases.

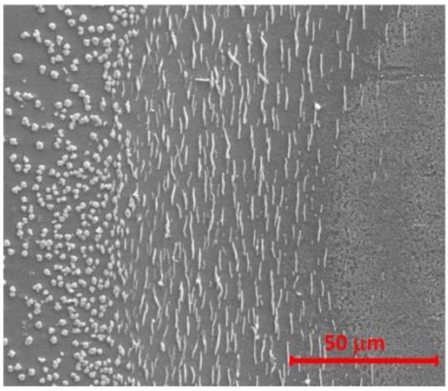


Fig.1: SEM image of $Cu_{10}(As_{20}S_{80})$90 thin film after laser irradiation at 244nm during 90min

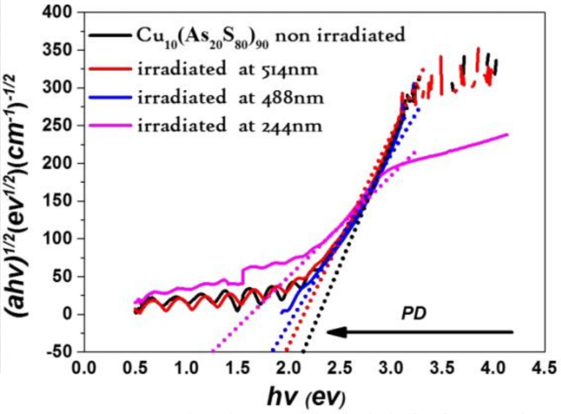


Fig.2: Tauc plot showing the red shift after irradiation at different wavelength

1. J.Z. Liu, and P.C. Taylor. "Absence of photodarkening in bulk, glassy $As_2S_3$ and $As_2Se_3$ alloyed with copper." Physical review letters 59.17 (1987)

VI O-2

# Physical properties and crystallization behaviours in $Ge_xTe_{1-x}$ films

X. Shen[1,*], Y. Chen[1,2], S. Dai[1], T. Xu[1,2]
[1]Laboratory of Infrared Material and Devices, Advanced Technology Research Institute, Ningbo University, Ningbo 315211, China
[2]Ningbo Institute of Material Technology and Engineering, Chinese Academy of Science, Ningbo 315201, China
*Corresponding author's E-mail: shenxiang@nbu.edu.cn

Driven by applications in data storage (phase change memories) and information transfer (optical waveguides), amorphous Ge-based tellurides have attracted considerable attention in recent decades. On the investigation of compositional dependence of structure and physical properties for amorphous Ge-based tellurides, Lucas *et al*. [1] carried out Maxwell rigidity transition from flexible to stressed rigid is determined to occur in the compositional range about $0.250<x<0.265$ at. % for $Ge_xTe_{1-x}$ glasses, which is the impact of fundamental glass properties on resistance drift phenomena. Piarristeguy *et al*. [2] exhibited two structural singularities at x~0.22 at. % and x~0.33-0.35 at. % in $Ge_xTe_{1-x}$ films, which are obtained by the study on the change of crystallization temperature and RMC simulations. On the other hand, using ultrafast calorimetry, the crystallization kinetics of suppercooled liquid $Ge_2Te_2Sb_5$ has been studied by Orava *et al*. [3] This indicated a novel and promising approach to study the crystallization kinetics at relatively high temperature for phase change material. In this work, the composition extended $Ge_xTe_{1-x}$ ($0.15 \le x \le 0.60$) films have been prepared by magnetron co-sputtering method. We used various diagnostic tools to explore the physical properties and structural evolution for these amorphous films. And the crystallization kinetics of supercooled liquid Ge-Te based on ultrafast DSC has been investigated. As shown in Figure 1(a), with the Ge content increasing, we can find the films' hardness and modulus are all increased. Obviously, one singularity can be found, which is $x$~0.28 at. %. The XRD results revealed the $Ge_xTe_{1-x}$ films with $x \le 0.28$ crystallize in two-stage due to segregation of Te and subsequent formation of GeTe crystallites, whereas those with $0.28<x<0.60$ show one stage amorphous to crystalline transformation with simultaneous formation of GeTe and Te phases. The Raman spectra of amorphous $Ge_xTe_{1-x}$ films evidenced the formation of heteropoloar GeTe bonds result in the singularity. More importantly, Kissinger plot with fittings by VFT equation for several Ge-Te films are shown in in figure 1(b), exhibiting a non-Arrhenius behaviour, especially in high Ge content sample. It implies that the more Ge content in Ge-based telluride, the more fragile in its supercooled liquid. If the singularity in property will show in the crystallization kinetics of supercooled liquid $Ge_xTe_{1-x}$, such as fragility, viscosity, crystal growth rate? This is research have to do in future.

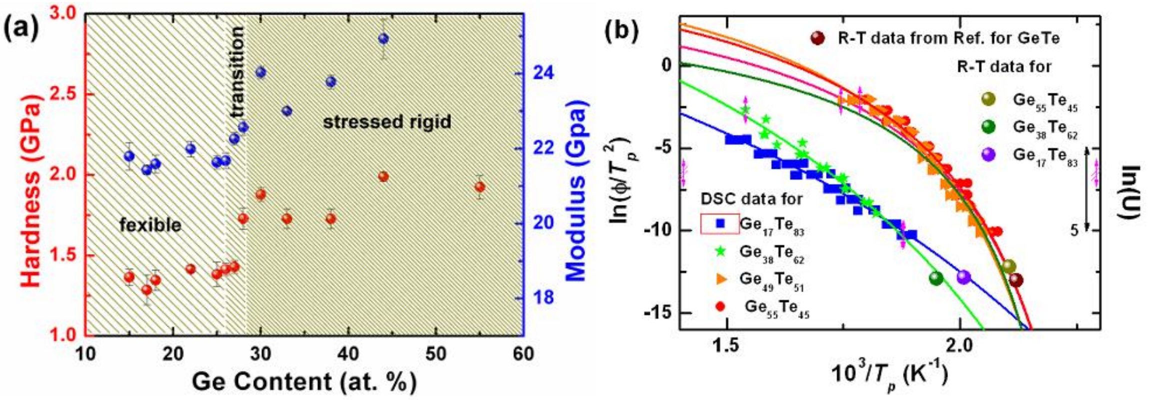


Figure 1: (a) Hardness and Modulus evolution plotted as a function of atomic percentage in Ge; (b) Kissinger plots for crystallization of supercooled liquid Ge-Te amorphous films.

1. Lucas J, Olk A, Jost P, Volker H, Alvarez J, Jaffré A, Zalden P, Piarristeguy A, Pradel A, Longeaud C, Wuttig M. Applied Physics Letters 2014;105:092108.
2. Piarristeguy AA, Micoulaut M, Escalier R, Jovari P, Kaban I, van Eijk J, Luckas J, Ravindren S, Boolchand P, Pradel A. The Journal of chemical physics 2015;143:074502.
3. Orava J, Greer A, Gholipour B, Hewak D, Smith C. Nature materials 2012;11:279.

# ISNOG 2016

## Tuesday, August, 23rd

## *Business Hall*

# Session V-1

**Session V-1: Luminescent Glasses, Optical Waveguides and Glass-Ceramics for active applications**

V-1-inv 1

# Glasses containing chalcogenide quantum dots

Jong Heo
Department of Materials Science and Engineering and Division of Advanced Nuclear Engineering
Pohang University of Science and Technology (POSTECH), Pohang, Republic of Korea

Glasses doped with PbS quantum dots (QDs) can absorb and emit light at wavelengths that can be controlled from ~0.7 ≤ λ ≤ ~2.0 μm by adjusting QDs' size from ~2 to ~10 nm [1]. They have possible applications as solid-state saturable absorbers for mode-locked lasers and as fiber-optic amplifiers in optical communication [2]. The average size of PbS QDs and their size distribution inside glasses can be tailored by carefully controlling the temperature and duration of thermal treatment [2]. This process, however, normally results in an uncontrolled spatial distribution of QDs in the glass matrix. Ion-implantation and femto-second laser irradiation techniques [3] were used to realize space-selective formation of QDs for micro- and nano-photonic devices. Doping of rare-earth ions was found effective to control the size of quantum dots [4]. Using Ag nano-particles (NPs) as nucleating agents to realize accurate control of PbS QD precipitation in glasses also has been investigated [5]. Adding $Ag^+$ ions allowed control of the size and size distribution of PbS QDs together a large increase of absorption and photoluminescence (PL) intensities. This work reviews the several methods applied to control the size, shape and spatial distribution of quantum dots in inorganic glasses.

A glass subjected to $Ag^+$ ion diffusion at 80 °C and heat-treated at 460 °C for 10 h was examined under TEM. PbS QDs formed in the $Ag^+$-diffused region were near-spherical shape with the average diameter of ~5.5 (±0.8) nm. PL spectra were recorded from the surface and cross-sectional areas of the glass to examine the effect of $Ag^+$ ion diffusion on the precipitation of PbS QDs. When the glass was in $AgNO_3$ solution at 80 °C and heat-treated at 460 °C for 10 h, two clear PL bands were recorded from the cross-sections. The wavelength of the PL peak from the diffused regions was ~1520 (±20) nm (Fig. 1). These results indicate that both diffusion conditions and heat-treatment conditions can influence sizes of PbS QDs formed in glasses.

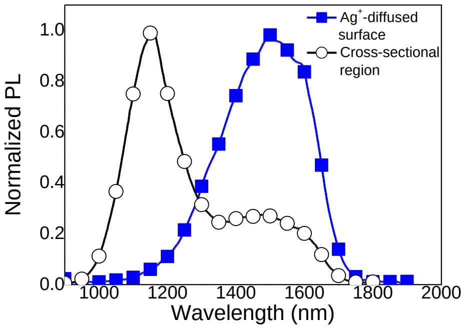


Fig. 1. Normalized PL spectra of glasses recorded from the cross-section of the entire glasses, and from the $Ag^+$-diffused surface. Specimens were kept in $AgNO_3$ solution at 80 °C, then heat-treated at 460 °C for 10 h. Symbols were added as guides to eyes.

Precipitation of PbS quantum dots (QDs) in silicate glasses were controlled by heat treatment, rare-earth ion concentrations and $Ag^+$ ion diffusion. Radii of PbS QDs were changed from 1 ~ 4 nm and wavelengths of the photoluminescence were in 1 ~ 2 μm range. Rare-earth and $Ag^+$ ions seem to provide heterogeneous nucleation sites for the precipitation of QDs. These glasses containing PbS QDs with controlled size distribution can provide potentials for amplification in the fiber-optic communication networks.

1. E. H. Sargent, Adv. Mater. 17 (2005) 515.
2. J. Heo, C. Liu, J. Mater. Sci.: Mater. Electron 18 (2007) S135.
3. Chao Liu, Yong Kon Kwon, Jong Heo, Bok Hyeon Kim, Ik-bu Sohn, J. Am. Ceram. Soc. 93 (2010) 1221.
4. Sang Min Shim, Chao Liu, Yong Kon Kwon and Jong Heo, J. Am. Ceram. Soc. 93 (2010) 3092.
5. Kai Xu and Jong Heo, J. Am. Ceram. Soc., 95 (2012) 2880 begin_of_the_skype_highlighting.

V-1-inv 2

# Recent progress in the development of ytterbium-doped oxyfluoride glass-ceramics for laser cooling application

Y. Ledemi,[1] K.V. Kummara,[1,2] Emmanuel Veron,[3] Cécile Genevois,[3] E. Soares de Lima Filho, [1,2]
G. Nemova,[2] Mathieu Allix,[3] R. Kashyap[2], Y. Messaddeq[1]
[1] Centre d'Optique, Photonique et Laser, Université Laval, Québec (QC) G1V 0A6, Canada
[2] Department of Engineering Physics and Department of Electrical Engineering, École Polytechnique de Montréal, Montréal H3C 3A7, Canada
[3]Conditions Extrêmes et Matériaux: Haute Température et Irradiation, CEMHTI – CNRS - UPR3079, 45071 Orléans Cedex 2, France.
Corresponding author: yannick.ledemi@copl.ulaval.ca

The first experimental demonstration of laser induced cooling of a solid through anti-Stokes fluorescence was realized more than 20 years ago in a fluoride ZBLANP glass doped with ytterbium $Yb^{3+}$ ions [1]. Since then, intensive research has been carried out, conducting to solid-state optical cooling down to cryogenic temperatures and very recently even below 100 K in $YLiF_4$:$Yb^{3+}$ single crystals [2]. In this work, we will present our recent advances on the fabrication and characterization of $Yb^{3+}$ doped oxyfluoride glasses, glass-ceramics and optical fibers belonging to the $SiO_2$-$Al_2O_3$-$CdF_2$-$PbF_2$-$YF_3$ system. Our strategy is to take advantage of the ease of fabrication and shaping of glassy materials (including optical fiber drawing ability) and of the enhanced optical properties of $Yb^{3+}$ doped glass-ceramics to propose novel solid-state cooling materials.

First, a systematic study of the photoluminescence quantum yield has been carried out in the bulk glasses as a function of the $Yb^{3+}$concentration [3]. Then, transparent glass-ceramics were produced with the formation of nanocrystals based on lead fluoride $PbF_2$ within the vitreous network by appropriate heat-treatment of the glass. These nanocrystals then constitute an ideal host for $Yb^{3+}$ ions owing to their local low phonon energy, providing superior luminescence properties to the glass-ceramics compared with its glassy counterpart. Last, vitreous and glass-ceramics optical fibers were obtained by the crucible technique (direct-melt process) and by the conventional glass preform drawing. Efforts have been focused on the purification of the raw materials in order to minimize the material background absorption. Optical characterization including anti-Stokes fluorescence spectra and photoluminescence quantum efficiency measurements was performed on the produced fibers. Structural characterization has been conducted by *in situ* and *ex situ* powder X-ray diffractions and transmission electron microscopy, evidencing the formation of nanocrystals smaller than 10 nm with appropriate thermal-treatment of the fiber. The potential of these nano-glass-ceramics for solid-state optical refrigeration will be discussed.

1. R.I. Epstein, M.I. Buchwald, B.C. Edwards, T.R. Gosnell, C.E. Mungan, Observation of laser-induced fluorescent cooling of a solid, Nature (Lond.) 377 (1995) 500.
2. S.D. Melgaard, A.R. Albrecht, M.P. Hehlen and M. Sheik-Bahae, Solid-state optical refrigeration of sub-100 Kelvin regime, Scientific Reports 6, (2016) 20380.
3. K.V. Kummara, E. Soares de Lima Filho, Y. Ledemi, G. Nemova, Y. Messaddeq and R. Kashyap, Development of ytterbium-doped oxyfluoride glasses for laser cooling applications, Scientific Reports 6, (2016) 21905.

V-1 O-1

# Photoluminescence properties of Er$^{3+}$ doped phosphate tungstate glass containing Ag-nanoparticles

S. H. Santagneli[1], M. Nalin[1], J. M. Caiut[2], L. Misoguti[3], S. J. L. Ribeiro[1]
[1]LAMF - Institute of Chemistry – UNESP
[2]Department of Chemistry- FFCLRP- USP
[3]Photonics Group - Institute of Physics of São Carlos – SP

Glass samples in the system $[(0.6KPO_3\text{-}0.4WO_3)]_{(1\text{-}x)}\text{-}AgCl_{(x)}$ embedded Er$^{3+}$ ions doped were prepared using the conventional melting-quenching method. Silver nanoparticle (Ag-NPs) formation in this system was obtained from the reduction of ionic Ag$^{+}$ followed by nucleation and growth using controlled thermal annealing. Thermal properties and the local structure were monitored as a function of AgCl content by DSC. Addition of AgCl leads to a pronounced decrease in the glass transition temperature. The formation process of the Ag-based NP has been investigated by UV-Vis spectroscopy. HRTEM, optical linear ($n_1$) and nonlinear ($n_2$) and photoluminescence were evaluated as a function annealing time below $T$g. The HRTEM-picture analysis indicated clearly homogeneous distribution of Ag-NP inside the glass matrix and they have almost ellipse shapes. The intensity of the emission in 1550 nm is influenced by the local field of silver nanoparticles, ie the emission intensity is associated with the effect of energy transfer of the Er$^{3+}$ ions to nanoparticles. The photoluminescence of Er$^{3+}$ ions evolution was studied as a function of time thermal nucleation and growth of Ag-NPs.

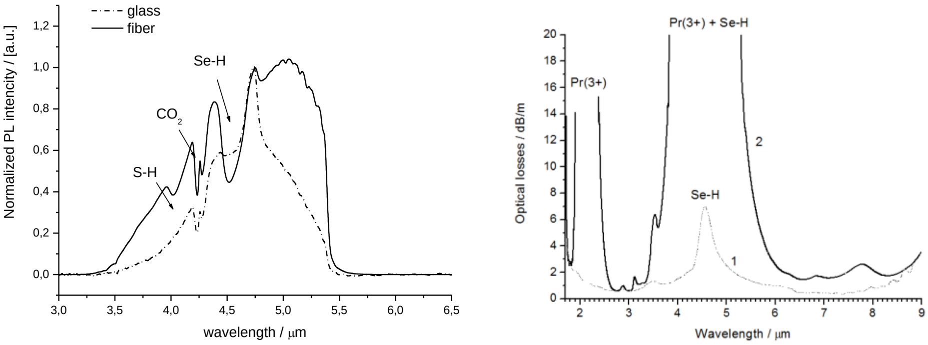
V-1 O-2

# Preparation and characterization of high purity Pr$^{3+}$-doped Ga(In)-Ge-As(Sb)-Se glasses and fibers

E.V. Karaksina, T.V. Kotereva
G.G. Devyatykh Institute of Chemistry of High-Purity Substances of RAS,
49 Tropinin Str., 603950 Nizhny Novgorod, Russia
e-mail: karaksina@ihps.nnov.ru

Chalcogenide glasses doped with rare-earth elements (REE) are promising for creation of mid-IR fiber and solid-state lasers [1]. In this work we propose the developed method for preparation of high-purity REE-doped Ga(In)-Ge-As(Sb)-Se(-I) glasses. This method is based on the use of chemical and distillation purification of the glass melt and the transport reaction technique to purify and to load the individual Ga or In components in the glass matrix [2, 3]. A more detailed attention was given to the possibility to decrease the concentration of the limiting impurities, such as hydrogen and oxygen.

The samples of high-purity multi-component Ga(In)-Ge-As(Sb)-Se(-I) glasses, doped with 1000 – 3000 ppmw praseodymium, have been synthesized. The data of DSC, XRD showed the absence of crystalline phases. In bulk samples of glasses, containing Sb in their composition, the micrometric size particles at the level of 0.1 ppmV were observed by optical microscopy method. The evaluated level of optical losses due to their presence is less than 0.1 dB/m near pump wavelength. For the prepared bulk glasses, the luminescence lifetimes were measured; their values at the wavelength of 4.7 μm are 5-10 ms depending on glass composition. From Ga(In)-Ge-As-Se(-I): Pr bulk glasses, the mono- and step-index (GeAsS-clad) fiber samples were prepared; the values of the fiber length are used to be more than 10 m. The spectra of optical losses and luminescence for 0.5 m length fiber pieces were investigated. For example, these data are shown in Fig. The absorption spectrum of Ga-Ge-As-Se:Pr (for the concentration of Pr-ions of 500-1300 ppmw) demonstrated the absence of absorption bands connected with oxygen impurities. This result shows the advantage of multi-stage method of synthesis of glasses in high-pure state, in comparing with the last data [4]. As for hydrogen impurity, we evaluated its concentration as less than 1 ppmw which meets the requirements of the fiber laser optics.



a b

Fig. Pl spectra (a) of the 1300 ppmw Pr(3+)-doped $Ge_{15}As_{16}Se_{63}In_3I_3$ glass and unclad fiber normalized at the wavelength of 4.7 μm, and optical losses (b):1- undoped, 2- Pr-doped

This work was supported by the Russian Foundation for Basic Researches, grant 15-03-03471a.

1. Seddon A.B., et.al. Optics Express, 2010, **18**, 26704.
2. Shiryaev V.S., Velmuzhov A.P., et,al., Optical Materials, 2014. **37**, 18.
3. Karaksina E.V., Shiryaev V.S., et.al., Journal of Luminescence, 2016, **170**, 37.
4. Z. Tang, D Furniss, M Fay, et al. Opt. Mat. Exp. 2015, **5 (4)**, 870.

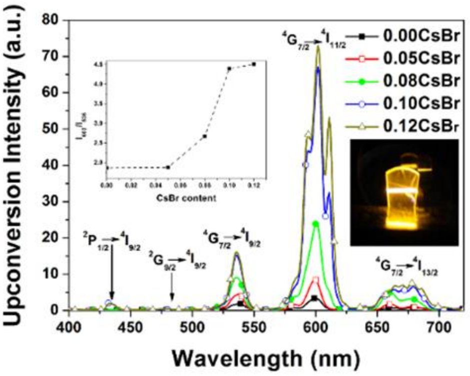
V-1 O-3

# Local environment dependence on the luminescence of rare earth doped chalcohalide glasses and glass ceramics

J. Zhang[1, 2, *], C. Liu [1], X. Zhao[1], B. Kim[2], J. Heo[3], M. Oh[2], N. Yu[2]
[1] State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, 122 Luoshi Road, Hongshan, Wuhan, Hubei 430070, P. R. China.
[2] Spectroscopy Sensor Laboratory, Advanced Photonics Research Institute (APRI), Gwangju Institute of Science and Technology, 123 Cheomdan - Gwagiro, Buk-gu, Gwangju, 500-712, Republic of Korea
[3]Division of Advanced Nuclear Engineering, Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH)San 31, Hyoja-dong, Pohang, Gyeongbuk 790-784, Republic of Korea
*E-mail: optinfo@whut.edu.cn

Chalcogenide glasses can be promising host materials for rare earth ions, for effective visible upconversion, near infrared and mid-infrared emission, for their high density, low phonon energy, and good transmittance in infrared region [1, 2]. The addition of alkali halide, which makes chalcohalide glasses, not only modifies the glass structure, improves the transparency in visible range, but also changes the local environment of rare earth ions [3]. The local environment changes have some effects on the luminescence properties of rare earth ions.

In present research, the effect of alkali halide addition on the luminescence properties of rare earth ions will be systemically investigated. $Nd^{3+}$, $Ho^{3+}$, $Er^{3+}$ single doped Ge-Ga-S-CsX (X=Cl, Br, I) chalcohalide glass, and $Nd^{3+}/Tm^{3+}$, $Nd^{3+}/Pr^{3+}$ co-doped chalcohalide glasses were prepared by conventional melt-quenching method. The micro-structure changes due to alkali halide addition were characterized by Raman spectroscopy. The results indicated that a new peak formed originated from Ga-X bond vibration in $[GaS_{3/2}X]^-$ group. The visible upconversion luminescence bands from $Nd^{3+}$, $Er^{3+}$ intensity was enhanced (Fig. 1), and novel upconversion from $Ho^{3+}$ was observed (Fig. 2). Moreover, different energy transfer processes were varied with different CsX content in chalcohalide glasses. The near infrared luminesce also observed from chalcohalide glasses, changed with different alkali halide and their content. The nanocrystals were fabricated in chalcohalide glasses. Visible upconversion and infrared luminescence were further enhanced. X-ray diffraction (XRD) patterns and transmission electron microscopy images proved that $Ga_2S_3$ nanocrystals were in glass matrix, with diameters ~20 nm – ~100 nm. The distributions of rare earth ions were directly observed using electron energy loss spectroscopy (EELS). And the local surroundings were confirmed.



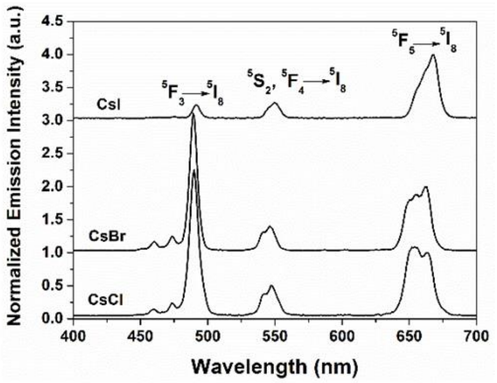


Fig. 1 Upconversion luminescence spectra of 0.1 mol % $Nd^{3+}$ doped chalcogenide and chalcohalide glasses with different CsBr content, under 810 nm laser excitation. Inset: digital image of glasses under 810 nm laser excitation, and the intensity ratio of emission bands centered at 602 nm and 535 nm.

Fig. 2 Upconversion luminescence spectra of $Ho^{3+}$ doped chalcohalide glasses, with different cesium halide. The intensity was normalized by the red emission centered at 660 nm. The spectra were vertically shifted for clarity. The excitation wavelength was 900 nm.

1. J. F. Suyver, A. Aebischer, D. Biner, P. Gerner, J. Grimm, S. Heer, K.W. Krämer, C. Reinhard, H. U. Güdel, Opt. mater., 27 (2005) 1111
2. D. Marchese, G. Kakarantzas, A. Jha, B. N. Samson, J. Wang, J. Modern Optics 43 (1996) 963
3. J. H. Song, Y. G. Choi, K. Kadono, K. Fukumi, H. Kageyama, J. Heo, J. Non-Cryst. Solids, 353 (2007)1676

---

V-1 O-4

# Studies of various praseodymium additives doped chalcogenide Se-based fibres

Z. Tang, L. Sojka, D. Furniss, H. Sakr, E.Barney, S. Sujecki, T.M. Benson and A.B. Seddon*
Mid-Infrared Photonics Group, George Green Institute of Electromagnetics Research, Faculty of Engineering,
University of Nottingham, University Park, Nottingham, NG7 2RD, UK.
*corresponding author: angela.seddon@nottingham.ac.uk

Due to the advantages of low-phonon energy, robust glass properties and good rare earth ion (RE) solution, RE-doped chalcogenide glasses are interesting and promising materials for achieving the mid-infrared (MIR) fibre laser [1]. Among different rare earth ion and host glass system, praseodymium ion ($Pr^{3+}$)-doped Ge-As-Ga-Se glass has been proposed as a promising candidate for MIR fibre lasing at 4-5 μm wavelength [2]. Based on our previous work [3, 4], crystallisation and optical scattering can occur in RE-doped Ge-As-Ga-Se glasses and further to affect the quality (*e.g.* optical loss) of the final fabricated optical fibres. In order to avoid Ga-related crystallisation during processing, a low Ga content is suggested in the host glass system for a proper RE solubilisation [3]. Also, it was found that RE additives had important influence on the properties (*e.g.* scattering loss) of RE-doped chalcogenide glass [5]. Therefore, this work investigates the influence of Pr additives on the $Pr^{3+}$-doped Ge-As-Ga-Se fibres with low Ga content. Techniques including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), fibre optical loss, photoluminescence (PL) spectra and PL lifetime were applied in the research.

500 ppm w $Pr^{3+}$(Pr foil, $PrI_3$ or $PrCl_3$) were doped in Ge-As-Ga-Se glasses (1 at % Ga; Ge, As and Se were distilled with both H and [O] getters) and the preforms were drawn into unstructured fibres. No crystallisation peak was found in powder XRD patterns of all the $Pr^{3+}$-doped fibres. Fibre loss spectra showed that the Pr foil-doped fibre had the lowest background optical loss without distinct scattering loss (lowest loss 2.0 dB/m at 6.8 μm wavelength); although the $PrCl_3$-doped fibre presented extra scattering loss below 4 μm wavelength, it gave the lowest loss of 1.8 dB/m at 6.9 μm wavelength; extra scattering loss was also observed in the $PrI_3$-doped fibre at below 4 μm wavelength but its scattering loss was lower than that of the $PrCl_3$-doped fibre. FTIR spectra of the preform bulk glass (*i.e.* the glass before fibre drawing) assisted the fibre study and it showed that the extra scattering loss in the $PrI_3$-doped and $PrCl_3$-doped fibres was (majorly) originally from the preform instead of being caused by the fibre drawing, and also, $Pr^{3+}$ absorption bands were structured in the $PrI_3$ and $PrCl_3$ doped Ge-As-Ga-Se glass preforms.

PL spectra and PL lifetime of the Pr foil-doped and $PrI_3$-doped Ge-As-Ga-Se fibres were investigated using pumping at 1.55 μm wavelength and the side PL collection of fibre was applied; the $PrCl_3$-doped fibre had too high background scattering loss (>100 dB/m) at 1.55 μm wavelength to achieve proper results. When pump power was increased from 19 mW to 65 mW, the PL intensity of the Pr foil-doped and $PrI_3$-doped Ge-As-Ga-Se fibres were increased linearly and the PL spectra shape kept the same. The PL intensity of Pr foil-doped fibre was more than 50 % higher than that of $PrI_3$-doped fibre. The PL lifetimes of the Pr foil-doped fibre and the $PrI_3$-doped fibre were 8.2-8.7 ms and 8.5-9.0 ms, respectively, when pump power was 19-65 mW.

This work was supported by the Framework Seven (FP7) project MINERVA of the European Commission http://minerva-project.eu/.

1. A. B. Seddon, Z. Tang, D. Furniss, S. Sujecki, and T. M. Benson, "Progress in Rare-Earth-Doped Mid-Infrared Fiber Lasers," Opt. Express, 18[25] 26704-26719 (2010).
2. Ł. Sójka, Z. Tang, H. Zhu, E. Beres-Pawlik, D. Furniss, A. B. Seddon, T. M. Benson, and S. Sujecki, "Study of Mid-Infrared Laser Action in Chalcogenide Rare Earth Doped Glass with $Dy^{3+}$, $Pr^{3+}$ and $Tb^{3+}$," Opt. Mater. Express., 2[11] 1632-1640 (2012).
3. Z. Tang, D. Furniss, M. Fay, N. C. Neate, Y. Cheng, E. Barney, L. Sojka, S. Sujecki, T. M. Benson, and A. B. Seddon, "First identification of rare-earth oxide nucleation in chalcogenide glasses and implications for fabrication of mid-infrared active fibers," J. Am. Ceram. Soc., 97[2] 432-441 (2014).
4. Z. Tang, N. C. Neate, D. Furniss, S. Sujecki, T. M. Benson, and A. B. Seddon, "Crystallization behavior of $Dy^{3+}$-doped selenide glasses," J. Non-Cryst. Solids, 357[11–13] 2453-2462 (2011).
5. Z. Tang, D. Furniss, S. Sujecki, T. M. Benson, and A. B. Seddon, "The effect of the nature of the rare earth additive on chalcogenide glass stability," pp. 79121F. in Proceedings of the SPIE, Solid State Lasers XX: Technology and Devices. , Vol. 7912. Edited by W. A. Clarkson, N. Hodgson, and R. Shori, San Francisco, California, USA, 2011.

---

V-1 O-5

# Fabrication and characterization of $Ge_{20}As_{20}Se_{15}Te_{45}$ chalcogenide glass for photonic crystal by nanoimprint lithography

Peiqing Zhang, Zheming Zhao, Xunsi Wang, Shixun Dai
Infrared Materials and Devices Laboratory of Ningbo University, Ningbo University, Ningbo, Zhejiang 315211,China
zhangpeiqing@nbu.edu.cn

Photonic crystals (PCs) are periodic dielectric materials exhibiting photonic band gaps (PBG), for which light of certain energies cannot propagate. Since their discovery in 1987 and especially these last few years

[1, 2], photonic crystals have been the objects of an intense activity [3]. Principally, the most important requirement for a material, which could be used for the fabrication of the photonic crystal with a complete photonic band-gap, is the high refractive index, which desirably should be higher than 2.7. In addition, the material should afford fabrication as a large bulk of an arbitrary shape; therefore, the material ought to be of glassy origin. Chalcogenide glasses (ChG) have been attracted recently a substantial interest as they have highest linear (2.0 to 3.5) and nonlinear refractive index (100 to 1000 times higher than silica) amongst glasses and allow fabrication of rib and fibre waveguides. Additionally, ChG possess very wide transmission window, which can be transparent from the visible region (sulfur-based glass) up to the mid-infrared region (25 μm for telluride glasses). These properties allowed to apply ChG for fabrication of efficient photonic band-gap crystals for visible to infrared applicaitons.

In this work, Te-enriched Ge-As-Se-Te glass (TeGAST), which has very high refractive index, up to 3.5, was fabricated and characterized for photonic crystal. The prepared glasses were measured to have other advantages of: a) broad transmission window from about 1.5 to 20 μm, b) very high nonlinearity of $6.17275\times10^{-18}$ m$^2$/W 3.5 μm in infrared, c) excellent glass-stability which enables applications of the surface moulding and hot pressing techniques to produce photonic devices. Photonic crystal of 1D gratings were fabricated by direct resist-free thermal nanoimprint on the surface of a 2 mm thick glass instead of the film. Remarkably, due to the low softening temperature of TeGAST, the nanoimprint was accomplished with a soft Polydimethylsiloxane (PDMS) stamp in contrast to hard stamps. By optimizing the imprint temperature, it is shown that a simple, low cost PDMS soft stamp can produce grating with excellent surface morphology.

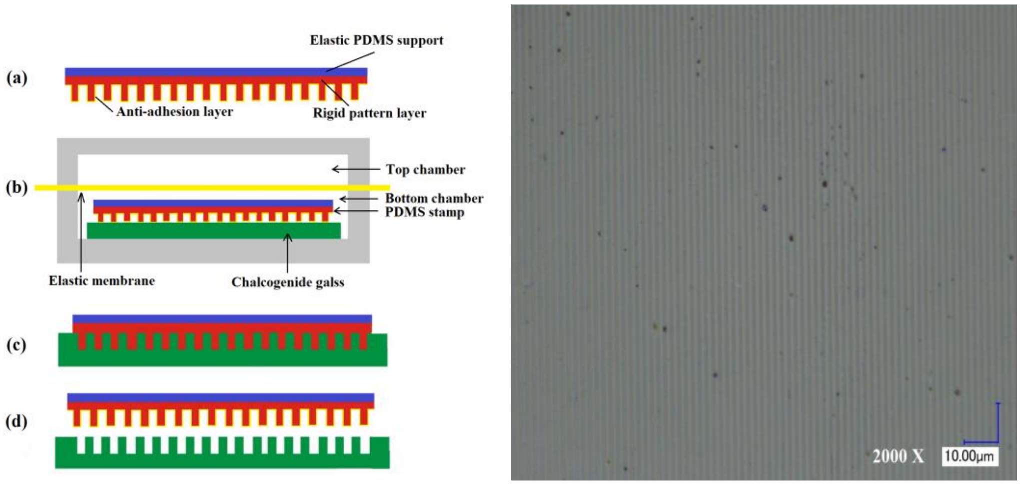


Fig. 1. The schematic of the nanoimprint lithography and the optical images of imprinted grating in $Ge_{20}As_{20}Se_{15}Te_{45}$ chalcogenide glass

1. A. Zakery, S.R. Elliott, "Optical properties and applications of chalcogenide glasses: a review," J. Non-Cryst. Solids 330, 1-12 (2003).
2. M. Solmaz, H. Park, C. K. Madsen, and X. Cheng, "Patterning chalcogenide glass by direct resist-free thermal nanoimprint," J. Vac. Sci. Technol. B 26(2), 606–610 (2008).
3. J. Orava, T. Kohoutek, A. L. Greer, and H. Fudouzi, "Soft imprint lithography of a bulk chalcogenide glass," Opt. Mater. Express 1, 796-802 (2011).

V-1 O-6

## Spectroscopic analysis of $Tm^{3+}/Yb^{+3}/Ho^{+3}$ tri-doped fluorophosphates glasses

O. Bentouila[1, 3] ,K.E. Aiadi[1] , F. Rehouma[2] and M. Poulain[3]
[1]Équipe Optoélectronique, Laboratoire LENREZA, Université Kasdi Merbah-Ouargla,30000 Ouargla, Algérie
[2] Université d'El-Oued, B.P 789 El-Oued R.P, 39000 El-Oued Algérie
[3] Matériaux Photoniques, UMR Sciences Chimiques, Université de Rennes 1,F-35042 Rennes, France
bentouila.om@univ-ouargla.dz

Fluorophosphates glasses, with compositions: (80-x-y-z)$NaPO_3$ -10$ZnF_2$ -10$SrF_2$ : x$HoF_3$ - y$YbF_3$ - z$TmF_3$ with x = 0.5, 0.75 (mol %), y = 2, 3 (mol %) and z =1, 1.5 (mol %), were prepared by melt-quenching technique. Stability criterion ($\Delta T = T_x\text{-}T_g$), calculated from the characteristic temperatures, indicate that these glasses exhibit a good thermal stability. According to the absorption spectra and by using Judd–Ofelt analyses, the spectroscopic properties, such as intensity parameters $\Omega_{2,4,6}$, spontaneous transition probability, branching ratio and radiative lifetime, of $Ho^{3+}$ and $Tm^{3+}$ ions in these glasses were calculated and compared with other glass hosts. Integrated emission cross-section and spectroscopic quality factor ($\Omega_4$ /$\Omega_6$) were evaluated to understand the lasing efficiency of these materials. According to the results, these glasses offer prospects for lasing materials and photonics applications [1].

1. G. Bai, Y. Guo, Y. Tian, L. Hu, and J. Zhang; Light emission at 2 m from Ho–Tm–Yb doped silicate glasses; Opt. Mater. 33 (2011) 1316 –1319.

V-1 O-7

## Spectral properties of $Er^{3+}$-doped high-purity tellurite glasses

V.V. Koltashev[2], V.V. Dorofeev[1], S.E. Motorin[1], A.V. Kharakhordin[2], E.B. Kryukova[2], V.G. Plotnichenko[2], B.I. Denker[3], B.I. Galagan[3], S.E. Sverchkov[3]
[1]Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, Nizhny Novgorod
[2]Fiber Optics Research Center of the Russian Academy of Sciences, Moscow
[3]Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow
e-mail: kvv@fo.gpi.ru

Rare-earth doped tellurite glasses are promising as an active medium for the bulk, planar and fiber coherent light sources in the near and middle IR ranges. The area of possible applications in the IR region is much wider than for silicate glasses and extends up to 5-6 μm for bulk and planar devices and up to 3.5-4.5 μm for step-index optical fibers. Glasses are also characterized by a high rare-earth oxide solubility and a sufficient stability against crystallization. The main obstacle for their widely using is the difficulty to obtain glasses with low concentration of 3d-transition metals and particularly OH-groups, as well as insufficient study of luminescent properties of such high-purity glasses.

In this paper tellurite glasses were prepared by melting a mixture of oxides in platinum crucible inside the quartz glass reactor in a purified oxygen atmosphere. After several hours of melting, the melt was poured into a quartz glass mould, and then the samples were annealed at glass transition temperature. The high-purity glasses were characterized by 2-3 ppm wt content of 3d-transition metals and extremely low OH-group absorption up to several thousandths of $cm^{-1}$ at the stretching vibrations peak of about 3.2 μm. Series of samples were prepared with different concentrations of erbium oxide and hydroxyl groups.

We investigated the optical, including luminescent properties of erbium ions in the near and middle IR ranges. The transmission spectra were measured using a spectrometer Lambda 900 (Perkin Elmer) in the 0.3-

2.5 μm range and a Fourier-spectrometer Bruker IFS-113v in the 1.5-8.0 μm range. The luminescence spectra were recorded on MDR-2 monochromator in the 1-3 μm range, fiber laser at 0.975 μm was used as a pump, and photovoltaic InSb detector P5968 was used as a receiver. The $4I_{11/2}$ Er level lifetimes were measured using 976 nm OPO excitation with pulse duration ~5 ns. The decay kinetics was measured in the spectral range of 1 micron by infrared PMT with C1 photocathode having time response ~20 ns.

Erbium-doped glasses are transparent in the 0.4-5.2 μm wavelength region, and the dependence of the absorption coefficient at the ~0.98 and ~1.5 μm band peaks on erbium oxide concentration is linear. When excited at 0.975 nm, an intense broadband photoluminescence with the peaks at ~1.6 and ~2.8 μm are obtained. The luminescence intensity increases with erbium oxide content, the dependences for both bands contain no extremes and are close to linear. Luminescence intensities and decay times increase with OH content decreasing. The luminescence decay times for 1.55 and 2.75 μm bands depend on the glass matrix compositions and the concentration of erbium oxide and hydroxyl groups, being for the best samples at the level of 8-10 and 0.2-0.25 ms, respectively.

The study was partly supported by the Russian Foundation for Basic Research (15-03-08324).

## V-1 O-8

# Visible and near-infrared luminescence of Pb-active centers in silica glass

A.V. Kharakhordin[1*], V.O. Sokolov[1], V.G. Plotnichenko[1], A.Yu. Laptev[2], A.N. Guryanov, E.M. Dianov[1].
[1]Fiber Optics Research Center of RAS, Moscow
[2]Institute of Chemistry of High-Purity Substances of RAS, Nizhny Novgorod
[*] E-mail: kharakhordin@fo.gpi.ru

Bi-doped glasses represent a new class of optically active materials, having a wide luminescence region in the near IR range. Investigation of glasses doped with other elements, similar to bismuth in their properties, can provide an additional information on the origin of Bi-centers, as well as the possibility of developing new active materials for use in fiber optics. One of such elements is lead. In [1, 2] the infrared luminescence was observed within 1.1-1.2 μm and near 1.4 μm in optical fibers based on silica and germanate-silicate glasses doped with lead, which preforms were fabricated by MCVD method. No valid models of lead infrared luminescence centers were suggested in these papers.

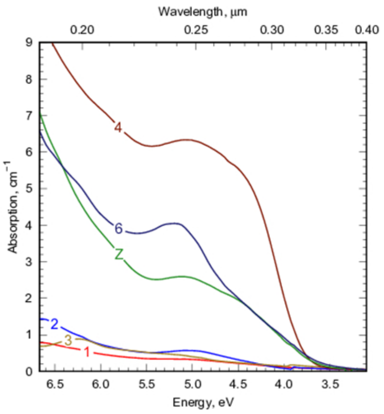


Fig. 1. Absorption spectra of the investigated samples

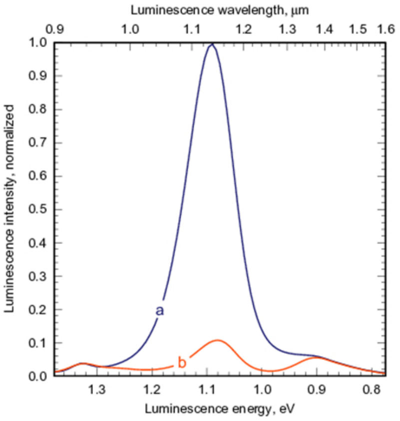


Fig.2. IR luminescence spectra excited at 300 nm in the №6 sample (a) before and (b) after γ-irradiation.

For our studies we used the optical fiber preforms produced by MCVD method with a $SiO_2$-glass core doped with lead. Experimental study of the transmission, luminescence and luminescence excitation spectra of $SiO_2$:Pb glasses has shown that at a relatively low PbO content (~ 0.1 wt. %) the visible luminescence within 300-450, 500-600 nm and infrared luminescence within 850-950, 1000-1200, 1300-1400 nm are observed in these glasses. According to our calculations, the luminescence in the 300-450 nm region is related to three- and twofold coordinated Pb atoms, and that within 500-600 nm is due to twofold coordinated Pb atoms. IR luminescence in the 1000-1200 nm region can be attributed to the center, representing an interstitial $Pb^+$ ion in the $SiO_2$ network, and that in the 850-950 nm and 1300-1400 nm regions is due to the center, being a complex formed by interstitial $Pb^0$ atom and two oxygen vacancies.

1. I. A. Bufetov, et al. "Luminescence and optical gain in Pb-doped silica-based optical fibers", Opt. Express 17(16), 13487-13892 (2009)
2. A. S. Zlenko, et al. "Optical properties of IR-emitting centers in Pb-doped silica fibers", Quant. Electronics 42(4), 310-314 (2012)

V-1 O-9

# The study of the state of bismuth ions in Bi-doped GeS$_x$ (1<$x$<2) and Ge-As-S glasses

R.P. Ermakov[1], L.D. Iskhakova[1], A.A. Mistonov[2], A.P. Chumakov[3], M.V. Sukhanov[4], M.F. Churbanov[4]
[1]Fiber Optics Research Center of the Russian Academy of Sciences (FORC RAS);
[2]Saint Petersburg State University (SPBU);
[3]European Synchrotron Radiation Facility (ESRF);
[4]G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences.

Bi-doped glasses have been found to be promising materials for production of new broadband fiber amplifiers and fiber lasers. The purpose of this study was to investigate the phase formation in Bi-doped GeS$_x$ (1<x<2) and Ge-As-S (with Ge content 35-÷40 at. %, As content 2÷15 at. % and S content 50÷60 at. %) of the crystalline phases formation, interphase distribution of bismuth activation ion and its state in glasses network. The Bi content varies from 0,25 to 5,0 at. %.

The synthesis of glasses was carried out using initial elementary substances of high-purity grade [1, 2]. The elements distribution in the samples was carried out by means of EDXA analysis (SEM JSM-5910LV, analytical system AZtecENERGY). XRD analysis was conducted at ambient (D2Phaser) and elevated (D8 Advance) temperature. Bi valence state and its nearest-neighbor coordination environment have been found from near edge X-ray absorption fine structure data. XANES experiments were performed from the Bi $L_I$ and $L_{III}$ edges at the European Synchrotron Radiation Facility in ID26 beamline with Si [111] monochromator crystals in fluorescence mode. It was shown the crystallization of GeS, $GeS_2$ and metallic Bi phases in Bi: GeS$_x$ glasses while at the Ge-As-S system crystallizes GeS and metallic Bi. The limits of glass stability for the synthesis technique used were established to correspond to 1,3 < $x$ < 1,6 concentration range. The system Ge-As-S is more resistant to crystallization. The dopant Bi was shown not to be incorporated into germanium sulfide crystal lattice. A reversible process of metallic bismuth formation and its subsequent dissolution was observed during thermal treatment of the glasses under ‘heating-cooling-heating" mode.

From XRD data have been estimated the intervals of short and intermediate range order in studied glasses. From XANES data Bi state in system GeS$_x$ remains invariable in the range 1,35<$x$<1,5and changes upon transition to $GeS_{2,3}$ glasses. X-ray fluorescence spectra of Bi from Ge-As-S glasses depends first of all from [S]/[Ge] relation. Based on the obtained experimental results and literature review (ERXAFS, high energy X-ray and neutron diffraction, computer simulation technique) is discussed the state of Bi ions in glasses networks.

1. L.D. Iskhakova, R.P. Ermakov, M.V. Sukhanov, V.V. Voronov, A.P. Velmuzhov, D.V. Phillipovsky, V.G. Plotnichenko, M.F. Churbanov // J. Non-Cryst. Solids. 2015. V. 428. P. 132-137
2. V. G. Plotnichenko, D. V. Philippovskiy, V. O. Sokolov, M. V. Sukhanov, A. P. Velmuzhov, M. F. Churbanov, E.M. Dianov //Opt. Mat. Express. 2014. V.4. No. 2. P. 366-374

# ISNOG 2016

# Thursday, August, 25th

## *Business Hall*

# Session V-2

**Session V-2: Optical Linear and Non-Linear Properties of Glasses and Fibers**

V-2 O-1

# Linear and nonlinear optical properties of chalcogenide glasses within Ge-Sn-Se system

Feifei Chen[1,2*], Beijing Qiao[1,2], Yicong Huang[1,2], Shixun Dai[1,2], Qiuhua Nie[1,2]
[1]Laboratory of Infrared Materials and Devices, The Research Institute of Advanced Technologies, Ningbo University, Ningbo 315211, China
[2]Key Laboratory of Photoelectric Materials and Devices of Zhejiang Province，Ningbo, 315211, China
*chenfeifei1@nbu.edu.cn

A systematic investigation on optical properties and network structure of chalcogenide glasses in Ge-Sn-Se ternary system is given. We find threshold behavior of optical properties, namely transitional composition of the Ge-Sn-Se glasses with progressive replacement of Se by Sn. Calculation of mean coordination number indicates that the transition-like feature of optical properties is associated with evolution of chemical ordering of the Ge-Sn-Se network. Analysis of Raman spectra of the glasses explains that such optical phenomenon comes from interactions between Se-Se chain bonds, $Sn(Se_{1/2})_4$ tetrahedra and Sn-Sn homopolar bonds.

We had also investigated the third-order optical nonlinearities of chalcogenide glasses Ge–Sn–Se ternary system and $As_2Se_3$ at a mid-infrared window of 3 and 3.5 μm with femtosecond Z-scan technique, and the highlights of our research are:

(1) Third-order optical nonlinearities of chalcogenide glasses at a mid-infrared window are presented in this study for the first time;

(2) performance improvement of optical nonlinearities of the chalcogenide glasses is observed at 3500 nm due to the absence of multiple photon absorption and impurity absorption;

(3) dependence of the mid-infrared optical nonlinearities on chemical composition of the chalcogenide glasses has been systematically investigated, and it has been well explained by a topological model.

V-2 O-2

# Study on the magneto-optical properties of $Ga_2S_3$ -$GeS_2$-based chalcohalide glasses

Y.T. Xu, H.T. Guo*, G. Chen, M. Lu, B. Peng
State Key Laboratory of Transient Optics and Photonics, Xi'an Institute of Optics and precision Mechanics, Chinese Academy of Science (CAS) , Xi'an, Shaanxi 710119, PR China
*Corresponding author: guoht_001@opt.ac.cn

Considerable attention was paid towards the study of the Faraday effect of magneto-optical materials in the past years due to their extensive applications such as optical isolators, magnetic field sensors, optical switching, and so on. Compared with other materials, magneto-optical glasses are of interest because they are transparent in a broad spectral region and can be readily formed into various shapes such as large-size plates or fibers. There are two kinds of magneto-optical glasses, i.e. paramagnetic glass and diamagnetic glass, in which the paramagnetic glasses are widely used because of their large Verdet constants. However, their disadvantage is also obvious, i.e. the Verdet constant is dependent of temperature. Diamagnetic glasses with temperature independent characteristic are therefore interested in. In various glass systems, chalcogenide glass has the highest refractive index and dispersion, and high Verdet constant is expected to be obtained. Moreover, it has the most broad transparent region from visible to ～20 um infrared wavelength, therefore can be used in infrared laser systems. Few works about the chalcogenide glass's magneto-optical properties were studied before, limited in some specific glasses such as $As_{40}S_{60}$ and $Ge_{20}As_{20}S_{60}$. In this work, several series of $Ga_2S_3$-$GeS_2$-based chalcogenide glasses were prepared and their magneto-optical properties were investigated. The relationships between the Verdet constant, glass composition and laser wavelength were studied and discussed. The figure of merit (*FOM*) was given for each composition glass finally.

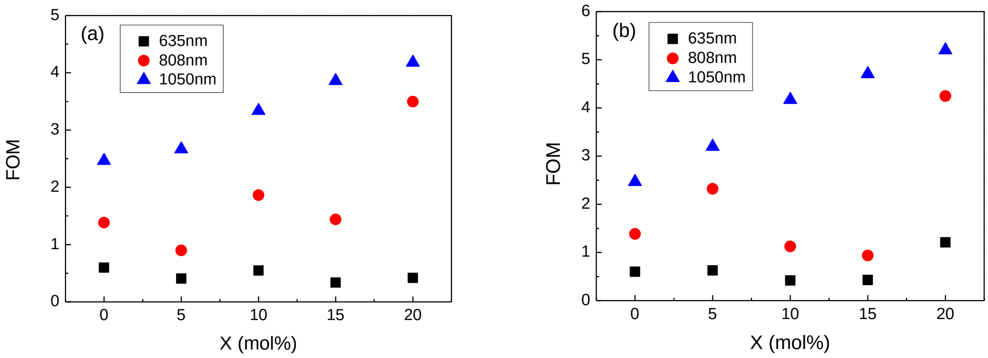


Figure. Magneto-optical figure of merits (*FOM*, $FOM=V(\lambda)/\alpha(\lambda)$) for the $80GeS_2\cdot(20\text{-}x)Ga_2S_3\cdot Sb_2S_3$ and (b) $80GeS_2\cdot(20\text{-}x)Ga_2S_3\cdot In_2S_3$ chalcogenide glasses.

### V-2 O-3

# Accurate measurement of the nonlinear optical constants of chalcogenide glasses

E.A. Romanova[1], Yu.S. Kuzyutkina[1], V.S. Shiryaev[2], T.M. Benson[3], A.B. Seddon[3], S. Guizard[4]
[1] Saratov State University, Saratov, Russia
[2]Institute of Chemistry of High Purity Substances of RAS, Nizhny Novgorod, Russia
[3] University of Nottingham, Nottingham, UK
[4] Ecole Polytechnique, Palaiseau, France
E-mail: romanova@optics.sgu.ru

Nonlinear coefficients of refraction and absorption are basic parameters in design of nonlinear optical devices and in development of the technology of materials processing by high-intensity laser pulses. For crystalline semiconductors, these coefficients can be evaluated by using the results of their nonlinear optical response theory developed in [1]. For non-crystalline semiconductors, in particular, chalcogenide glasses, such a theory has not been yet developed. The nonlinear optical constants of chalcogenide glasses measured mainly at the wavelengths 1.064 μm, 1.25 μm and 1.55 μm of available ultra-fast lasers exhibited a large scatter of magnitudes [2]. These results depended on duration of laser pulses used in the measurements. Uncertainty of the results increased near the fundamental absorption band (FAB) edge of a particular glass.

In this work, we present a thorough analysis of the nonlinear optical response of chalcogenide glasses of the systems As-S-Se and Ge-Se by using a time-resolved pump-probe method [3]. As has been shown in [4], at large pump pulse energies this response includes the Kerr nonlinearity and photo-induced charge carriers kinetics. The latter process significantly depends on where a glass composition was illuminated – near or far from the fundamental absorption band edge. If the pump pulse wavelength corresponds to the Urbach tail, the time of charge carriers trapping by bound states in the bandgap does not depend on the pump pulse energy. In a glass composition illuminated far from the fundamental absorption band edge, the trapping time increases with the pump pulse energy decrease. This means that upon the photo-excitation, electrons can exist in a free state over tens of picosecond. The structural changes, which are usually associated with the electrons trapping process, can develop from the pico- to micro- second time scale. Using of the pump pulses of the pico- or nano- second duration for measurements of the nonlinear optical constants does not provide accurate and reliable magnitudes.

By analysis of the time-resolved nonlinear optical response, conditions have identified when the density of photo-induced charge carriers in a glass sample is small and can be neglected in calculations of the Kerr constant $n_2$ and two-photon absorption coefficient $\beta_2$. These coefficients have been evaluated for the compositions $As_{40}S_xSe_{60-x}$ ($x = 0, 15, 30, 45, 60$) and $Ge_{20}Se_{80}$, $Ge_{12}Se_{88}$ at the pump laser wavelength of 790 nm. Our results of $n_2$ evaluation and literature data reveal that $n_2$ magnitudes are always positive-valued that is different from the direct-gap crystalline semiconductors having negative-valued $n_2$ in some spectral range near the FAB edge [1]. Spectral dependence of $\beta_2$ of the direct-gap crystalline semiconductors exhibit an agreement (within an experimental error) with literature data and our results of $\beta_2$ measurements for the glass samples illuminated in the range of their weak absorption tails. For the samples illuminated at their Urbach tails, when electron transitions through the gap states are possible, the magnitudes of $\beta_2$ differ substantially from that calculated by using the results of the theory of the direct-gap crystalline semiconductors.

This work was supported by the Russian Science Foundation (Russia, Grant No. 16-13-10251).

1. Sheik-Bahae M, Hagan D J, and Van Stryland E W 1990 Phys. Rev. Lett. **65** 96
2. Zakery A and Elliot S R 2007 Optical nonlinearities in chalcogenide glasses and their applications (Springer-Velag, Berlin, Heidelberg, New York)
3. Martin P, Guizard S, Daguzan Ph, Petite G, D’Oliveira P, Meynadier P and Perdrix M 1997 Phys. Rev. B **55** 5799
4. Romanova E A, Kuzyutkina Y S, Konyukhov A I, Abdel-Moneim N, Seddon A B, Benson T M, Guizard S, Mouskeftas A 2014 Opt. Eng. **53** 071812

V-2 O-4

# Optical and thermal properties of monoisotopic glasses on the basis of arsenic sulfide, germanium sulfide and arsenic selenide

M.V. Sukhanov, M.F. Churbanov
G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Science,
Nizhny Novgorod, Russia
sukhanov@ihps.nnov.ru

An interest to monoisotopic chalcogenide glasses is due to possibility to get new data on their structure and optical properties, on chemical state of their impurities, on their interaction with glass network. Semiconductor engineering and opto-electronics can be the possible field of application of these glasses.

The aim of investigation is to prepare monoisotopic $GeS_{1.35}$, $As_{35}Se_{65}$ glasses, characterization of the isotopic effect in their optical and thermal properties as well as specification of structure of these glasses.

Monoisotopic $^{72}Ge$, $^{73}Ge$, $^{74}Ge$, $^{32}S$, $^{34}S$ and $^{80}Se$ with enrichment of 99.6–99.9 at. %, highly enriched $^{72}Ge$, $^{76}Ge$ (52 and 88 at. %) and germanium with the maximum isotopic disorder, containing 72 and 76 isotopes, were used in this work. The content of metal impurities in the samples of the initial simple substances did not exceed $(0.02–2)\cdot 10^{-4}$ wt. %, the impurities of light elements C, O, H – $(0.1–1.5)\cdot 10^{-4}$ wt. %. Glasses of the given elemental composition were prepared by melting simple substances in evacuated quartz ampoules by the known techniques. The mass of the prepared samples was 0.5–4 g. The samples of glasses were investigated by the methods of Raman spectroscopy, visible and IR-spectroscopy and by differential scanning calorimetry.

In IR-spectra of polished samples of $GeS_{1.35}$ glasses with thickness of ~300 μm and 5.5 mm the intrinsic absorption bands were identified at 382, 765, 1101 $cm^{-1}$. It is shown that the band position at 765 $cm^{-1}$ linearly depends on $M^{-1/2}$ value (M is the reduced mass of $^{M}Ge–^{32}S$ pair) which makes it possible to connect it with Ge – S vibration in glass network. The observed isotopic shift of bands at 382 and 1147 $cm^{-1}$ proves their composite nature. One of vibrational modes also refers to Ge – S vibration. The dependence of bandwidth 765 cm$^{-1}$ on the value of isotopic disorder in cation constituent of glass network was found. In IR-spectra of $Ge^{32}S_{1.35}$ and $Ge^{34}S_{1.35}$ glasses the isotopic shift was observed in the position of impurity band S – H at 2511 cm$^{-1}$ by 1.7 cm$^{-1}$ for glass with heavy isotopic species of sulfur.

On the basis of the position of short-wave absorption edge of glasses their band-gap width was calculated as 1.55–1.58 eV. Its value has a weak tendency to decrease with the increase in average atomic mass of germanium but this change remains within the limits of measurement accuracy. Raman spectroscopy absorption spectra of $GeS_{1.35}$ glasses are typical of chalcogenide glasses. The bands at 295, 368.5 and 412 cm$^{-1}$ are identified in glass spectra by mathematical decomposition. Their frequencies are shifted by 2–6 cm$^{-1}$ with the change in mass of Ge isotope. Analysis of isotopic effect in the position of these bands made it possible to interpret them as vibration of Ge – Ge, Ge – S bonds in tetrahedrons connected with edges and of Ge – S – in chains. There were no significant differences in glass transition temperature and in start of crystallization of $GeS_{1.35}$ glasses determined by the method of differential scanning calorimetry.

In IR absorption spectra of $As_{35}{}^{nat}Se_{65}$ and $As_{35}{}^{80}Se_{65}$ glasses the intrinsic (Se–Se) and impurity (Se–H, As–O, Se–O, and water) absorption bands were identified. With the increase of atomic mass of selenium, a shift in the intrinsic absorption band by ~2.8 cm$^{-1}$ at 481 cm$^{-1}$ into the low-frequency range was observed. The glasses are characterized with band-gap width of 1.51 eV. For purification of glasses from impurities of water, As–O, Se–O they were subjected to melting with getter (Al) and to subsequent distillation in dynamic vacuum. Macro-composition of the purified glasses, determined by the method of chemical-atomic-emission spectral analysis with ICP, within the limit of error meets the composition set during synthesis. Optical fibers were drawn from the melt and their optical losses were measured.

In IR spectra of optical fiber obtained from $As_{38}{}^{32}S_{62}$ and $As_{38}{}^{34}S_{62}$ glasses isotopic shift of bands in the region 5.26–5.87 μm was observed. The value of this shift corresponds to theoretical value calculated for S-S vibration in glass network.

V-2 O-5

# A portable luminescent thermometer based on green up-conversion emission of $Er^{3+}/Yb^{3+}$ co-doped tellurite glass

D. Manzani*, J. F. S. Petruci, K. Nigoghossian, A. A. Cardoso, S. J. L. Ribeiro
Institute of Chemistry, São Paulo State University, UNESP, CP 355, Araraquara, SP, Brazil
*danilo.manzani@gmail.com

The determination of temperature is an essential parameter in several application scenarios, such as in the biomedical, technological and industrial fields. Optical thermometry appears as an excellent alternative for conventional electric-based temperature sensors, featuring advantages such as non-contact methods, fast response, no interference of the electromagnetic field and high temperature sensitivity. In this contribution, we have proposed an optical thermometer probe comprised of an $Er^{3+}/Yb^{3+}$ co-doped tellurium glass attached on the tip of an optical fiber and optically coupled to a laser source and a portable USB-spectrometer. The ratio of the up-conversion green emission integrated peak areas when excited at 980 nm is temperature dependent and employed for thermometer calibrations purposes. The thermometer was operated in the range of 5 – 50 ºC and 50 – 200 ºC, revealing excellent linearity ($r^2 > 0.99$), suitable accuracy and precision of ±0.5 and ±1.1 ºC, respectively. The high thermal sensitivity presented by the obtained probe results from the optimization study on $Er^{3+}$ concentration to obtain high green emission intensity and thus higher sensitivity. The described probe presented suitable properties for its application as a temperature sensor and superior performance among others $Er^{3+}$-based optical thermometers, in terms of thermal sensitivity.

# ISNOG 2016

## Thursday, August, 25th

## *Business Hall*

# Session VII

**Session VII: Glass-Ceramics and Optical Ceramics**

VII O-1

# Synthesis, structure and optical properties of transparent glass-ceramics with nanocrystals of rare-earth niobates

I. Alekseeva[1], O. Dymshits[1], M. Tsenter[1], A. Zhilin[1], A. Vasilevskaya[1], P. Loiko[2],
N. Skoptsov[2], K. Yumashev[2], E. Vilejshikova[2], K. Bogdanov[3]
[1]NITIOM Vavilov State Optical Institute, Saint-Petersburg, Russia
[2]Center for Optical Materials and Technologies, Belarusian National Technical University, Minsk, Belarus
[3]National Research University of Information Technologies, Mechanics and Optics, St. Petersburg, Russia
e-mail: vodym@goi.ru, vodym1959@gmail.com

Rare-earth ortho-niobates, RENbO$_4$, demonstrate promising luminescent, chemical and mechanical properties. They are synthesized by growth of single crystals, fibers or powders by solid state reactions, by combustion method, via sol-gel route, etc. However, their technological applications are often limited by poor homogeneity. Formation of transparent glass-ceramics with rare-earth ortho-niobate nanophase [1] is a convenient route for preparing the nanosized RENbO$_4$ crystals homogeneously dispersed in the matrix.

Initial glasses of the lithium aluminosilicate system doped by 2-5 mol % RE$_2$O$_3$ (where RE is Y, Eu, Tm, Ho, Er, Yb or their combination) and 2-5 mol % Nb$_2$O$_5$ were prepared by conventional melt-quenching at 1580 °C with stirring and casted on a metal plate. To prepare glass-ceramics, they were heat-treated in the temperature range of 700 – 1400 °C. The structure of the initial glasses and its transformation with heat-treatment were characterized by X-ray diffraction analysis (XRD), high-temperature X-ray diffraction, differential scanning calorimetry, Raman spectroscopy, absorption and luminescence spectroscopy. According to Raman spectroscopy findings, inhomogeneous regions enriched by rare-earth niobates are formed during the glass cooling and annealing. Depending on the composition of the initial glass, concentrations of RE and niobium oxides, and on the nature of the rare-earth element, they are either completely amorphous or contain nanocrystals with a defect fluorite structure. Upon heat-treatments at 720–740 °C, the size and volume fraction of these crystals increases. At elevated temperatures, the crystal structure transforms to a tetragonal one (at 800–900 °C). At 1000 °C and above, the high-temperature tetragonal phase with a sheelite structure is formed. According to in-situ high-temperature XRD study, this phase transforms to a monoclinic (M) form at cooling down the sample below 600 °C, while the tetragonal phase does not show any prove of such kind of transformation and retains even after cooling down. Crystals of β-quartz solid solutions (ss) appear at 800 °C, their transformation to β-spodumene ss begins at above 1100 °C, so that glass-ceramics prepared at 1350 °C contain the crystals of M-RENbO$_4$ and β-spodumene ss.

It was demonstrated that the RENbO$_4$ nanocrystals play a role of nucleating agents and they are the promising luminescent crystals. The spectral-luminescent properties of glass-ceramics are directly linked to their structure and reflect all the above mentioned structural transformations. Co-precipitation of crystals of β-quartz and β-spodumene solid solutions does not influence the optical properties of the rare-earth ortho-niobates as the rare-earth ions do not enter the structure of aluminosilicate solid solutions. Transition metal ions enter the crystals of β-quartz and β-spodumene ss. By these means, transparent multifunctional materials containing RE ions in niobate crystals and transition metal ions in crystals of β-quartz ss are prepared. Crystallization of lithium aluminosilicate ss ensures high thermal shock resistance of these glass-ceramics.

This work was partly supported by the RFBR (Grant 13-03-01289 A).

1. O.S. Dymshits, I.P. Alekseeva, A.A. Zhilin, M.Ya. Tsenter, P.A. Loiko, N.A.Skoptsov, A.M. Malyarevich, K.V. Yumashev, X. Mateos, A.V. Baranov, J. Lumin. 160 (2015) 337–345.

VII O-2

# Effect of LiF sintering aid on the properties of $MgAl_2O_4$ ceramics

A.V. Novikova[1,2], S.S. Balabanov[1,2], E.M. Gavrishchuk[1,2], A.V. Belyaev[1,2], D.A. Permin[1,2]
[1] G.G. Devyatykh Institute of Chemistry of High-Purity Substances RAS, Nizhny Novgorod, Russia
[2] N.I. Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, Russia
E-mail: anastasia93novikova@yandex.ru

Magnesium aluminum spinel ($MgAl_2O_4$) ceramics is well-known optical material for industrial and military applications. $MgAl_2O_4$ possesses the unique combination of optico-mechanical characteristics: high hardness, optical transmission in a broad spectral range (0.2-6 μm), chemical stability.

The properties of such ceramics are significantly determined by the characteristics of the starting powder: its stoichiometry, impurities content, morphology and sintering aids. According to literature data [1], the most effective sintering aid is lithium fluoride. The aim of this work is to investigate the effect of lithium fluoride content in starting powders on the optico-mechanical properties of produced $MgAl_2O_4$ ceramics.

The magnesium aluminum double isopropoxide ($MgAl_2(O^iPr)_8$) was used as the precursor to obtain $MgAl_2O_4$ powder. It was synthesized by interaction of activated magnesium-aluminum alloy with isopropyl alcohol [2] and then purified by vacuum distillation. The hydrolysis of $MgAl_2(OPr^i)_8$ was performed by azeotropic mixture isopropyl alcohol–water with equimolar ratio 1:8. Lithium fluoride was added as a solution during the hydrolysis. Magnesium aluminum spinel powders with LiF content up to 1 wt % were obtained by calcination of the hydrolysis products in air at 750 °C for 3 h.

According to the scanning electron microscopy results, the particles of both undoped and LiF-doped powders were spherical with the average size of 30-50 nm and aggregated into soft agglomerates up to 50 μm in size.

The resulting powders were used to sinter transparent $MgAl_2O_4$ ceramics by hot-pressing at a temperature of 1600 °C and pressure of 50 MPa. It was found that optical properties and microstructure of ceramic samples correlate with LiF content in starting powders. The LiF concentration at which maximum light transmission value was reached amounted to 0.5 wt %.

The ceramics microstructure was characterized by the linear dependence of the average grain size on the LiF content. Ceramics made from powder with 0.5 wt % LiF had the average grain size of 25 μm. The hardness of undoped spinel samples (11.9±0.7 GPa) was lower than that of LiF-doped samples (up to 14.6±0.5 GPa), which is connected with more homogeneous structure of ceramics with LiF and less defects content (pores, microcracks).

Thus the effect of LiF content on the properties of obtained $MgAl_2O_4$ ceramics was investigated. The optimal concentration of sintering aid was determined. It was shown that lithium fluoride improves microstructure homogeneity and optical characteristics of spinel ceramics.

This work was supported by the Russian Foundation for Basic Research, grant no. 15-03-04299.

1. S.S. Balabanov et al. Fabrication of transparent $MgAl_2O_4$ ceramics by hot-pressing of sol-gel-derived nanopowders. Ceramics International, 2015, v. 41, p. 13366–13371.
2. E.M .Gavrishchuk, V.V .Drobotenko. A method for producing a magnesium-aluminum double isopropoxide, RU Patent 2471763 (2013).

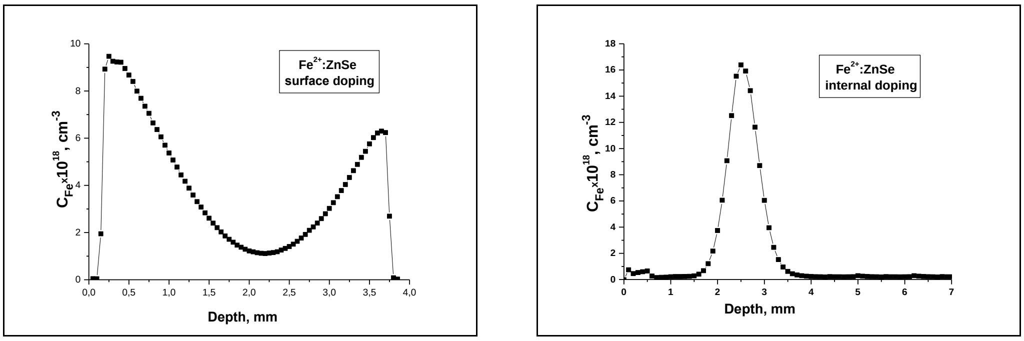
VII O-3

# Fabrication of $Fe^{2+}$:ZnSe polycrystalline samples with different geometry of doping and investigation of generation characteristics of synthesized materials

N.A. Timofeeva[1], K.N. Firsov[2], E.M. Gavrishchuk[1], V.B. Ikonnikov[1], S.Y. Kazantsev[2],
I.G. Kononov[2], S.A. Rodin[1], D.V. Savin[1]
[1]G.G. Devyatykh Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences,
49 Tropinina Str., 603950 Nizhny Novgorod, Russia
[2]A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, 38 Vavilova Str., 119991
Moscow, Russia
e-mail: timofeeva@ihps.nnov.ru

Creation of high-power $Fe^{2+}$:ZnSe-lasers operated in the 3.5-5 μm spectral range is in great demand for many practical applications. In recent years, the efforts in investigations are focused on increasing the power and efficiency of $Fe^{2+}$:ZnSe-laser radiation at room temperature. Advancement in this direction is mainly determined by active medium characteristics, such as structural and optical homogeneity, purity of crystals, total concentration of active ions and the character of their distribution over the depth of the sample. The complex of all these properties essentially depends on the method of material preparation.

The original approaches of fabricating polycrystalline $Fe^{2+}$:ZnSe samples with the controlled profile of distribution of $Fe^{2+}$ concentration in the sample have been presented in this work. High optical quality CVD-ZnSe was utilized as a base matrix. In the first approach suggested in this work the doping was realized by the method of high temperature diffusion involving HIP-treatment (hot isostatic pressing) from the thin-film source of metallic iron preliminarily deposited on both flat surfaces of the sample (“surface doping”). The HIP-treatment in conditions of high isostatic pressure makes it possible to elevate the temperature during the doping process up to 1200-1300 °C without any noticeable mass transfer due to sublimation and to reduce the duration of the process. In the second approach samples with a zero dopant concentration at the surface and a maximum concentration inside the sample were fabricated (“internal doping”). In order to create such samples, the three-layer ZnSe–$Fe^{2+}$:ZnSe–ZnSe structures were preliminarily obtained with the use of the chemical vapor deposition process in the commonly employed CVD-reactor. After that, the obtained preforms were subjected to HIP-treatment. Variation in the conditions of $Fe^{2+}$:ZnSe layers preparation, CVD-process and HIP-treatment made it possible to control the total concentration of $Fe^{2+}$ ions and the geometry of their concentration profile. In the figure given below one can see the distribution of $Fe^{2+}$ concentration over the depth of ZnSe samples with “surface” and “internal” doping.



Distribution of $Fe^{2+}$ ions concentration over the depth of ZnSe samples

Impurity composition has been analyzed, optical properties of synthesized materials have been studied and the generation characteristics of $Fe^{2+}$:ZnSe-lasers excited at room temperature by an electric-discharge HF laser have been investigated. $Fe^{2+}$:ZnSe samples with “internal” doping gave the generation energy

E=298 mJ with the slope efficiency $\eta_{slope}$=45 % and efficiency with respect to the absorbed energy $\eta_{abs}$=40 %. A sample 63 mm in diameter doped on both sides provided the generation energy E=1.43 J with the slope efficiency $\eta_{slope}$=52 % and $\eta_{abs}$=48 %. The great efficiency value is a proof to the high optical quality of the investigated laser elements. At the present time, the obtained values of generation energy and efficiency are the highest for $Fe^{2+}$:ZnSe-lasers operating at room temperature.

The work was supported by the RSF grant №15-13-10028 in the part concerning development and manufacturing ZnSe:$Fe^{2+}$ samples.

VII O-4

# Luminescent glass-ceramics containing fluoride, aluminate and borate subphases for WLED application

X. Qiao[1]*, J. Zhao[1], R. Ma[1], J. Du[2], X. Fan[1]
[1]State Key Laboratory of Silicon Materials, School of Materials Science and Engineering,
Zhejiang University, Hangzhou 310027, China
[2]Department of Materials Science and Engineering, University of North Texas, Denton, Texas, U.S.
*Corresponding author: qiaoxus@zju.edu.cn

The trend of LED lighting nowadays is high power, general lighting and intelligent lighting, which bring up new requirements for the white light emitting phosphor materials with high quantum yield (QY), high color rendering index (CRI), low correlated color temperature (CCT) and high stability. The luminescence quantum yield of the glass doped with molecule-like Ag ($Ag_m^{n+}$, ML-Ag) can reach 96.7 % [1-4], and the co-doping with Eu ions could well improve its CCT and CRI. However, the QY and CRI cannot be improved synchronously. Here we prepared one type of luminescent glass containing fluoride, aluminate nanocrystals and borate subphases simultaneously. In this glass, $Eu^{2+}$ ions enrich in fluoride crystals, $(Ag^+)_2$ in aluminate crystals, emitting blue and red light respectively, while ML-Ag enrich in borate subphase regions, emitting green light [5, 6]. By this means, there is no mutual interference between different kinds of luminescent center, thus it could enhances QY and CRI simultaneously. Therefore, such type of luminescent glass could be potential candidate as high power LED lighting materials.

1. Tikhomirov, V.K., et al., Preparation and luminescence of bulk oxyfluoride glasses doped with Ag nanoclusters[J]. Optics Express, 2010. 18(21): p. 22032-22040.
2. Jiménez, J., S. Lysenko, and H. Liu, Photoluminescence via plasmon resonance energy transfer in silver nanocomposite glasses[J]. Journal of Applied Physics, 2008. 104(5): p. 054313.
3. Eichelbaum, M. and K. Rademann, Plasmonic Enhancement or Energy Transfer? On the Luminescence of Gold-, Silver-, and Lanthanide-Doped Silicate Glasses and Its Potential for Light-Emitting Devices[J]. Advanced Functional Materials, 2009. 19(13): p. 2045-2052.
4. Guo, H., et al., Origin of White Luminescence in Ag-Eu Co-doped Oxyfluoride Glasses[J]. Journal of the Electrochemical Society, 2011. 158(6): p. J165-J168.
5. Ma, R., et al., Enhancing NIR emission of Yb 3+ by silver nanoclusters in oxyfluoride glass[J]. Journal of Luminescence, 2014. 152: p. 222-225.
6. Ma, R., et al., Eu 2+ promoted formation of molecule-like Ag and enhanced white luminescence of Ag/Eu-codoped oxyfluoride glasses[J]. Journal of Non-Crystalline Solids, 2016. 432: p. 348-353.

# ISNOG 2016

Monday, August, 22nd

***Hall Standard 1***

# Session VIII

**Session VIII: Glasses for Medicine, Biotechnology, Sensors, Energy applications**

VIII-inv 1

# Russian neodymium phosphate glasses for the laser controlled fusion research: technology and limit properties

V.I. Arbuzov
Research and Technological Institute of Optical Materials Science,
All-Russian Scientific Center “S. I. Vavilov State Optical Institute”, St.-Petersburg
National Research University of Information Technologies, Mechanics and Optics, St-Petersburg
arbuzov@goi.ru, arbuzov@oi.ifmo.ru

Multichannel pulse high-energy and high-peak-power amplifier systems such as the ***NIF*** (***National Ignition Facility***) in the USA and the ***LMJ*** (***Laser Megajoul***) in France have been put into operation early in the 21st century. To take one example, each of 192 channels of the *NIF* has 16 big-sized active elements (AE), they are arranged in the channel under the Brewster angle. A light beam with an aperture of 400*400 mm (and even more) four times passes through the channel. 192 amplified beams bear 1.8 MJ of energy in a pulse lasting 3.5 nanoseconds with an average peak power of $5.0*10^{14}$ W. The output energy of the *LMJ* exceeds .2.0 MDzh. Simultaneously, a 4-channel laser system “Luch” was constructed in Russia at the *Russian Federal Nuclear Center, Sarov, Region Nizhnii Novgorod*. It used AEs with light aperture of 200*200 mm. With this facility, the physical and technical principles of creation of a 192-channel pulse laser facility *UFL-2M* with output energy of 2.8 MJ were worked out. The *UFL-2M* is going to use AEs with light aperture of 400*400 mm (810*460*40 mm in size). The *NIF*, the *LMJ*, and the *UFL-2M* are dedicated, first of all, for the research in the field of controlled nuclear fusion but they can be also used in the fields of plasma physics, physics of high energy densities, physics of interaction of laser radiation with matter.

Commercial phosphate laser glasses with neodymium concentration up to $4.2*10^{20}$ $cm^{-3}$ (LG-750 (Schott, USA), LHG-8 (Hoya, Japan), KGSS 0180/35 (*Research and Technological Institute of Optical Material Science, RTIOMS, RF*), and KNFS-3 (*Lytkarino Plant of Optical Glasses, LPOG, RF*) of the methaphosphate system $K_2O$–BaO-$Al_2O$-$P_2O_5$ [1–4] proved to be the most suitable materials to manufacture big-sized AE of such multichannel pulse laser systems. To be used in such systems, these glasses must meet a wide variety of stringent requirements. Some of their characteristics (probabilities of radiative electron transitions, reduced concentration quenching of $Nd^{3+}$ luminescence due to cross-relaxation, heightened (up to $3.6*10^{20}$ $cm^{-2}$) emission cross-section, non-linear reflection index, appropriate optical properties, glass melt resistance to crystallization) depend on the glass composition. Another part of functional properties of neodymium phosphate glasses is determined by the technology of their production. The most important quantitative requirements are as follows: 1). as high as possible optical homogeneity (absence of gas bubbles, dielectric and platinum inclusions), 2). high (up to 80 %) quantum yield of luminescence (luminescence life time - up to 300 – 320 μs) in dehydrated glasses, 3). big (≥20 J/$cm^2$ at the pulse length of 3.0 – 3.5 ns) surface damage threshold, 4). as small as possible (<0.002 $cm^{-1}$) natural coefficient of inactive absorption, $a_{1053}$, at the generation wave length (1053 nm) caused primarily by impurities of $Cu^{2+}$ and. $Fe^{2+}$ ions.

Phenomena of parasitic generation and super-luminescence caused by luminescence quanta that propagate along big sides of a AE lead to a release of inverse population density in the ensemble of excited activator ions and – as a result – to a reduction of output energy. To suppress these phenomena plates of copper containing glass (cladding) with special properties are pasted to lateral sides of the AE.

One- and two-stage technologies of getting both neodymium and copper glasses that meet all the requirements developed at the *RTIOMS* and the *LPOG* are described in the lecture. The main technological operation while glass melting is glass melt dehydration as structural water proved to be the most effective quencher of neodymium luminescence in phosphate glasses.

1. Campbell J.H., McLean M.J., Hawley-Fedder R., Saratwala T., Ficini-Dorn G., Trombert J.H. Development of Continuous Glass Melting for Production of Nd-doped Phosphate Glasses for the NIF and LMJ Laser Systems //SPIE, 1999. V. 3492. P. 778–786.
2. Campbell J.H., Suratwala T.I. Nd-doped Phosphate Glasses for High-energy/High-peak-power Lasers // J. Non-Cryst. Sol., 2000. V. 263 – 264. p. 318 – 431.
3. Arbuzov V.I., Lunter S.G., Nikitina S.I., Petrovskii G.T., Semenov A.D., Fedorov Yu.K., Shashkin V.S., Shashkin A.V. Large disc-shaped active elements made from neodymium phosphate glass for powerful high-energy lasers // Journal of Optical Technology, 2003. V. 70. P. 361 – 369.
4. Avakyants L.I., Arbuzov V.I., Babina T.O.et al. Phosphate glasses for making rod and disc active elements of lasers and high-pick-power/high-energy radiation amplifiers //Book of Abstracts of the 23 International Congress on Glass. 2013. Prague. P. 75-76.

VIII O-1

# Chalcogenide glass fibre-optics for the *in-vivo* mid-infrared optical biopsy

H. Parnell, D. Furniss, Z. Tang, T.M Benson and A.B Seddon*
Mid-Infrared Photonics Group,
George Green Institute for Electromagnetics Research, Faculty of Engineering, University Park,
University of Nottingham, Nottingham NG7 2RD, UK.
*Corresponding author: angela.seddon@nottingham.ac.uk

Recent statistics released by Cancer Research UK now reveal that 1 in 2 people born after 1960 will develop some form of cancer within their lifetime [1]. Diagnosing patients whilst in their early stages drastically improves their chances of survival but up until now the Gold Standard for cancer detection is *via* a lengthy excision biopsy procedure [2, 3], which relies solely on the skill of the conducting histopathologist. The mid-infrared (MIR) spectral region covers the wavelengths 3-25 μm [4] and the characteristic vibrational spectral unique to each molecular type, known as the molecular fingerprint. Subtle changes within this fingerprint are directly related to changes within the cells relative to the normal cells hence, signifying the presence or absence of a disease. Therefore, our goal aims to use these characteristic changes to carry out real-time disease diagnosis *in vivo*.

Reaching these wavelengths has previously presented difficulties as conventional MIR blackbody light sources are weak and optical fibres for transmitting MIR to and from tissue *in vivo* is often limited by strong material absorption for example, silica glass >2.4 μm and heavy metal fluorides, >4.7 μm. However chalcogenide glasses have been shown to transmit MIR light out to 25 μm and moreover, have recently been demonstrated capable of bright, wideband supercontinuum (SC) emission across the MIR region [5]. Based on one or more of the elements sulfur (S), selenium (Se) and tellurium (Te), these low phonon chalcogenide glasses exhibit high optical non-linearity [6] as well as a large optical window covering the two atmospheric windows lying from 3 to 5 and 8 to 12 μm [7].

Chosen for its superior glass formability over the telluride glass system [8]; this paper reports on several glass compositions from the Ge-Sb-Se and Ge-Sb-Se-S glass systems and their suitability as optical fibres for the transmission of MIR light for sensor probes. Physical properties of candidate glass pairs are assessed *via* thermal and structural analysis as well as fibre loss measurements for the associated optical fibres.

1. Cancer Research UK. Accessed: [01, 2016]]; Available from: http://www.cancerresearchuk.org/about-cancer/what-is-cancer
2. Kwak, J.s., S.M. Hewitt, S. Sinha, and R. Bhargava, Multimodal microscopy for automated histologic analysis of prostate cancer. BMC Cancer, 2011. **11**(1): p. 1-16.
3. Irving J. Bigio, J.R.M., Optical Biopsy, in Encyclopedia of Optical Engineering R.G. Driggers, Editor. 2003, Marcel Dekker: New York. p. 1577-1593.

4. Seddon, A.B., A Prospective for New Mid-Infrared Medical Endoscopy Using Chalcogenide Glasses. International Journal of Applied Glass Science, 2011. **2**(3): p. 177-191.
5. Petersen, C.R., U. Møller, I. Kubat, B. Zhou, S. Dupont, J. Ramsay, T. Benson, S. Sujecki, N. Abdel-Moneim, Z. Tang, D. Furniss, A. Seddon, and O. Bang, Mid-infrared supercontinuum covering the 1.4–13.3 μm molecular fingerprint region using ultra-high NA chalcogenide step-index fibre. Nat Photon, 2014. **8**(11): p. 830-834.
6. Zakery, A. and S.R. Elliott, Optical properties and applications of chalcogenide glasses: a review. Journal of Non-Crystalline Solids, 2003. **330**(1–3): p. 1-12.
7. Bruno Bureau , X.H.Z., Frederic Smektala, Jean-Luc Adam, Johann Troles, Hong-li Ma, Catherine Boussard-Ple`del, Jacques Lucas, Pierre Lucas, David Le Coq, Mark R. Riley, Joseph H. Simmons, Recent advances in chalcogenide glasses. Non-crystalline solids, 2004: p. 276-283.
8. Bureau B., C.Boussard-Pledel, P.Lucas, X.Zhang, and J.Lucas, Forming Glasses from Se and Te. Molecules, 2009. **14**(11): p.4337.

VIII O-2

# Fabrication of high and low numerical aperture optical fibre for sensing, mapping and imaging

D.M Jayasuriya, D. Furniss, Z. Tang, T.M Benson, A.B Seddon*
Mid-Infrared Photonics Group,
George Green Institute for Electromagnetics Research, Faculty of Engineering, University Park,
University of Nottingham, Nottingham NG7 2RD, UK.
Corresponding author: angela.seddon@nottingham.ac.uk

Global energy demand is driven by population growth, and it is projected increase of 1.6 % annually over the next 25 years for oil and gas [1]. Moreover according to a recent market survey report [2], it is projected that 70 % associated with oil and gas segments will turn to distributed therma l fibre optic sensing (light pulses are reflected down a fibre optic and monitored real time from multiple points along a pipeline) by 2018. Fibre optic sensors are taking up a leading role in the energy industry (geothermal applications, sub surface monitoring) [2].

Chalcogenide glass fibres, which are based on chalcogen elements S, Se and Te, are being actively pursued worldwide. High optical non-linearity, ≥ 20 μm multiphonon absorption edge, meaning a wide transmission range, and a relatively high optical damage threshold enable numerous applications [3, 4]. Novel chalcogenide glass based fibre opens up the mid-infrared region (MIR) for remote, real time monitoring and control in medical diagnostics and chemical processing. Fibres with long wavelength cut-off are of interest here. Telluride based chalcogenide glass optical fibres have a significantly longer wavelength cut off than selenide based or sulphide based glasses and are therefore of interest for chemical sensing. In general sulphide and selenide glasses have greater glass stability as compared to telluride glasses; selenide-telluride glasses are a good compromise.

The Ge-As-Se-Te glass system is a good potential candidate, which has intrinsic transparency from 1.5 ≥ 20 μm [5, 6]. This paper will address several interim objectives in glass development towards high numerical aperture (NA) small-core step index optical fibre for MIR supercontinuum generation and low NA step-index fibre-optic sensor head.

1. D. Simonits and A. Franzen, “Permanent downhole temperature sensing succeeds for low cost wells,” World Oil, vol. 228, no. May, pp. 37–44, 2007.
2. H. Pan, “2015 Photonic sensors consortium market survey report,” Light Wave Venture, LLC, 2015.
3. J.P.D. Lezal and J. Zavadil, “Chalcogenide glasses for optical and photonics application,” Optoelectron. Adv. Mater., no. 6, pp. 133–137, 2004.

4. A.B. Seddon, "Chalcogenide glasses: a review of their preparation, properties and applications," J. Non. Cryst. Solids, vol. 184, pp. 44–50, May 1995.
5. C. Vigreux-Bercovici, E. Bonhomme, and a. Pradel, "Te-rich Ge–As–Se–Te bulk glasses and films for future IR-integrated optics," J. Non. Cryst. Solids, vol. 353, no. 13–15, pp. 1388–1391, May 2007.
6. V. K. Tikhomirov, D. Furniss, a. B. Seddon, J. a. Savage, P. D. Mason, D. a. Orchard, and K.L. Lewis, "Glass formation in the Te-enriched part of the quaternary Ge-As-Se-Te system and its implication for mid-infrared optical fibres," Infrared Phys. Technol., vol. 45, pp. 115–123, 2004.

## VIII O-3

# Nano-layered solid electrolyte prepared by laser ablation

Yu. Tver'yanovich, A.Bandura, S.Fokina
St. Petersburg State University, Department of Laser Chemistry and Laser Material Science
tys@bk.ru

General aim of solid state ionics is the development of solid electrolytes with maximum conductivity. It is well-known that extensive interphase surface promotes ion conductivity. Nano-layered thin films are suitable for investigation of interphase surface promoting ion conductivity phenomenon [1] because the interphase boundary area and all geometry parameters of such object are known and controllable. Of course, it is only true if thickness of every layer is controlled during deposition procedure.

Films composed of alternating AgI and chalcogenide glass ($0,4AgI\text{-}0,3GeSe_2\text{-}0,3Sb_2Se_3$) nanolayers were prepared via laser ablation. Thickness of two nearby layers is 30 nm. Total film thickness is 1 μm. Temperature dependencies of multilayered film specific conductivity (Fig. 1) were studied using impedance spectroscopy method. After the third cycle it reaches 0,3 $Ohm^{-1}cm^{-1}$ and its activation energy decreases to 0.07 eV.

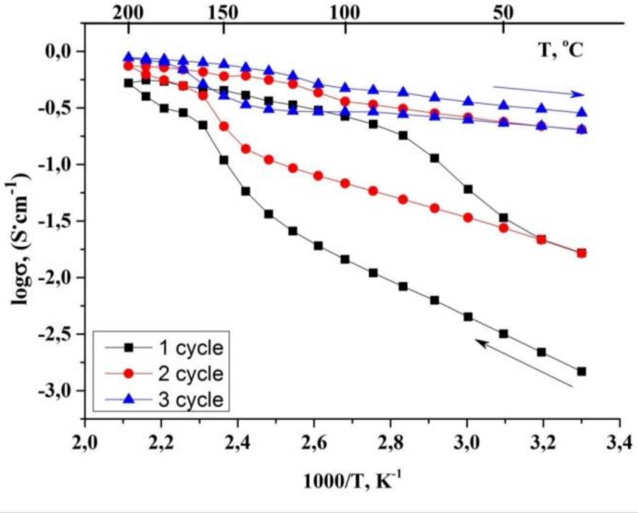


Fig. 1 The results of measurements of specific conductivity of AgI/CG multilayered film with 10 nm layer thickness during three thermal treatment heating-cooling cycles.

To specify phase transitions occurring in the thermal treated film, dependencies of XRD spectra on temperature were studied. For explanation of obtained results the calculations of eight AgI layers structure transformations were also performed using hybrider exchange-correlation functionals PBE0 in frame of density functional theory (DFT) approach.

The research is supported by RFBR (grant 14-03-00822). The measurements were performed at the following Research Centers of the SPSU: “X-ray Diffraction Studies”, “Nanotechnology Interdisciplinary Center”, “Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics” and “Optical and Laser Materials Research”.

1. N. Sata, K. Eberman, K. Eberl,J. Maier. Mesoscopic fast ion conduction in nanometre-scale planar heterostructures. // Nature**,** V. 408, 946-949 (2000) doi:10.1038/35050047.

X. X. Guo, I. Matei, J.-S. Lee,c and J. Maier. Ion conduction across nanosized CaF2 /BaF2 multilayer heterostructures. // Applied Physics Letters, 91, 103102, (2007).

VIII O-4

# Bipolar resistive switching in capacitor-like structures based on ionic and covalent oxide dielectrics

O.N. Gorshkov[1*], A.N. Mikhaylov[1], A.P. Kasatkin[1], S.V. Tikhov[1], A.I. Belov[1], M.E. Shenina[1],
M.N. Koryazhkina[1], D.V. Guseinov[1], V.I. Okulich[1], D.S. Korolev[1], I.N. Antonov[1], D.A. Antonov[1],
A.I. Bobrov[1], D.A. Pavlov[1], D.I. Tetelbaum[1], E.G. Gryaznov[1,2], A.P. Yatmanov[2]
[1] Lobachevsky University, 23/3 Gagarin prospect, 603950 Nizhny Novgorod, Russia
[2] Sedakov Scientific-Research Institute, GSP-486, 603950 Nizhny Novgorod, Russia
*E-mail: gorshkov@nifti.unn.ru

Considerable attention has been paid recently to the development of nonvolatile resistive memory devices (memristors) based on metal–insulator–metal (MIM) or metal–insulator–semiconductor (MIS) capacitor-like structures. Oxides with high mobility of oxygen ions/vacancies are often used as the insulators in such structures. A number of physical models has been proposed to describe the electroforming and resistive switching (RS) processes in memory cells that includes the formation of conductive pathways (filaments) in oxide matrix and induced by the electric-field-driven migration of oxygen vacancies or mobile oxygen ions in nonstoichiometric oxides. The nature and mechanisms of RS are still a subject of debates and depend strongly on the structure and composition of oxide material, as well as on the kind of metal electrodes and metal-insulator interface.

The present report is focused on the analysis of RS properties and mechanisms for the capacitor-like structures based on oxide dielectrics with ionic ($ZrO_x$, $HfO_x$) and covalent ($SiO_x$) bonding. A particular case is the RS in structures composed of yttria-stabilized zirconia (YSZ) and yttria-stabilized hafnia (YSH) that has been reported to a lesser extent so far. The advantage of using YSZ and YSH instead of $ZrO_x$ and $HfO_x$ in memristive structures is related to the possibility of strict control of oxygen vacancies concentration by varying the content of $Y_2O_3$ stabilizing oxide. The use of silicon oxide as a switching material is also very challenging due to its natural compatibility with the silicon-based electronics technology.

All the oxide films covered with Au or Au/Zr top electrodes were deposited by the methods of magnetron sputtering on the $TiN/Ti/SiO_2/Si$ substrate commonly used in CMOS technology. After electroforming that leads to the change in morphology and composition of oxide film (evidenced by various microscopic techniques), the MIM structures demonstrate reproducible bipolar RS between the high-resistance state (HRS) and low-resistance state (LRS) at atmospheric conditions. In contrast to the structures with covalent $SiO_x$ oxide, the YSZ- and YSH-based capacitors reveal RS either in vacuum or in air and show better HRS-to-LRS resistance ratios up to $10^3$. The nature of the observed RS is discussed in the framework of the filamentary model that is supported by the kinetic Monte-Carlo computer simulation of the redox processes for different oxide structures. To elucidate the concurrent ion and electron transport phenomena in the ionic and covalent oxides by analyzing the state of semiconductor/oxide interface, the corresponding MIS-structures were also studied.

The study is supported by the Ministry of Education and Science of the Russian Federation (applied research project with unique identifier RFMEFI57514X0029).

VIII O-5

# $AlF_3$-based glasses as promising material for mid-IR solid state lasers

Huang Feifei, Ying Tian, Shiqing Xu, Junjie Zhang
College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, China

Mid-infrared 3-5 μm laser has important application value in fields of communication and distance measurement, remote sensing, gas detection, spectral analysis, medical treatment. Therefore, development of 3 μm laser material of rare earth doped glass fiber has important research significance. Fluoride glass shows the unique advantages as Mid-infrared materials. ZBLAN fluoride system is the only matrix which obtained 3 μm laser output in recent years. However, poor chemical and mechanical properties of ZBLAN make it difficult to meet the present requirements of efficiency and power of the laser output. In our study, $AlF_3$-based glasses with enhanced thermal and chemical stability were synthesized and compared with the well-known fluorozirconate glass (ZBLAN). The 2.7 μm mid-infrared emission in the $AlF_3$-based glasses was also investigated. Therefore, these results showed that this kind of fluoride glass has a promising application for Mid-infrared solid state lasers.

# ISNOG 2016

## Tuesday, August, 23rd
## Wednesday, August, 24th

# Poster session

P1

# Preparation of tellurite-molybdate glasses containing of lanthanum oxide from precipitated batch

I.G. Fedotova, A.A. Sibirkin, O.A. Zamyatin
N.I. Lobachevski Nizhny Novgorod State University,
G.G. Devyatykh Institute of Chemistry of High-Purity Substances
of the Russian Academy of Sciences

The promising method for preparation of tellurite-molybdate glasses comprising lanthanum oxide is based on the fusion of the substances precipitated by action of ammonia to hydrochloric solution of tellurium (IV) oxide, ammonium heptamolybdate, and lanthanum (III) oxide.

The purpose of the study is the preparation of tellurite-molybdate glasses containing of lanthanum oxide from precipitates mentioned and the optical properties test of these glasses.

The regularities of co-precipitation of tellurium, molybdenum, and lanthanum compounds from hydrochloric acidic solution subjected the action of ammonia were studied in the course of the batch deposition. The precipitate enriched in tellurium and molybdenum compounds if the precipitation was completed in the pH range from 2 to 3, as it was proved by using of X-ray fluorescence analysis. The percentage of molybdenum compounds in the precipitate decreased at $pH > 4$ as a result of their partial dissolution due to the formation of molybdenum isopolycompounds. The proportional precipitation took place at $pH = 4$ if the relative lanthanum content in the mixture was not over 25 mol %.

It was shown by using of X-ray diffraction analysis that the precipitates prepared were amorphous at the temperatures below 300 °C. At the temperatures over 400 °C the binary and complex tellurium, molybdenum and lanthanum oxides formed. These compounds were detected in the system by their characteristic reflections. The residues after calcination described were hold at 500 °C in the oxygen flow and were used as a batch for synthesis of the $TeO_2 – MoO_3 – La_2O_3$ glasses. The homogenising fusion was carried out at 850 °C for 15 minutes.

The short-edges of glass transmission elicited from the optical spectra were found to be in the wavelength range from 520 to 1300 nm corresponding to the glass composition. These short-wave boundaries shifted toward longer wavelengths while the molybdenum trioxide content increased in the system. Moreover, the short-edge of the $(TeO_2)_{0.58}(MoO_3)_{0.29}(LaO_{1.5})_{0.13}$ glass transmission was equal to 522 nm if the glass was made from precipitated batch whereas it was at 780 nm for the glass of the same composition prepared from binary oxides.

So, the method proposed provides a possibility in reduction the temperature and the duration of homogenising fusion and allows to prepare the tellurite-molybdate glasses of high lanthanum oxide content which possess higher optical transparency in short wavelength range in comparison with the glasses of the same composition prepared from binary oxides mixtures.

P2

# Preparation of the $TeO_2 - WO_3$ glasses by using of the batches precipitated from aqueous solutions

Gavrin S.A.[1,2], Sibirkin A.A.[1,2], Suchkov A.I.[2]
[1]Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, Russia
[2]Devyatykh Institute of Chemistry of High-Pure Substances of Russian Academy of Sciences, Nizhny Novgorod, Russia
E-mail: sa-gavrin@yandex.ru

The ordinary method for preparation of optically homogeneous tungstate-tellurite glasses from the binary oxides includes the fusion of the batch components at the temperature of 800 − 1000 °C for several hours.

The purpose of this work is to develop the technique for preparation of transparent tellurite-tungstate glasses which possess lower temperature and duration of homogenising fusion. It allows to expand the assortment of materials for crucibles, to reduce contamination due to crucible materials used, and to make possible the preparation of glasses with lower content of metallic elements.

The precipitates manufactured through the addition of aqueous ammonia to the hydrochloric acidic solutions of tellurium dioxide and tungstic acid were used as batches after drying and calcination.

The co-precipitation peculiarities of tellurium (IV) and tungsten (VI) compounds from these solutions was elucidated. The X-ray fluorescence analysis proved that the precipitate composition is equal to the initial solution one if the precipitation finished in the pH range from 2 to 7.

X-ray diffraction analysis revealed that the precipitates remain amorphous after thermal processing at the temperatures lower than 350 °C. At higher temperatures the batch converted to a mixture of the crystalline $TeO_2$ and $WO_3$. These products do not undergo any chemical changes and turned into glass forming melt. The batch homogenising fusion was carried out in the temperature range of 650 − 850 °C for 5 − 10 minutes correspondingly to the glass composition. After casting the transparent tungstic-tellurite glasses of 9 – 27 mol % $WO_3$ content were prepared. The boundaries of transparency region of the glasses moulded were within the range of 0.44 - 5.4 micrometres, and slightly shrank with the increase in tungsten oxide content.

So, the use of precipitated batch reduces the temperature and the duration of homogenising fusion in comparison with those for the melts for preparation of $TeO_2 - WO_3$ glasses from binary oxides.

P3

# Thermal and crystallization properties of fluorozirconate-phosphate glasses doped with rare earths

V.K. Goncharuk[1,2], V.Ya. Kavun[1], A.B. Slobodyuk[1], V.E. Silant'ev[1], A.Yu. Mamaev[1], I.G. Maslennikova[1]
[1] Institute of Chemistry, FEB RAS, Vladivostok, Russia
[2] Pacific S.O. Makarov Higher Naval School, Vladivostok, Russia
gon@ich.dvo.ru

The glass formation and crystallization in the mixed fluorozirconate-phosphate system $ZrF_4$–$BaF_2$–$NaPO_3$ doped with fluorides of erbium, neodymium and europium were studied. Physical properties of the glasses were characterized by differential thermal analysis (DTA), nuclear magnetic resonance (NMR) and transmission electron microscopy (TEM).

Sodium metaphosphate $NaPO_3$ was introduced by two ways: grinding and melting of the $60ZrF_4$-$40BaF_2$ (ZB) and $NaPO_3$ glasses initially prepared and melting of starting reagents directly. In systems ZB-$NaPO_3$ and $ZrF_4$-$BaF_2$-$NaPO_3$, comprising two glass-formers, transparent glass samples were obtained up to 20 mol. % $NaPO_3$. Further increasing concentration of the phosphate component led to crystallization. The area of glass formation in the $ZrF_4$-$BaF_2$-$NaPO_3$ system depends on the $ZrF_4$ / $BaF_2$ ratio, which is within 1.13-2.5. At higher or lower ratios, the crystallization is observed with the formation of barium and zirconium phosphates, indicating the interaction of two glass networks. Introduction of sodium metaphosphate slightly lowers the glass transition temperature Tg, while the Tc1 values somewhat increase.

According to NMR data, introduction of sodium metaphosphate $NaPO_3$ to the fluorozirconate glass does not effect significantly on the temperature onset of emergence of ionic movements in its fluoride sublattice. At 500 - 520 K all fluoride ions in the glass become mobile, which enables to consider the glass as high-temperature ionic conductor. It is found that the resonance lines of $^{19}F$ MAS NMR spectra belong to the fluorozirconate glass network. Increasing $NaPO_3$ concentrations in the glass doped by rare earths results in an increase of luminescence intensity.

The structure of a number glasses obtained in these systems was studied by TEM method. It was shown that the glass consists of crystallites with a spherical shape of 20-350 Å in diameter. Fluorides of erbium, neodymium and europium promote the formation of crystallites and appear as nucleation agents. It was shown previously by atomic force microscopy and laser diffraction spectroscopy [1] that in the ZBLAN system the glass particle sizes varied in a range of 20-180 Å depending on a cooling rate of the melt that was also consistent with our data. From a practical point of view, there is a possibility of selective crystallization conditions to obtain a mixed optical nanoceramics.

This work was supported by grant of FEB RAS N 0265-2015-0009.

1. E. Yu. Mikhteeva, E. G. Savchuk, E. A. Tararako, E. B. Merkulov, V. K. Goncharuk, Structure inhomogeneities of medium-range order in fluorozirconate glasses, J. Struct. Chem. 46 (2005) 1082-1085.

P4

# Peculiarities of structure, crystallization and luminescence in the $TeO_2$-$PbO•P_2O_5$-$PbF_2$:$EuF_3$ glasses

L.N. Ignatieva, N.N. Savchenko, Yu.V. Marchenko, I.G. Maslennikova, G.A. Zverev, V.K. Goncharuk
Institute of Chemistry, Far-Eastern Branch, Russian Academy of Sciences
E-mail: ignatieva@ich.dvo.ru

Glasses of the composition $(100–\boldsymbol{x}–y)TeO_2–PbO·P_2O_5–yPbF_2$-:$0.5EuF_3$ ($\boldsymbol{x}$ = 42.5–30 mol %, $y$ = 5–25 mol %) have been investigated. It has been demonstrated that a glasslike network composed of mixed tellurite and phosphate polyhedra is formed in the glass: the network medium-range order area does not change significantly in the range of the examined compositions, despite changes occurring inside the network. Lead difluoride has a modifying effect on the structure of the glasslike network at large, i.e., both tellurite and phosphate groups.

The process of crystallization of glass of the composition $42.5TeO_2$-32.5 $PbO·P_2O_5$-$25PbF_2$:$0.5EuF_3$ has been studied. It has been shown that crystallization starts in the area of location of phosphate groups with partial destruction of the glasslike network. Only phosphate phases ($Pb_3(PO_4)_2$) crystallize upon thermal treatment of this glass at 500 °C. Crystallization in the area of tellurite groups starts upon sample heating at the same temperature for 1 hour.

At the scattering excitation by a laser with the wavelength $\lambda_0$=532 nm in glass of the composition $42.5TeO_2$-$32.5PbO{\cdot}P_2O_5$-$25PbF_2$:$0.5EuF_3$, the europium luminescence corresponding to the emission levels 578, 585, 590, and 612 nm was revealed.

Entering of the rare earth element into the crystalline phase has been revealed: for instance, it could be the formation of REE crystalline compounds, which cannot be detected by the XRD method because of their small quantity and, possibly, nanosized nature of the formed phases.

Band frequencies (cm$^{-1}$) ν (Te-O), ν (P-O) and boson peak positions in Raman spectra of glasses in the system $TeO_2$–$PbO{\cdot}P_2O_5$–$PbF_2$-$0.5EuF_3$

| Glass composition | ω | ν (Te-O) | ν (P-O) |
|---|---|---|---|
| $52.5TeO_2$-$42.5PbO{\cdot}P_2O_5$-$5PbF_2$:$0.5EuF_3$ | 45 | 696 751 | 911 1083 |
| $50TeO_2$-$40PbO{\cdot}P_2O_5$-$10PbF_2$:$0.5EuF_3$ | 45 | 697 750 | 916 1083 |
| $47.5TeO_2$-$37.5PbO{\cdot}P_2O_5$-$15PbF_2$:$0.5EuF_3$ | 45 | $697_{bend}$ 751 | 913 982 936 1085 |
| $45TeO_2$-$35PbO{\cdot}P_2O_5$-$20PbF_2$:$0.5EuF_3$ | 46 | 751 | 913 989 1028 1076 |
| $42.5TeO_2$-$32.5PbO{\cdot}P_2O_5$-$25PbF_2$:$0.5EuF_3$ | 46 | $690_{bend}$ 752 | 913 980 1030 1071 |
| $42.5TeO_2$-$57.5PbO{\cdot}P_2O_5$:$0.5EuF_3$ | 45 | 702 747 | 907 $984_{bend}$ 1121 |

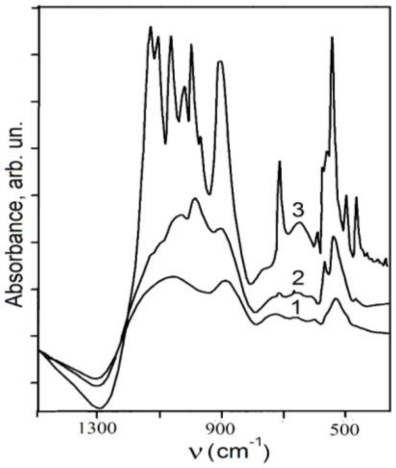


Fig. 1. IR spectra of samples $42.5TeO_2$-$32.5PbO{\cdot}P_2O_5$-$25PbF_2$:$0.5EuF_3$: 1 - initial glass, 2 - sample heated up to 500 °C, 3 - sample held at 500 °C for 1 hour.

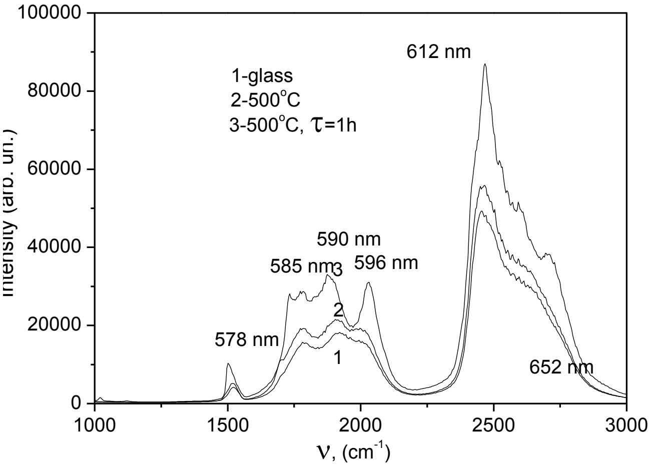


Fig. 2. Spectra of inelastic scattering for samples $42.5TeO_2$-$32.5PbO{\cdot}P_2O_5$-$25PbF_2$:$0.5EuF_3$: 1 - initial glass, 2 - sample heated up to 500 °C, 3 - sample held at 500 °C for 1 hour.

P5

# Synthesis and study of new In-containing oxyfluoroniobate glasses

Savchenko N.N[1]., Ignateva L.N.[1], Marchenko Yu.V.[1], Zverev G.A.[1], Bouznik V.M.[2]
[1]Institute of Chemistry FEB RAS, Vladivostok, Russia
[2]All-Russian Scientific Research Institute of Aviation Materials
savchenko@ich.dvo.ru

The glasses in the system $MnNbOF_5$-$BaF_2$-$InF_3$ have been firstly synthesized and studied. The conditions of formation, the structure and thermal stability of the glasses obtained were identified by DSC, IR, Raman and XRD methods. It was found that the introduction of InF3 does not affect virtually the glass transition temperature, according to composition *T*g of all glasses obtained is varied from 289 to 305 $^o$C. In the system $MnNbOF_5$-$BaF_2$-$InF_3$ the glass $40MnNbOF_5$-$40BaF_2$-$20InF_3$ is characterized by the highest thermal stability range ($\Delta T$, °C) equal 109 and degree of glass stability to crystallize (S,K) ~2.

By Raman and IR spectra analysis we revealed that the networks of glasses in the system are built by structural type of glasses in $NbO_2F$-$BaF_2$ system: ($NbO_nF_m$) polyhedra joined oxygen bridges. Indium trifluoride forms $InF_6$ polyhedra, which are embedded between oxyfluoroniobate ions, forming a common networks or form its own layers from $InF_6$ polyhedra. Such structure of glass networks is possible reason of found single and multi-stage crystallization of these glasses. One can be expect that crystal phases obtained will contain simultaneously In-compounds, fluorides and oxyfluoroniobates. This assumption is in satisfactory agreement with the results of X-ray analysis: the main crystalline phases at the thermal treatment of In-containing glasses are $Ba_3In_2F_{12}$(α- and β- modifications) and $BaNbOF_5$.

This research was supported by the Russian foundation for basic research (Project No 15-03-01626) and FEB RAS grant (Project No15-I-3-016).

P6

# Fluorozirconate and fluorohafnate glasses, doped with europium

M. Brekhovskikh[1], S. Batygov[2], I. Zhidkova[1], L. Moiseeva[1,2], S.Yurtaeva [1]
[1]N.S.Kurnakov Institute of General and Inorganic Chemistry RAS, Russia
[2]A.M.Prokhorov Institute of General PhysicsRAS, Russia
mbrekh@igic.ras.ru

Heavy metals halides glasses exhibit a wider IR transmission range as compared to the known oxide glasses and fluoride glasses remain an attractive material in shorter optical devices with application lying in the visible and mid IR spectral range. Europium-doped glasses and glass-ceramics appeared to be promising as photostimulated X-ray phosphors for ionizing radiation detection in medical imaging. We studied the X-ray luminescence (RL) of undoped and Eu-doped fluorozirconate and fluorohafnate glasses in the systems $ZrF_4$-$BaF_2$-$LaF_3$-$AlF_3$-NaF (ZBLAN) and $HfF_4$-$BaF_2$-$LaF_3$-$AlF_3$-NaF (HBLAN), respectively, as well as in the chlorine-substituted glasses in which $F^-$ anions are partly replaced by $Cl^-$ anions by substitution $BaF_2$ for $BaCl_2$. The undoped glasses have wide intrinsic luminescence bands peaked between 250 and 450 nm, correspond to transitions between local levels in the band tails. Partial substitution of chlorine for fluorine causes the bands shift to the longer wavelengths (Fig. 1).

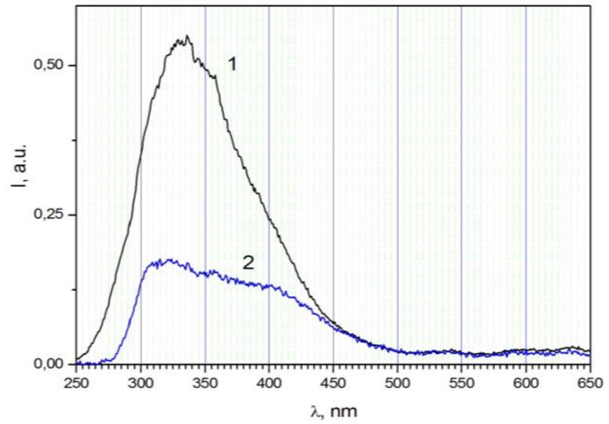


Fig. 1 ZBLAN intrinsic luminescence – 1; ZBLAN chlorine-substituted intrinsic luminescence – 2.

Theses bands correspond to the chlorine levels in the valence band tail. Glass samples, doped with $EuF_2$, contained both $Eu^{2+}$ and $Eu^{3+}$ ions. RL spectra contain the lines of $Eu^{3+}$ luminescence in the whole visible range, associated with transitions from different levels of the $^5D$ multiplet. At the same time no emission which could be attributed to the $Eu^{2+}$ ions was observed in the RL spectra as well as in the photoluminescence spectra. The absence of luminescence of $Eu^{2+}$ in fluorozirconate glasses is due to the overlap of the excited level of $Eu^{2+}$ with the conduction band of the glass, which leads to non-radiative relaxation of the excited level through the conduction band.

The publication was supported by the Federal Agency of Scientific Organizations within the State Assignment on Fundamental Research to the Kurnakov Institute of General and Inorganic Chemistry and the Russian Foundation for Basic Researches RFBR grant No. 15-03-02507.

P7

# The use of the ICP-AES method to determine matrix components and impurity elements in the As-S, As-Se chalcogenide glass systems

Fadeeva D.A., Yevdokimov I.I., Pimenov V.G.
G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences,
Nizhny Novgorod , Russia
pim@ihps.nnov.ru, atstsky@yandex.ru

The As-S, As-Se et al. chalcogenide glass systems, including the isotopically enriched ones are promising materials for IR-optics and optoelectronics. The characteristics of glasses strongly depend both on the content of matrix components and on broad range of impurities. At the present time, the express multi-element methods of the analysis of chalcogenide glasses and their precursors allowing to detect a wide range of impurities at the level of $10^{-7}$–$10^{-5}$ wt. % (in accordance with modern requirements) are actually absent. The content of macro-components in glasses is usually determined by the methods of X-ray fluorescence and X-ray spectral analysis. These methods require the sets of reference samples identical to the analyzed probes. Preparation of these reference samples is a time-consuming and difficult task. Therefore, the development of new available methods for determination of macro-components and impurities in chalcogenide glasses with the required metrological characteristics is of current actuality.

The purpose of this research work is to investigate the ICP-AES potentialities of determining: 1) a wide range of impurities, including the elements whose volatility is similar to the matrix elements volatility (P, S, Sb, Se, Te) at the level of $10^{-7}$–$10^{-5}$ wt. %; 2) the macro-components with a relative expanded uncertainty value 0.001–0.003 in high purity chalcogenide glasses. Potentialities of the ICP-AES method are examined in the analysis of the As-S, As-Se glass systems. The ICP-AES method is selected due to the following advantages: 1) the possibility to obtain information both on matrix composition and impurities; 2) the ability to analyze low-mass samples (1–100 mg), which is important in case of analysis of expensive isotopically enriched samples; 3) the possibility to use reference samples in the form of solutions, which are much easier to prepare than solid reference samples of complex composition; 4) the availability and prevalence of equipment.

Sub-boil distilled nitric acid (68 wt. %) was used to dissolve the samples. The As-Se glass samples were dissolved under the atmospheric pressure and at the temperature of 80–100 °C in glass flasks. The samples of As-S glasses were dissolved under the pressure of 0.4–0.5 MPa and at the temperature of 130–140 °C using the microwave digestion system. The prepared solutions were analyzed with the use of the ICP-AES spectrometer iCAP 6300 Duo. Due to the relatively weak matrix interference, the solutions of the glasses were introduced into inductively coupled plasma with a high content of matrix elements – 0.1 g/mL. The absence of significant spectral interferences made it possible to take into account the matrix effect by the standard addition technique, instead of the use of the blank solutions containing matrix elements. Analytical lines of the impurities and analysis conditions were selected. The limits of detection of impurities (3*s*-criterion) were $n \cdot 10^{-8}$ wt. % for Ba, Be, Cd, Li, Sr, Y, were $n \cdot 10^{-7}$ wt. % for Ag, Au, Co, Cr, Cu, Fe, Mg, Mn, Na, Sc, Ti, V, Zn, were $n \cdot 10^{-6}$ wt. % for Al, As, B, Ca, Ga, In, K, La, Nb, Ni, Pb, Sb, Se, Sn, Ta, Te, Tl, W, were $n \cdot 10^{-5}$ wt. % for Bi, Ge, P, S, Si ($n$ = 1–9).

Within the framework of development of the technique for determination of matrix components, the factors affecting the accuracy of analysis results were found. The optimum operating range of concentration of macro-components in the 10–250 μg/mL solution was selected. In this operating range the calibration functions are linear and the relative standard deviation of the analytical signal attains the minimum value ($S_r \approx 0.002$). The analytical lines for As, S, Se and operation conditions which ensure the maximal accuracy of analysis results, were selected. The methodological approaches to improving the accuracy of results of the matrix elements determination, as compared to the typical ICP-AES accuracy, were analyzed and developed. Calibration curves were plotted in relative concentrations. Calibration solutions were prepared using the batches of elementary As, S and Se (5*N* purity). These approaches make it possible to determine the matrix components in the As-S, As-Se glass systems with a relative expanded uncertainty value not exceeding 0.001–0.003. The ICP-AES method compares favourably with the X-ray method with respect to determination of macro-components of the glasses. In addition, one more advantage of the ICP-AES method is that it does not require the sets of adequate solid reference samples.

P8

# Optical, thermal and crystallization properties of high-purity $TeO_2$-ZnO-$La_2O_3$-$Na_2O$ glasses

S.E. Motorin[1], V.V. Dorofeev[1], A.D. Plekhovich[1], A.M. Kutyin[1], V.V. Koltashev[2], V.G. Plotnichenko[2], A.F. Kosolapov[2]
[1]G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, Tropinina st. 49, 603950 Nizhny Novgorod, Russia
[2]Fiber Optics Research Center of the Russian Academy of Sciences, Vavilova St. 28, 119333 Moscow, Russia
e-mail: motorin@ihps.nnov.ru

Tellurite glasses compositions with low phonon energy, which do not contain oxides of heavy metals such as W, Mo, Nb and etc. are the most suitable for the near and mid-IR applications. One of these systems are zinc-tellurite glasses that contain up to 30 % mol. ZnO as well as modifying components such as oxides of alkali and rare earth metals.

Series of $TeO_2$-ZnO based glasses with the addition of $La_2O_3$ and $Na_2O$ was synthesized in a stream of purified oxygen from high purity initial oxides. The technique allows to obtain the zinc-tellurite glasses with a total content of 3d-transition metals of less than 1-2 ppm wt. and hydroxyl groups absorption level as low as 0.001-0.002 cm$^{-1}$ [1-3].

The glass transition temperatures, crystallization stability, transmission spectra, spectral dependences of the refractive index and fiber optics applicability for series of glasses were studied. Transmittance of the prolonged zinc-tellurite glass samples significantly higher near short-wave boundary and in the mid-IR as compared with tungstate-tellurite glasses. The transmission spectra present absorption bands of the dissolved platinum near 450 nm and of the hydroxyl groups around 2.3, 3.3 and 4.6 µm with a width dependent on the concentration of OH-groups and the glass composition. A number of $TeO_2$-ZnO-$La_2O_3$-$Na_2O$ glasses are stabl to crystallization, there were no thermal effects of crystallization and melting of crystals at heating rates of 10, 5, 2.5 K/min according to differential scanning calorimetry data. The glass transition temperature and therefore viscosity of glass were essentially independent on the composition inside this series, while the refractive index change according refractometry data is sufficient to create multimode and singlemode step-index fibers.

The multimode optical fiber produced by high-purity zinc-tellurite glass preform stretching is characterized by optical loss less than 100 dB/km at wavelengths range of 1.4-1.7 µm, that demonstrates high fiber optics applicability of the developed glasses.

The study was partly supported by the Russian Foundation for Basic Research (15-03-08324).

1. A.N. Moiseev, V.V. Dorofeev, A.V. Chilyasov et. al, Production and properties of high purity $TeO_2$-ZnO-$Na_2O$-$Bi_2O_3$ and $TeO_2$-$WO_3$-$La_2O_3$-$MoO_3$ glasses // Optical Materials 33 (2011) 1858–1861
2. M. F. Churbanov, A. N. Moiseev et. al, Production and properties of high purity glasses of $TeO_2$–$WO_3$, $TeO_2$–ZnO systems, Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B, December 2008, 49 (6), p. 297-300
3. M.F. Churbanov, A.N. Moiseev, A.V. Chilyasov et. al, Production of high-purity $TeO_2$-ZnO and $TeO_2$-$WO_3$ glasses with the reduced content of OH-groups, J. Optoelectr. Advanced Mater. 2007, v. 9, No 10, p. 3229-3234

P9

# Methodology to evaluate the crystallization stability of the tellurite glasses by DSC methods

K.V. Balueva[1], A.D. Plekhovich[2], V.V. Dorofeev[2], A.M. Kutyin[1,2]
[1]Lobachevsky State University, pr. Gagarina 23, Nizhny Novgorod, 603950 Russia
[2]Devyatykh Institute of Chemistry of High_Purity Substances, Russian Academy of Sciences,
Tropinina str. 49, Nizhny Novgorod, 603950 Russia
e_mail: plehovich@gmail.com

Differential scanning calorimetry (DSC) analysis of tellurite glasses doped with lanthanum oxide, which improves their crystallization resistance, has revealed a phase transformation specific to such glasses, in which beyond partial crystallization of a sample follow the melting of the resulting crystals. The experimentally observed decrease of crystallization - melting peaks with increasing particle size in a series of disperse samples of tellurite glass together with extrapolation to the size of a bulk sample has been used to assess the crystallization resistance of tellurite glass promising for optical applications.

The assessment technique comprises DSC characterization of particle-size-classified glass samples and the use of a mathematical model for obtaining the degree of crystallization as a function of temperature and time, $\alpha(T, t)$ through analysis of non-isothermal DSC peaks representing a partial glass crystallization process with transferring to melting. The crystallization resistance of glass is estimated by extrapolating the maximum $\alpha$ values as a function of particle size to a preform size.

The tested technique offers the possibility to select preforms for producing fibers from compositionally new, chemically pure tellurite glasses at a given phase purity level and to accelerate a search for additives increasing the crystallization resistance of glasses for fiber-optic applications.

The increasing current interest in such an independent, nonoptical test for crystallization behavior, which requires samples as small as 30 mg in weight, is aroused, in particular, by the revival - on a modern basis - a production technology for sintering a mixture of inorganic oxide powders. A modern version of such technology, based on high-purity components, employs approaches for the fabrication of microstructured fibers.

To characterize proposed technique, it is reasonable to conclude that it describes crystallization mainly on existing after crushing surface, heterogeneous centers of the forming a new phase. At the same time, the semiempirical version of the used here crystallization theory effectively takes into account homogeneous constituent without detailing her share. Note that the processing procedure of the experimental DSC data requires no identification of the forming phase.

The proposed model for analysis of crystallization-melting DSC peaks, with the possibility of determining $\alpha(T,\ t)$, is of interest on its own for characterization of glass-forming systems, whose characteristics are typically related to the degree of crystallinity of glass.

The study was partly supported by the Russian Foundation for Basic Research (15-43-02185, 15-03-08324).

### P10

## Removing the defective surface layer by magnetorheological treatment

Khudoley A.L., Kolpashchikov V.L., Aleksandronets A.S., Gorodkin G.R.
A.V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus
khudoley@hmti.ac.by

Traditional methods of treatment of optical materials are grounded on using bonded or non bonded abrasives polishing processes. The main disadvantages of these methods are mechano-chemical transformation of surfacing layer properties in particular imbedding of K, Ce ions from polishing fluids into the glass structure [1]. After grinding depth of subsurface damage in optical glasses can rise to 30 μm [2]. Recently focused ion-beam (FIB) technique is widely used for treatment of optical surfaces. However it should be noted that FIB method leads to surface contamination: concentration of Ga ions can reach 0.7 g/cm$^2$ with depth penetration 700 nm. These factors dramatically decrease the quality of optical components: laser damage, transmission capacity, refraction index and etc.

The problem of automatically controlled polishing and generation of geometry of precision optical surfaces by small-size tool based on magnetorheological fluid is discussed in this report. Due to structure control of magnetizable medium magnetorheological polishing (MRP or MRF) allows adaptively to treat the surface largely any shape. MRP is the method of treatment of surface without high-powered stresses and modification of surfacing layer. The advantages of MRP are precision, possibility to conduct treatment of surface without overheating and destruction of the material and alternatively to FIB MRP doesn't require utilizing of vacuum. At present time bulk materials and thin film that made from water soluble crystals, polymers, glasses, nonmagnetic metals are successfully polished by MRP. Compared to other methods MRP allows to improve component geometry to λ/100, to remove extremely thin layers of material and to treat surface to it morphology with value of roughness up to 0.2 nm.

Experiments connected with MRP of optical glasses (fused silica and K8, diameter of samples 25 mm) are fulfilled on the 5-axis CNC machine. Its established that the removal rate of fused silica is 0.17 μm/h and it of K8 is 1.48 μm/h. Results of 3D-interferometric analysis on KLA-Tencor MicroXAM-800 profilometer of surfaces showed the decrease of roughness Rq in 33 times to 0.97±0.14 nm for K8 glass and in 44 times to 0.84±0.17 nm for fused silica.

Finally technical characteristics of whole range of automated MRP machines engineered in the Institute are given. It shown that equipment allows to treat oxygen-free glasses, mono- and polycrystals and microelectronic components. The high-precision surfacing laboratory designs, fabricates and supplies universal and unique 3-5-axis CNC MRP machines for polishing and shaping of component with flat, spherical and aspherical shape of surface from 3 mm to 2.5 m [3].

1. Suratwala, T. Chemistry & formation of the Bielby layer during polishing of fused silica glass / T. Suratwala // Journal of the American Ceramic Society. – 2015. – Vol. 98. – P. 2395-2402.
2. Hed, P.P. Optical glass fabrication technology. 2: Relationship between surface roughness and subsurface damage / P.P. Hed, D.F. Edwards // Applied Optics. – 1987. – Vol. 26. – P. 4677-4680.
3. The high-precision surfacing with magnetorheological fluids / A.L. Khudoley [et. al.] // The Science and Innovations. – 2015. – No. 6. – P. 20-23.

P11

# Is the term “Polyamorphism” correct for noncrystalline substance?

V.S. Minaev[1,2], S.P. Timoshenkov[1], V.V. Kalugin[1], N.E. Korobova[1], S.N. Novikov[1], O.N. Kalashnic[2]
[1]National Research University of Electronic Technology MIET, Zelenograd, Russia.
[2]Research institute of Materials science and technology, Moscow, Russia.
korobova3@mail.ru

We must have at least the most common representation about the structure of "amorphous" analogue (Kobeko P.P.), or in private case about the structure of non-crystalline material (Mott N.F. and Davis E.A.) discussing "polymorphism" phenomenon (or artifact?). The possibility of amorphous polymorphism existence was first formulated by E. Lell et al. in 1966. In 1992 Wolf G.H. et al. have proposed the term "polyamorphism". The paper Hancoc B.C. et al. gives the following polyamorphism definition – “substance ability to exist in several different amorphous modifications”. Polyamorphism is the analogue of crystalline materials polymorphism. In the textbooks of crystallography you can find crystalline polymorphs modification definition and their crystallographic characteristics, but the authors did not give a definition of amorphous polymorphs modification, and their characteristics. The term "amorphous" (Greek ἄμορφος - formless, vague) consists of denial "a" and the root "morphe", which translates as “form” and means outer appearance, outer contours, structure of something. Thus, the term "amorphous" means without form structure, and structureless. In modern Condensed Matter Physics the term "amorphous" is characterized by an absence of strict substance periodicity, which inherent for crystals, that is, long-range order. At the same time "in an amorphous substance" there is consistency in the arrangement of neighboring atom particles - short-range order, as well as the intermediate order, which is distributed in 5 - 20 Å. Thus, the "amorphous" material does not have strictly defined structure or disordered ("amorphous") - at the macro and micro level, but ordered (it has a certain structure - not amorphous) on the nanoscale - the level of intermediate and short-range order. The proof of these modern science principles demonstrates the unacceptability of "amorphous", "amorphism" terms at this level of Condensed Matter Physics development. No wonder the international community has named its main magazine «Journal of Non-crystalline Solids», rather than «Amorphous Solids» in the discussed area. It has been shown on the $As_2S_3$, $GeSe_2$, $BeCl_2$ etc. examples, that there were no «amorphous» substances similar to separate compositions of polymorphs modifications in accordance with our concept of nano-heteromorphic polymer-polymorphoide structure of non-crystalline substances [1]. The "polyamorphism" data of amorphous materials in [2-4] do not correspond to reality.

1. V.S. Minaev, S.P. Timoshenkov, N.E. Korobova, el al. J. Optoelectron. Adv. Mat. V. 18, №1-2, p.10-23 (2016).
2. E. Lell, N. Kreidl, J. Hensler, in: Progress in Ceramic Science, 4, Pergamon Press, New-York – Toronto. P.4, (1966)
3. G.H.Wolf, S. Wang, C.A. Herbst, D.J. Durben, W.F. Oliver, Z.C. Kang, K. Halvorson, in: High-Pressure Research: Application to Earth and Planetary Science; Ed. Syono Y.; American Geophysical Union; Terra Scientific publishing company: Washington D.C.; pp. 503-517, (1992)
4. B.C. Hancock, E.Y. Shalaev, S.L. Shamblin, The Journal of Pharmacy and Pharmacology, 54 (8), 1151, (2002)

P12

# Structural characterization and electrical conductivities of highly ion-conducting glasses and glass ceramics in the system $Li_{1+x}Al_xSn_yGe_{2-(x+y)}(PO_4)_3$

S.H. Santagneli[1], S.J.L. Ribeiro[1], S. Kundu[2], A.C.M. Rodrigues[2], C. Doerenkamp[3], H. Eckert[3]
[1]LaMF, Instituto da Química, UNESP, Araraquara, SP, Brazil
[2]LaMaV, Universidade Federal em São Carlos, SP, Brazil
[3]Instituto de Física em São Carlos, Universidade de, São Carlos, SP, Brazil & Institut für Physikalische Chemie, WWU Münster, Germany
santagneli@iq.unesp.br

Highly ion conducting glass ceramics, crystallizing in the Na.super-ion conducting (NASICON) structure have been prepared in the system $Li_{1+x}Al_xSn_yGe_{2-(x+y)}(PO_4)_3$ by crystallization of glassy precursor samples. For modest substitution levels ($y = 0.25$), these crystalline solid solutions show higher electrical conductivities than corresponding samples without Sn, supporting the rationale that the lattice expansion associated with the substitution of Ge by its larger homologue Sn can enhance ionic mobilities. The glass-to-crystal transition has been characterized in detail by multinuclear single and double resonance NMR experiments. While substantial changes in the $^{31}P$ and $^{27}Al$ MAS-NMR spectra indicate that the crystallization of the glasses is accompanied by significant modifications in the local environments of the phosphate and the aluminum species, the dipolar solid state NMR experiments indicate that the structures of both phases are dominated by Ge-O-P, Sn-O-P and Al-O-P connectivities. Substitution of Ge by Al and Sn in the crystalline NASICON structure results in a binomial distribution of multiple phosphate environments, which differ in the number of P-O-Ge, P-O-Al, and P-O-Sn linkages. While there is no chemical shift discrimination between P-O-Al and P-O-Sn linkages, an unambiguous distinction is possible on the basis of $^{31}P\{^{27}Al\}$ rotational echo adiabatic passage double resonance (REAPDOR) experiments.

P13

# Effect of silver and sodium ions on optical properties and structure $TeO_2$-$WO_3$-$La_2O_3$ glass

Stepanov B.S.[1], Shenina M.E.[2], Antonov I.V.[2], Churbanov M.F.[1], Frumarova B.[3]
[1] Devyatykh Institute of Chemistry of High_Purity Substances, Russian Academy of Sciences, Tropinina str., 49, Nizhni Novgorod, 603950 Russia
[2] Research Institute of Physics and Technology, Lobachevsky State University, pr. Gagarina 23, Nizhni Novgorod, 603950 Russia
[3] Pardubice University, Studentska 95, Pardubice, Czech Republic.
e_mail: boris1885@gmail.com

Data are presented on the influence of silver and sodium ions on the refractive index and structure of $TeO_2$–$WO_3$–$La_2O_3$ glasses. Using ellipsometry, we have obtained dispersion dependences of the refractive index of the tellurite glasses. Structural changes in the glass network have been assessed using the Wemple–DiDomenico model and Raman spectra.

Increasing the mole fraction of $Na_2O$ from 3 to 12 % increases the refractive index of the glasses by 4 %, whereas increasing the mole fraction of $Ag_2O$ from 5 to 12 % at $Na_2O$ content of 3 % increases the refractive index by 1 %.

Raman spectra of tellurite glass having equal ion-modifier concentrations (Ag and Na) exhibit notable difference. Ag-containing tellurite glasses are characterized by a red shift of the band at 360 cm$^{-1}$ and a blue shift of the band at 450 cm$^{-1}$ comparing with Na-containing glasses. Ag-containing glasses have higher peak intensities in the range 150-500 cm$^{-1}$ than the Na-containing glasses. The bands in the range 650-920 cm$^{-1}$ demonstrate the opposite behavior.

Ag-containing glasses have lower values of FWHM than Na-containing glasses that imply the less level of disorder in the glass network.

We connect dissimilarities in raman spectra with formation of $W–O–Ag^+$ and Te–O–W units in silver-containing tellurite glasses, while sodium ions interact preferentially with Te-containing units, resulting formation $Te–_{eq}O–Na^+$ и $Te–_{ax}O–Na^+$ bonds and leading to concentration increase of trigonal pyramid $TeO_3$ and concentration decrease of trigonal bipyramid $TeO_4$ [1,2].

Thus adding of the sodium ions leads to more active transformation of Te-containing units ($TeO_4$->$TeO_{3+1}$->$TeO_3$). Silver ions preferentially interact with $WO_4$, $WO_6$ units with formation $W–O–Ag^+$ and W–O–Te bonds.

1. C. Y. Wang, Z. X. Shen and B. V. R. Chowdari, Raman Studies of $Ag_2O$-$TeO_2$-WO3 Ternary Glasses, J. Raman Spectrosc., 1998, vol. 29, pp. 819-823
2. Lim, J.W., Jain, H., Toulouse, J., et al., Structure of alkali tungsten tellurite glasses by X-ray photoelectron spectroscopy, J. Non-Cryst. Solids, 2004, vol. 349, pp. 60–65.

P14

# Isothermal and laser crystallization of amorphous thin films of PCM materials: comparative analysis of the two mechanisms.

S. Kozyukhin[1,2], A. Sherchenkov[3], P. Lazarenko[3], Yu. Vorobyov[4], M. Presniakov[5], O. Boytsova[1]
[1]Kurnakov Institute of General and Inorganic Chemistry, RAS, Moscow, Russia
[2]National Research Tomsk State University, Tomsk, Russia
[3]National Research University of Electronic Technology, Zelenograd, Russia
[4]Ryazan State Radio Engineering University, Ryazan, Russia
[5]NBICS-Centre Kurchatov Institute, Moscow, Russia
E-mail: sergkoz@igic.ras.ru

Chalcogenide compounds of Ge-Sb-Te system are currently in use as materials for the phase-change memory (PCM) application, and one of the most promising among them is $Ge_2Sb_2Te_5$ (GST225) composition.Clarification of the various aspects of crystallization phenomena is an important scientific and practical task as these issues are directly related with the reliability of data storage in the PCM devices based on this material. In this study we investigated the isothermal and laser crystallization processes of amorphous films and performed a comparative analysis of these two mechanisms.

Thin films were prepared by thermal evaporation of pre-synthesized polycrystalline material on the c-Si substrates. The structures of synthesized materials and thin films were investigated by XRD. The composition of thin films was determined by Rutherford Backscattering Spectroscopy (RBS) and Energy Dispersive X-Ray Analysis (EDXRA). Isothermal crystallization of thin films was carried out in an inert atmosphere at varying time-temperature regimes: $\Delta T$=423-493 K, $\Delta t$=15-180 min. The choice of these regimes was based on the earlier published data and our preliminary experiments. We also used for crystallization of amorphous films laser irradiation at room temperature. For this purpose we used laser ($\lambda$ = 532 nm, $P$ = 13 mW), the beam diameter is of about 5μm, exposure time is a few seconds. This allowed us to compare the two processes of phase transition: in isothermal conditions and under external influence. We used the complex of methods to determine the evolution of the amorphous thin films: 2θ scan (thin film XRD, Rigaku), DSC-50 (Shimadzu), AFM (Solver Pro, NT-MDT), SEM (JEOL), Raman spectroscopy and optical microscopy (NTEGRA Spectra NT MDT). For the TEM analyses, the cross-sections of thin films were prepared using Focused Ion Beam (FIB) milling technique in a Helios (FEI) scanning electron/ion microscope system, a FIB/SEM dual beam system equipped with C and Pt gas injectors and micromanipulator (Omniprobe). All specimens were studied using a transmission/scanning electron microscope (TEM/STEM) Titan 80-300 (FEI). The TEM analyses were performed at 300 kV. RAPID CCD camera was used to record energy-dispersive patterns. We also used a liquid nitrogen cooling holder (Gatan 636 Double Tilt) to prevent potential sample decomposition and/or amorphization during the study.

The presence of crystalline phase in thin films was determined by the appearance of reflexes in X-Ray spectrum, changes in the Raman spectrum, and increasing of the reflectance and roughness ($R_{ms}$) of thin film. It was found that noticeable crystallization begins for the temperature range of 423-453 K after the annealing during several hours, whereas at $T$=453 K and above it crystallization process happen almost immediately, and after 30 min. of heat treatment thin film became completely crystalline. The time-temperature regimes were also identified in which the films were crystalline only partly. The correlation between the experimental data and results of the calculations of information reliability of PCM cells was revealed. Comparison of the Raman spectra of GST225 amorphous thin film, crystalline thin films after thermal annealing and after laser irradiation showed that the strongest changes were observed after laser irradiation. As these results indicate, the process of phase transition is dependent on the driving force of the process and its nature. TEM results also indicate that in the case of laser crystallization process takes place only in a thin surface layer (about 15 nm), whereas when the isothermal crystallization it covers the whole volume of thin film. The analysis showed that for the description of the isothermal crystallization Kolmogorov's model can be used. In the case of laser irradiation the progress of crystallization $x(t)$ was analyzed using the Johnson–Mehl–Avrami model (JMA model).

The study was supported by RFBR (14-03-00314).

P15

# Excitation induced NIR emission analysis in $Pr^{3+}$ single and $Pr^{3+}$, $Yb^{3+}$ co-doped TZYN glasses for optical amplifiers

Dagupati Rajesh* M. Reza Dousti, Raja J. Amjad, A. S. S. de Camargo*
Physics institute of São Carlos, University of São Carlos, São Paulo 13566-590, Brazil
E-mail: rajeshdagupati00@gmail.com; andreasc@ifsc.usp.br

Nowadays, the interest in broadband optical amplifiers has continually motivated the research into NIR emitters, because their potential applications in the C-, S-, O- and E-bands [1, 2]. To purse that purpose, different concentrations of $Pr^{3+}$ and $Pr^{3+}/Yb^{3+}$ doped oxyfluoro tellurite glasses with composition $TeO_2$+ZnO+$YF_3$+NaF (TZYN) were synthesized and characterized to investigate their potential application as amplifier media operating at 1.04, 1.3 and 1.48 μm. Optical absorption and NIR emission spectra of $Pr^{3+}$ and $Pr^{3+}/Yb^{3+}$ active ions in TZYN glass were recorded at room temperature. Based on optical absorptions, the three phenomenological Judd–Ofelt parameters $\Omega_2$, $\Omega_4$ and $\Omega_6$ have been derived and, by using them, we calculated radiative parameters such as spontaneous emission probabilities (A), lifetimes ($\tau_R$), branching ratios ($\beta_R$) and integrated absorption cross sections ($\Sigma$) for all the studied excited states. For $Pr^{3+}$ doped glasses, two prominent bands around 1.04 and 1.49 μm (see below Fig.), originating from $^1D_2$ state, were observed, upon excitation at 440 nm. Another broad NIR emission band around 1.30 μm originating from $^1G_4$ state has been observed upon excitation at 978 nm for $Pr^{3+}/Yb^{3+}$ co-doped glasses. The experimental stimulated emission cross-sections were evaluated for all the observed NIR emission transitions. These results suggesting that $Pr^{3+}$ and $Pr^{3+}/Yb^{3+}$ doped TZYN glass is potential candidate for optical amplifiers application.

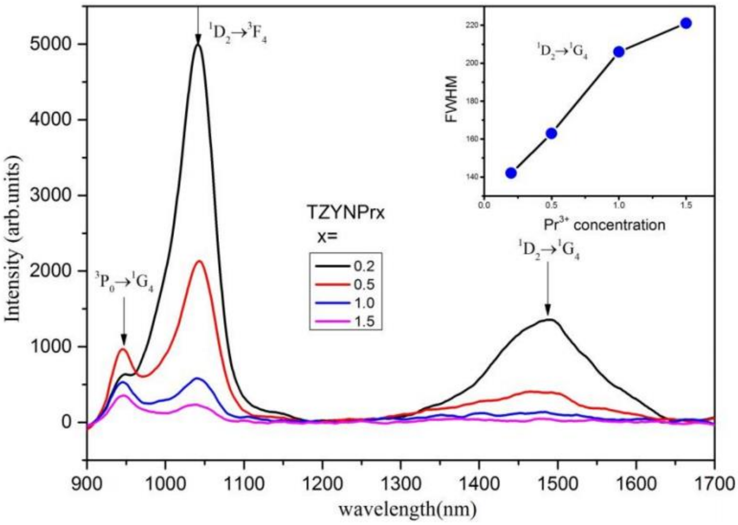


Fig. 1 (color online) NIR emission spectra for different concentration of $Pr^{3+}$ doped samples.

1. B. Zhou, L. Tao, Y.H. Tsang, W. Jin, E.Y.-B. Pun, Opt. Exp. 20 (2012) 3803–3813.
2. Q. Sheng, X. Wang, D. Chen, J. Lumin. 135 (2013) 38–41.

P16

# Photoluminescence and thermal lens spectroscopic investigations of highly efficient fluorophosphates glasses doped with $Nd^{3+}$ and $Er^{3+}$

T.S. Gonçalves, J. Santos, T. Catunda, A. S. S. de Camargo
São Carlos Institute of Physics, University of São Paulo, Av. Trabalhador Sãocarlense 400, 13566-590,
São Carlos – SP, Brazil.

Currently, glasses and glass ceramics doped with trivalent rare earth $RE^{3+}$ ions represent the most important class of materials for laser and other optical applications in the visible and near-infrared spectral regions. In this context, one of the challenges is to find host matrices that assure good optical quality and optimum performance of the dopant ions (high absorption and emission cross sections, low probability of non-radiative decays, sufficiently long excited state lifetimes), while still maintaining thermal and mechanical stabilities. In this study, we present the synthesis by melt quenching and the structural/spectroscopic investigation of new glasses with composition $25BaF_2 25SrF_2 10Al(PO_3)_3 20AlF_3 (20-z)YF_3{:}zREF_3$, where x = 20 or 25, RE = $Er^{3+}$ and $Nd^{3+}$ and z = 0.25 – 5.0 mol %. Glass transition temperature ($T$g), crystallization temperature ($T$c), and melting temperature ($T$m) were determined by DSC. Long excited state lifetime values ($\tau$ = 10 ms for $Er^{3+}$ level $^4I_{13/2}$, $\tau$ = 266 μs for $Nd^{3+}$ level $^4I_{11/2}$) and high fluorescence quantum efficiencies $\varepsilon$ (up to 85 %) were verified for all the glasses. Thermal lens signal amplitude presented a linear dependence with $Er^{3+}$ concentrations resulting in a decrease of about 40 % when going from 1 to 5 mol % doping. Thermal diffusivity value is around 3.5 x $10^{-3}$ $cm^2/s$ for $Er^{3+}$-doped samples and $Nd^{3+}$ doped samples are under study.

P17

# Luminescent lead tungsten fluorophosphate glasses and glass-ceramics

Nardi, R. P. R. D., Cassanjes, F. C., Poirier, G.
Research Group in Materials Chemistry, Institute of Science and Technology, Federal University of Alfenas, campus Poços de Caldas – MG, UNIFAL-MG, Brazil.
gael.poirier@unifal-mg.edu.br

Phosphate compounds are interesting glass formers and are largely investigated for their specific properties with respect to other classical glass formers such as silicate, borate or germanate glasses. Particularly, they are well known for their small liquidus viscosity, softening temperatures, large UV transparency and high solubility for other glass modifiers or intermediaries such as alcaline, rare earth or transition metal compounds [1-3]. Another interesting behavior of phosphates glasses is their ability to incorporate fluoride compounds without reduction of the glass forming ability. These vitreous materials are known as fluorophosphate glasses and are of great interest for rare earth luminescence since the fluoride compounds strongly reduce the phonon energy of the glass host [2, 3]. Heavy metal fluoride compound were also incorporated in several other glass formers and these materials were used to prepare the well-known ultratransparent glass ceramics [4-6]. These rare earth doped materials exhibit highly efficient luminescent properties since rare earth ions tend to migrate to the heavy metal fluoride crystalline phase during heat-treatment. On the other hand, tungsten phosphate glasses based on the binary system $NaPO_3$-$WO_3$ are well-known for their great glass forming ability and very high thermal stability against devitrification due to the intermediary behavior of tungsten octahedra inside the metaphosphate network [7, 8].

For these reasons, this work investigated the glass forming ability in the ternary system $NaPO_3$-$WO_3$-$PbF_2$ doped with rare earth ions in order of obtaining transparent glass-ceramics containing lead fluoride nanocrystallites. Synthesis conditions such as melting time and melting temperature were improved for the formation of transparent, homogeneous and stable glasses with low fluorine loss during the melting process. Glass samples were obtained in this ternary system $(40-x)NaPO_3$-$xWO_3$-$60PbF_2$ varying $x$ of 14 to 34. Subsequently, these samples were characterized by DSC, in order to determine the characteristic temperatures and thermal stabilities. The XRD analyzes prove the non-crystalline state of the samples. A crystallization study identified the preferential crystallization of the cubic phase β- $PbF_2$ with dominant volumetric crystallization and two-dimensional growth. Luminescence measurements of $Eu^{3+}$ in glasses and glass-ceramics obtained by heat treatment suggest migration of $Eu^{3+}$ to the β-$PbF_2$ crystalline phase only for the most $WO_3$ concentrated samples with a decreasing intensity of the hypersensitive emission $^5D_0 \rightarrow {}^7F_2$ at 612 nm.

1. B.C. Sales, Materials Research Bulletin,1987; 12: 32.
2. L. Bih, N. Allali, A. Yacoubi, A. Nadiri, D. Boudlich, M.Haddad, A. Levasseur, Journal of Physics and Chemistry of Glasses,1999; 40: 229.
3. R.K. Brow, D.R. Tallant, Journal of Non Crystalline Solids,1997; 222: 396.
4. Y. Wang, J. Ohwaki, Applied Physics Letters, 1993; 63: 3268.
5. K. Hirao, K. Tanaka, M. Makita, N. Soga, Journal of Appied Physics, 1995; 78: 3445.
6. P.A. Tick, N.F. Borrelli, L.K. Cornelius, M.A. Newhouse, Journal of Applied Physics, 1995; 78: 6367.
7. G. Poirier, M. Poulain, Y. Messaddeq, Journal of Non Crystalline Solids, 2005 ; 351-4 : 293.
8. S.H. Santagneli, C.C. Araujo, H. Eckert, G. Poirier, S.J.L Ribeiro, Y. Messaddeq, Journal of Physical Chemistry B, 2007; 111: 10109-10117.

P18

# Superposition spectra and interionic energy migration in fluorophosphate:$Ho^{3+}/Er^{3+}$ glass

L.Y. Zhang*, L. Wen, D.B. He
Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics,CAS, Shanghai,201800,China.
*Corresponding author:jndxzly@hotmail.com

$Ho^{3+}$ is an efficient de-sensitizer to $Er^{3+}$:$^4I_{11/2}\rightarrow{}^4I_{13/2}$ transition, and the energy transfer (ET) between $Ho^{3+}$ and $Er^{3+}$ is a phonon-assisted process [1]. Theoretically, phonon-assisted ET is benefit for the population accumulation on $^4I_{11/2}$, which is the upper laser level of $Er^{3+}$:2.7 μm emission. It is necessary to investigate the energy migration mechanisms between $Ho^{3+}$ and $Er^{3+}$. Studies on superposition spectra [2, 3] of $Er^{3+}$:1.5 μm reveal the possibility of the interionic energy migration between the two $RE^{3+}$ ions. Emission cross section ($\sigma_{emi}$) superposition of $Er^{3+}$:1-phonon overlaps largely with $Ho^{3+}$ absorption cross section at 2.0 μm, while the 1-phonon and 2-phonons assisted $\sigma_{emiEr3+@1.5\mu m}$ are 1/3 and 1/33 of the 0-phonon assisted $\sigma_{emiEr3+@1.5\mu m}$, respectively, proving that 1-phonon assisted ET is principle for $^4I_{13/2}\rightarrow{}^5I_7$ energy migration. Calculation indicates that ET coefficient is not a constant but varies with $Ho^{3+}$ concentration. ET rate of $^4I_{13/2}\rightarrow{}^5I_7$ enhances largely with increasing $Ho^{3+}$ concentration, but combined with the strengthened ET rate of $Ho^{3+}$-$Ho^{3+}$ interaction and the correspondingly decreased 2.7 μm and 2.0 μm emission, Ho:Er ratio is recommended to be lower because intensive interactions between $Ho^{3+}$ induce large energy loss and inefficient 2.7μm emission. ET rate of $^4I_{13/2}\rightarrow{}^5I_7$ is much larger than that of $^4I_{11/2}\rightarrow{}^5I_6$, and the energy back transfer rate of $^5I_7\rightarrow{}^4I_{13/2}$ is very low, which overcomes the bottleneck of the lower lasing $^4I_{13/2}$ level, and promote the 2.7 μm emission efficiently.

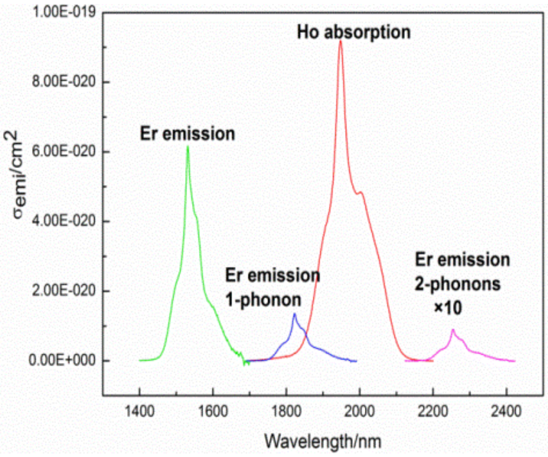


Fig.1 Spectral cross section superposition between $Er^{3+}$:$^4I_{13/2}\rightarrow{}^4I_{15/2}$ emission and $Ho^{3+}$:$^5I_8\rightarrow{}^5I_7$ absorption under room temperature.

1. L. Zhang, Z. Yang and Y. Tian, *J. of Appl. Phys*., **110** 093106-1-6 (2011).
2. L. Tarelho, L. Gomes, Physical Review B, **56** 14344–51(1997).
3. T. Förster , Annalen der Physik, **2** 55–75 (1948).

P19

# Up-conversion detection of 1.908 micron radiation of Tm: YLF in the glass composition $TeO_2$-$PbF_2$-$Ho_2O_3$-$Yb_2O_3$

A.P. Savikin, A.S. Egorov, A.V. Budruev, I.Y. Perunin, I.A. Grishin
N.I. Lobachevsky State University of Nizhny Novgorod, 603950 Nizhny Novgorod, Russia
e-mail: savikin@rf.unn.ru

By setting up and working with near IR laser systems it is convenient to use up-conversion detectors at the 2 μm band with conversion of the IR radiation into visible radiation light. This phenomenon named as anti-Stokes luminescence (ASL). Due to this purpose the best approach is to use ions of rare earth elements (i.e. ions $Ho^{3+}$). They have the absorption band from the ground state located near 1870 – 2150 nm. The ASL intensity largely depends on the choice of matrix in which holmium ions are embedded. So, the phonons energy of $PbF_2$ ($h\nu_{phon} \approx 257 cm^{-1}$) makes this material a promising matrix for efficient conversion of the 2 μm radiation in the visible range of the spectrum to be realized. For the first time the observation of ASL excited radiation 2.051 μm in a fluoride fiber doped with $Ho^{3+}$ reported in [1].

In this paper, we report the results of the experiments and quantitative estimates of the probabilities of two mechanisms: non-resonant Stokes and anti-Stokes excitation and cooperation of $Ho^{3+}$ ions energy with matrix phonons. Synthesized glasses had the following composition: (99-x-y)$TeO_2$-x$PbF_2$-1$Ho_2O_3$-y$Yb_2O_3$, where x= 40,50,60 mol %; y = 0,1,2,3 mol %. To study the Raman scattering the glasses had a composition of (100-x)$TeO_2$-x$PbF_2$, where x=40,50 мол %. Excitation of ASL of samples (λ = 650 nm) was performed on the wavelength at 1908 nm via emission of $Tm^{3+}$:YLF laser with diode-pumped operating in free-running generation mode. The experimentally minimum (threshold) of power density of Tm:YLF laser, in which a sample spot (ASL) was observed visually was determined. The values of population levels involved in the transitions were found by solving the system of the balance equations. The estimates of probability are non-resonant absorption and probability of the exchange of excitation energy between the ions, lead to the conclusion about the prevalence of the co-operation mechanism of excitation energy in the population levels $^5F_5$ of the holmium ions. These estimates are made according to the method described in [2], as well as the time dependence of the luminescence decay obtained in the experiment.

1. A. Guhur, and S. D. Jackson, Opt. Express, **18**(19), 20164 (2010).
2. F. Auzel, Phys. Rev. B **13**, 2809 (1976).

---

P20

# Study of magnetooptic properties of high-purity tellurium dioxide based glasses

Yakovlev A.I.[1],*, Snetkov I.L.[1], Dorofeev V.V.[2], Motorin S.E.[2], Palashov O.V.[1]
[1]Institute of Applied Physics of the Russian Academy of Sciences, 46 Ulyanova st., Nizhny Novgorod, 603950, Russia
[2]G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, Tropinina st. 49, 603950 Nizhny Novgorod, Russia
* yaknnalex@gmail.com

Active researches are now actively carried out to develop a magneto-active material for magneto-optical filters, operating in the visible and infrared ranges. Tellurite glasses offer an advantages of high transparency range (approximately from 0.35 to 6 μm), considerable magneto-optical properties [1, 2], sufficient mechanical strength and seem to be the attractive material. The possibility of obtaining of tellurite glass elongated samples with a very low level of optically active impurities of 3d-transition metals and hydroxyl groups with low optical loss was already demonstrated [3]. It can afford to produce the samples of sufficient length for Faraday rotators with the required parameters creation. One of the key characteristics of the magneto-active material is the wavelength dependent Verdet constant. The tellurite glasses compositions diversity allows to vary the value of the Verdet constant by introduction of the modifying component s, such as zinc, molybdenum, tungsten and bismuth oxides.

In the present work a spectral dependence of the Verdet constant was measured for tellurite glasses of different composition within wavelength region of 450 – 1530 nm.

The glasses were produced by melting the high-purity initial oxides inside a sealed silica reactor in the atmosphere of purified oxygen. The melt was poured into silica glass moulds and annealed during several hours at glass transition temperature. The founded samples were extracted from the moulds and mechanically treated by grinding and polishing for subsequent investigations. The samples prepared had the form of plates of several mm thick.

The scheme of the experiment is presented on the Fig. 1. The linear polarized radiation after calcite wedge propagated through the sample placed in the magnetic system. Without the sample installation the Glan prism was crossed relatively calcite wedge. The angle of the rotation was measured by the Glan prism rotating dawn to achieving minimal signal at CCD-Cam while the sample was located in the magnetic system.

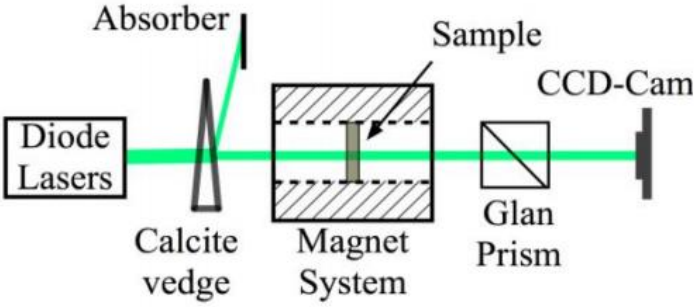


Fig. 1. Scheme of the experiment.

According to measurements, the Verdet constant was obtained from the expression: $V = \varphi / (\int H(x) \cdot dx)$ for each wavelength. Also, the approximation $V(\lambda) = (1 / \lambda) \cdot (A + B / (\lambda^2 - \lambda_0^2))$ was obtained for wavelength region of 450 – 1530 nm and coefficients $A$, $B$ and $\lambda_0$ for tellurite glass samples were determined. The data can be useful for tellurite glass based Faraday devices creation.

The fabrication of the samples was supported by the Russian Foundation for Basic Research (15-03-08324). Measurements of the Verdet constant of the samples was supported by the mega-grant of the Government of the Russian Federation No. 14.B25.31.0024 executed at the Institute of Applied Physics of the Russian Academy of Sciences.

1. Borrelli, N.F., Faraday Rotation in Glasses. The Journal of Chemical Physics, 1964. 41(11): p. 3289-3293.
2. Westenberger, G., et al. Verdet constant and its dispersion in optical glasses, 1991. Proc. SPIE 1535, Passive Materials for Optical Elements, p. 113.
3. V.V. Dorofeev, et al., High purity TeO2-WO3-(La2O3, Bi2O3) glasses for fiber-optics, Optical Materials, 2011. 33(12): p. 1911–1915.

P21

# Thermal and optical properties of niobium phosphate glasses and glass-ceramics

B.L. Pastena, F.C. Cassanjes, G. Poirier
Research Group in Materials Chemistry, Institute of Science and Technology, Federal University of Alfenas,
campus Poços de Caldas – MG, UNIFAL-MG, Brazil.
gael.poirier@unifal-mg.edu.br

The work has been devoted to the preparation of glass samples based on potassium polyphosphate and niobium oxide doped with luminescent rare earth ions for obtaining new glass compositions with potential photonic applications. The glass forming domain of the binary system $KPO_3$-$Nb_2O_5$ was investigated and the glass samples were doped with 0.5 % $Eu^{3+}$. Homogeneous and transparent glasses were obtained for niobium oxide contents ranging from 20 mol % to 50 mol %. The different synthesis conditions such as melting temperature, time and atmosphere were determined and optimized.

The glass samples were characterized by DSC in order to determine the thermal behavior as a function of $Nb_2O_5$ content as well as the characteristic temperatures $T_g$, $T_x$, $T_c$ and $T_f$. Higher niobium oxide contents resulted in higher glass transition temperatures and consequently lower thermal stability against devitrification.

The glass composition $50KPO_3$-$50Nb_2O_5$ exhibited two crystallization peaks associated with precipitation of hexagonal niobium oxide at lower temperature due to phase separation and precipitation of potassium niobium phosphate $K_3Nb_6P_4O_{26}$ corresponding to the remaining glass matriz at higher temperature. DSC measurements on powder and bulk samples also allowed to determine a volume crystallization for the hexagonal niobium oxide phase, justifying the selection of this glass composition for glass-ceramic preparation.

Optical characterizations by UV-Vis spectroscopy were useful to determine that higher $Nb_2O_5$ contents promote a decrease of the bandgap energy due to higher overall polarizability of the glass matrix. Finally, $Eu^{3+}$ emission data in the visible pointed out a strong dependence of the $Eu^{3+}$ symmetry, experimental lifetimes and quantum efficiency with respect to the niobium oxide content crystallinity degree related with hexagonal $Nb_2O_5$ precipitation.

P22

# NMR spectroscopy of the fluoride glasses in the $BiF_3$–Rb(Cs)F–$ZrF_4$ systems

V. Kavun, A. Slobodyuk, E. Merkulov, M. Polyantsev, R. Yaroshenko, V. Goncharuk
Institute of Chemistry, FEB RAS, Vladivostok, 690022, Russia
kavun@ich.dvo.ru

One of priorities in research of glass materials is a direction associated with a study of ion mobility and ion transport in the fluoride glasses. High conductivity of these glasses causes good prospects of their application in the development of functional materials including solid state electrochemical devices. A glassy state is characterized by a certain kind of structural disordering in amorphous solids, which resulted in glasses with high ionic conductivity (up to $10^{-2}$-$10^{-4}$ S/cm) were obtained in a number of inorganic systems. In recent years much attention is paid to research of fluoride glasses containing $Bi^{3+}$ ions, an addition of which into the fluorozirconate glasses extends application abilities of these glasses: the refractive index increases, the ionic conductivity grows, an optical transparency window increases. We have previously studied the dynamics of ion motion, structure, and electrical and physical properties of $BiF_3$–$MF_n$–$ZrF_4$ (M =

Li, Na, K, Ba, Pb) glasses [1–3]. In this work, we present the results of the study of ionic mobility in (55–**$x$**)BiF$_3$–**$x$**RbF–45ZrF$_4$ (**$x$** = 10, 20 and 30 mol. %) and (90–**$x$**)BiF$_3$–10CsF–**$x$**ZrF$_4$ (**$x$** = 55, 50, 45 and 40 mol. %) glasses.

The nature of cations of stabilizing additives (in this case, fluorides of alkali cations) is known to be one of the main factors determining the nature of ion motions in glass materials. A typical transformation of NMR spectrum shape of the studied glasses at temperature variations is shown in Fig. 1. The $^{19}$F NMR data made it possible to assess the temperature effect on the nature of ion motions in the fluoride sublattice, identify types of ionic mobility, and determine the respective temperature ranges (150–500 K). It has been established that the fluorine ions transition from rigid lattice (below 320 K) to diffusion (above 450 K) takes place through an intermediate stage associated with the occurrence of local motions. Analysis of temperature dependences of a shape and the second moment of $^{19}$F NMR spectra of the (55–**$x$**)BiF$_3$–**$x$**RbF–45ZrF$_4$ glasses shows that the fluoride sublattice remains "rigid" (in NMR terms) up to a temperature of 300–320 K. The observed below 300 K asymmetric shape of $^{19}$F NMR spectra of glasses with different alkali cations is caused by a structural non-equivalence of resonating nuclei and a chemical shift anisotropy. An appearance of the "narrow" component in the NMR spectrum (Fig. 1) indicates an emergence of local motions of fluorine-containing groups in the temperature range of 320–350 K (Rb → Cs). According to NMR data, the larger is a cation M$^+$ size, the lower is energy of activation of local motions is, and the more intensive dynamic processes occur in the glass fluoride sublattice at the same glass compositions.

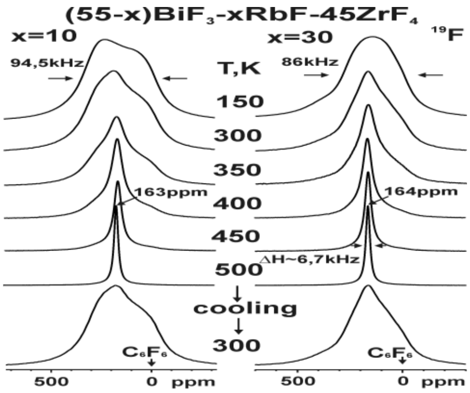


Fig.1. Evolution of $^{19}$F NMR spectrum shape vs tempera-ture for the some glasses

Taking into account a line shape, the second moment values, and component widths in $^{19}$F NMR spectra, in the temperature range of 350–450 K the local motions (along with the rigid lattice) can be assumed to be the main type of ion motions in the fluoride sublattice for glasses with any alkali cation. In the fluoride sublattice of the studied glasses the local movements are mainly observed - reorientations of fluorine-containing groups which form the glass network. The results showed that in (55–x)BiF$_3$–xRbF–45ZrF$_4$ glasses at temperatures above 490 K the dominant type of ion motion was diffusion of fluoride ions.

The factors contributing to the development of local mobility (diffusion) in the fluoride sublattice of the glasses in the BiF$_3$–RbF–ZrF$_4$ and BiF$_3$–CsF–ZrF$_4$ systems were considered, and a role of fluorides in forming the character of ion motions in these glasses was determined. It was found that the specific conductivity of glasses depends largely on the concentration of cations with high polarizability.

This work was supported by the Russian Foundation for Basic Research (grant No. 14-03-00041)

1. V.Ya. Kavun, E.B. Merkulov, N.A. Logoveev, A.B. Slobodyuk, V.K. Goncharuk, Ionic Mobility in Glasses in the ZrF$_4$–BiF$_3$–MF Systems (M = Li, Na, K) as Probed by $^7$Li, $^{19}$F, and $^{23}$Na NMR, Russ. J. Inorg. Chem. 53 (2008) 418–424.
2. V.Ya. Kavun, E.B. Merkulov, S.L. Sinebryukhov, S.V. Gnedenkov, V.K. Goncharuk, Ionic Mobility and Electrical Transport in 45ZrF$_4$–35BiF$_3$–20MF (M - Li, Na, K) Glasses Studied by NMR and Impedance Spectroscopy, Inorg. Mater. 45 (2009) 315–321.
3. V.Ya. Kavun, E.I. Voit, R.M. Yaroshenko, V.K. Goncharuk, Structure and ion mobility in glasses in the BiF$_3$–PbF$_2$–ZrF$_4$ systems studied by Raman and NMR spectroscopy, J. Non–Cryst. Solids, 401 (2014) 224-231.

P23

# Investigation of heterophase inclusions as a source of optical losses in high-purity chalcogenide and tellurite glasses for fiber optics

L.A. Ketkova, V.S. Shiryaev
Institute of Chemistry of High Purity Substances, Russian Academy of Science, 49 Tropinin st.,
Nizhny Novgorod, 603950, Russia, E-mail: ketkova@ihps.nnov.ru

The search for sources of extrinsic optical losses is one of the main objectives in the technology of high-purity materials for fiber optics. This problem is especially relevant for a number of prospective materials for the mid-IR fiber and nonlinear optics - tellurite and chalcogenide glasses. The optical loss spectra of the fibers obtained from the most pure samples of such glasses show regions where the bands of selective absorption typical for homogeneous impurities are weak or are absent. At the same time, the level of losses remains rather high, exceeding, as a rule, by orders of magnitude the intrinsic losses of the material. The determination of the heterogeneous component contribution to optical losses in these materials is, therefore, of significant interest. Such a component is due to the presence of the impurity inclusions resulting from the contamination and the phase inclusions arising from the crystallization and phase separation.

3D laser ultramicroscopy (3D LUM) is the most suitable method for the study of the impurity and phase inclusions in high-purity materials for fiber - optic applications [1, 2]. This technique is based on the registration of the light scattered by individual inclusions in the direction orthogonal to the incident laser beam. The method is characterized by a low size detection limit (~$n$*10 nm) and a wide range of the detectable concentrations ($1\text{-}10^{10}$ см$^{-3}$). 3D LUM can scan a sample up to a few centimeters depth and can be used to control inclusions in the materials transparent not only in the visible but also in the near IR region. The measurement of the light scattered by inclusions at a varied probe beam wavelength and polarization and at a varied scattered light collection angle makes it possible in some cases to determine the inclusion refractive indices. There are, however, glass samples where 3D LUM reveals no individual scattering centers, only so called background scattering is detected. This can be interpreted as scattering on optical inhomogeneities with the concentration above the maximum available for 3D LUM. In such cases the information required for the estimation of the background scattering contribution to optical losses is provided by measurements of integral scattering relative to a known standard (the quartz glass). The 3D LUM apparatus makes it possible to determine most elements of the $90^o$-scattering matrix as well as to measure the integral scattering coefficient, depolarization of the scattered radiation and the asymmetry coefficient of the scattering indicatrix.

Potentialities of the techniques are demonstrated by dispersion analysis of the chalcogenide glasses based on arsenic, antimony, and germanium sulfides, selenides (glass samples prepared by the direct synthesis from elements in a quartz container), as well as of the $TeO_2$-$WO_3$ and $TeO_2$-ZnO tellurite glasses with the $La_2O_3$, $Na_2O$ additives (the synthesis in a platinum container). It was found that the concentration of the $n\times(10\text{-}100)$ nm heterophase inclusions in the chalcogenide glasses is $10^3\text{-}10^7$ cm$^{-3}$ depending upon the degree of purity and synthesis conditions (time and temperature regimes). The most part of registered inclusions correspond to the inclusions with the refractive indices close to that of the silicon dioxide. A small part is identified as the bubbles. The maximum inclusion contribution to the optical loss calculated on the basis of dispersion analysis is ~ $10^3$ -$10^4$ dB/km at wavelengths of 2-7 μm. All the tellurite glass samples studied reveal only background scattering. The scattering intensity exceeds that in the quartz glass by over an order of magnitude. Substantial depolarization of the scattered radiation is observed. Measurements of the $90^o$-scattering matrix ($\lambda$=0.63 μm) are indicative of non-spherical shapes of the optical inhomogeinities and of the Rayleigh nature of scattering ($A/\lambda^4$). Estimated scattering losses is A=30-100 dB/km·μm$^4$, which is higher than the known theoretical intrinsic scattering in tellurite glasses [3] by over two orders of magnitude.

This work was supported by the Russian Science Foundation (Russia, Grant No. 16-13-10251).

1. L.A. Ketkova, M.F. Churbanov, Inorg. Mater. 50 (2014) 1301-1316.
2. L.A. Ketkova, Opt. Mater. 47(2015) 251–255.
3. J.S. Wang, E.M. Vogel, E. Snitzer, Opt. Mater. 3(1994) 187–203.

P24

# A study of glasses in the $TeO_2$-$P_2O_5$PbO-$PbF_2$-$MF_3$ (M-Er, Eu, Nd) system by light nonelastic scattering method

Marchenko Yu.V., Ignatieva L.N., Savchenko N.N., Maslennikova I.G.
Institute of Chemistry FEB RAS, Vladivostok, Russia
gor_dvo@mail.ru

In this work the glasses in the $TeO_2$-PbO·$P_2O_5$-$PbF_2$-$MF_3$(M-Er, Eu, Nd) system were studied with the aim of revealing the rare earth elements trifluorides influence on the structural, optical and crystallization characteristics of the glasses of this system. In the $TeO_2$-PbO·$P_2O_5$-$PbF_2$-$MF_3$ system the REE content has changed from 0.5 to 3 mol %. The main attention focuses on the study of low frequency range of the Raman spectra, which is responsible for the information about middle range order in the glasses studied.

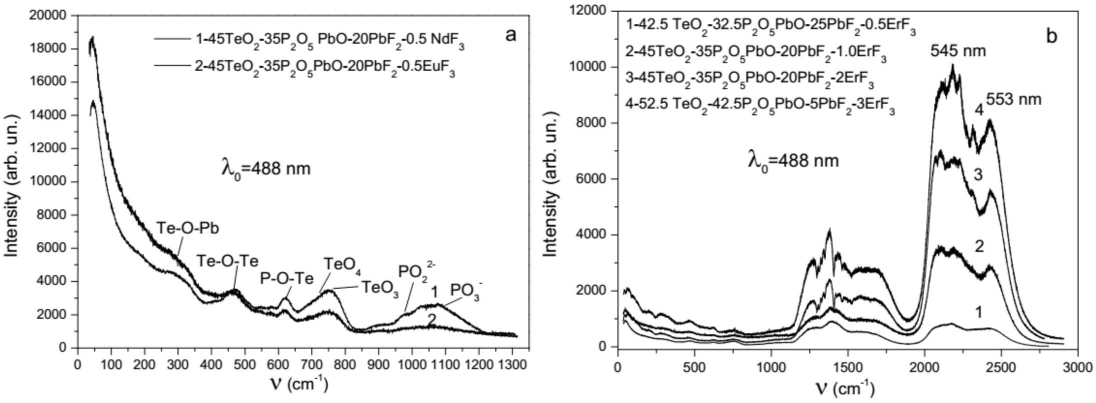


Fig1. Spectra of the light nonelastic scattering for glasses in the $TeO_2$-PbO·$P_2O_5$-$PbF_2$-$MF_3$ systems

The boson peak location in the Raman spectra of the glasses containing different REE (fig 1a) was analyzed. The boson peak location in the Raman spectra of the glasses with different content of the glassforming components $TeO_2$, $P_2O_5$PbO and REE trifluorides was analyzed. The contribution of REE photoluminescence in to the spectra of nonelastic scattering of the systems is discussed.

At the excitation of spectrum by laser with wavelength $\lambda_o$= 488 nm in glasses containing 0.5 mol % $ErF_3$ the bands in the range 2000-2700 cm$^{-1}$ (fig. 1b) increasing in intensity with increasing erbium trifluoride content in the system are observed. It was expected, that these bands correspond to contribution of Er photoluminescence in to the spectrum of the light nonelastic scattering. The bands correspond to the emission levels 530, 545 nm ($^4S_{3/2}\rightarrow{}^4I1_{5/2}$ transition). At the increasing of the erbium trifluoride concentration from 0.5 mol % to 3 mol %, judging by the changes in the Raman spectra (the shape of the boson peark and the bands, corresponding to the vibrations of the glassforming polyhedra, changes) in the glasses the crystallization occurs. The crystallization begins in the range of the phosphate groups.

P25

# Nonlinear optical properties of high-purity tellurite glasses

M.P. Smayev[1], V.V. Dorofeev[2], A.N. Moiseev[2], A.G. Okhrimchuk[1]
[1]International Centre of Laser Technology, D. Mendeleyev University of Chemical Technology of Russia,
Miusskaya sq. 9, 125047 Moscow, Russia
e-mail: smayev@gmail.com
[2]G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences,
Tropinina st. 49, 603950 Nizhny Novgorod, Russia

Tellurium dioxide based glasses are characterized by low phonon energy as compared with silica glasses, and can be obtained with an extremely low 3d-transition metals and hydroxyl groups impurities content, which ensures high transparency in the near and mid infrared regions [1, 2]. In addition, convenient viscosity parameters, sufficient mechanical strength and especially high non-linear refractive index make them a very promising material for bulk and waveguide devices for infrared optics.

The nonlinear optical properties of high-purity zinc- and tungstate- tellurite glasses modified with molybdenum, lanthanum or bismuth oxides were studied.

The glasses were produced by melting the oxides in gold or platinum crucibles inside a sealed silica chamber filled with purified oxygen. $TeO_2$, $WO_3$, $MoO_3$ fabricated in our laboratory by original techniques and commercial high-purity ZnO, $La_2O_3$, $Bi_2O_3$ were used for glass synthesis. The total content of the 3d-transition metals impurities in raw materials and in glasses did not exceed 1-2 ppm wt. High stability of glasses against crystallization was confirmed by DSC at a heating rate 10 K/min and there were no thermal effects of crystallization and melting of crystals. The hydroxyl groups absorption at ~3 μm, being calculated from transmission spectra by the Beer–Lambert–Bouguer law equation, was as low as 0.001-0.01 $cm^{-1}$ in the glass samples prepared.

We have experimentally determined nonlinear coefficient $\gamma$ that characterizes refractive index change $\Delta n$ due to Kerr lens effect: $\Delta n = \gamma \times I$, where $I$ is light intensity in the sample. The measurements were performed with Z-scan technique [3]. The femtosecond laser beam was focused by a lens with focal distance of 250 mm, and this way a beam with waist radius of 50 microns and Relay distance of 7.5 mm is formed. Laser operation wavelength was 1030 nm, pulse duration was as low as 180 fs, and repetition rate equaled 1 kHz. A glass sample with thickness of 1.5 mm was installed on a motorized translation stage, and scanned along the beam waist on the distance 120 mm.

All samples exhibit positive nonlinearity. The maximal $\gamma$ values were obtained for bismuth oxide modified glasses: $\gamma = 5.6 \times 10^{-6}$ $cm^2$/GW, lowest non-linear coefficients among glasses investigated were obtained for zinc-tellurite glasses ($\gamma \approx 10^{-6}$ $cm^2$/GW). In conclusion high values of the nonlinear coefficient combined with low absorption in NIR make tellurium glasses an attractive material for applications in devices of non-linear photonics, such as Kerr-lens mode-locked laser, waveguide optical switchers, super-continuum generators.

The study was supported by the Ministry of Education and Science of the Russian Federation (grant no. 14.Z50.31.0009). The fabrication of the samples was partly supported by the Russian Foundation for Basic Research (15-43-02185, 15-03-08324).

1. A.N. Moiseev, V.V. Dorofeev, A.V. Chilyasov et al., Optical Materials 33, 2011, p. 1858–1861
2. V.V. Dorofeev, A.N. Moiseev, M.F. Churbanov et al., Journal of Non-Crystalline Solids 357, 2011, p. 2366–2370
3. M. Sheik-Bahae, Ali A. Said, T.H. Wei, D.J. Hagan, E.W. Stryland, IEEE J. Quantum Electron. 26, 1990, p. 760

P26

# Glass formation region and optical properties of $TeO_2$-$MoO_3$-$Bi_2O_3$ system

O.A.Zamyatin[1,2], C.G.Bodrova[1], E.V.Zamyatina[1]
[1]Lobachevsky State University of Nizhni Novgorod,
23 Prospekt Gagarina (Gagarin Avenue), Nizhny Novgorod, 603950, Russia
[2]G.G.Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences,
49 Tropinin Str., Nizhny Novgorod, 603950, Russia
E-mail: xef7@mail.ru

Tellurite glasses combine unique physical and chemical properties such as a wide window transparency, good glass stability, rare-earth ion solubility, slow corrosion rate, high refractive index and high nonlinear refractive index. It makes theme an attractive material for optoelectronics and photonics to create fiber amplifiers, lasers and other devices. One of the interesting subject of study is tellurite-molybdate glasses. This binary system has a wide glass formation region and glasses demonstrate sufficiently low glass transition temperature, which makes their useful for production of fibers with low optical losses. Addition of bismuth trioxide is capable to increase the stability of glass to crystallization and improve optical characteristics. In the literature, information about the system $TeO_2$-$MoO_3$-$Bi_2O_3$ is no detailed, so the purpose of this paper was to determine the boundaries of the ternary glasses and determine of optical and thermal properties.

Samples of the ternary glass system were obtained by crucible method from binary oxides at a temperature of 800° C and then annealing at 300°C. Crystalline phases and amorphous nature of the samples was carried out by X-ray analysis. The nature of phases, preparing by heating the starting mixture $TeO_2$, $MoO_3$ and $Bi_2O_3$ to the melting temperature, was established. The formation of a complex oxide $Te_2MoO_7$ occur in the mixture oxides with a low content of bismuth before the melting of the charge. The composition of the resulting bismuth molybdates determined by the initial ratio between molybdenum and bismuth oxides.

The thermal properties of glasses were studied by DSC methods. Glass transition and crystallization temperature of the samples was found. Stable compositions for crystallization in terms of registration DSC was discovered. Optical properties of the glasses in the visible and infrared region was studied by spectrophotometric methods. Window transparency of glasses narrows and the short-transmission border shifted to longer wavelengths with increasing molybdenum trioxide content in the glass. In the NIR wide band of absorption at 3300 nm due to the presence of water was found.

P27

# Optical absorption of *d*-elements in the tellurite-molybdate glasses

O.A.Zamyatin[1,2]*, M.F.Churbanov[1,2], E.V.Zamyatina[1]
[1]Lobachevsky State University of Nizhni Novgorod,
23 Prospekt Gagarina (Gagarin Avenue), Nizhny Novgorod, 603950, Russia
[2]G.G.Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences,
49 Tropinin Str., Nizhny Novgorod, 603950, Russia
*Corresponding author: xef7@mail.ru

$TeO_2$-based glasses possess attractive thermal, physical and optical properties such as a low glass transition temperature and a high refractive index. Binary system with molybdenum trioxide has a high glass forming ability and is regarded as a promising material for linear and nonlinear photonics and optoelectronics. However, the widespread application of such glasses is still prevent a high level of optical losses. In the visible and near infrared region of the spectrum it may be associated with the absorption of the transition elements. Therefore, the study of 3*d*-elements behavior in the matrix of tellurite glass is an actual scientific problem.

In this paper the glasses $(TeO_2)_{0.80}(MoO_3)_{0.20}$, containing a predetermined amount of nickel(+2), cobalt(+2), copper(2), chromium(+3) and iron were prepared by melt at 800 °C in a porcelain crucible. Polished samples with different thickness were made from cylinders, 9 mm in diameter, and transmission spectra of the glasses in the wavelength range from 450 to 2800 nm were measured.

Transmittance of glasses containing impurity atoms in the visible and near infrared region of the spectrum decreases with increasing concentration of d-element. It is shown that the elements of the iron subgroup in the specified range of the spectrum appear in the double-charged cations and have an intense absorption band. In particular, $Ni^{2+}$-ions are characterized by two bands with maxima at 1320 and 810 nm [1], $Co^{2+}$ has a broad band with a maximum at 1380 nm [2], and two bands with maxima registered for $Fe^{2+}$ ions at about 600 and 860 nm. Investigation of the transmission spectra of copper(+2) in glass revealed a strong absorption band at 830 nm [3] and for chromium-containing glass a relatively narrow band at 660 nm.

The specific absorption coefficients of impurity atoms for the entire range of wavelengths were calculated based on the law of light absorption. The full compliance position peaks in the absorption spectra with spectral dependence of the specific absorption coefficient for all the ions of 3d-elements was established. The specific absorption coefficients for each impurity atom increases with decreasing wavelength and short-wave approximation to boundaries of the glass transmission window. This indicates that an intense absorption band outside the area transparency of glasses, with a peak at a wavelength less than 450 nm, is present. Based on the specific absorption coefficient minimum content of impurity atoms to achieve the desired level of optical losses in glass and fibers was estimated. Total content of impurity atoms in the spectral range from 600 to 2800 nm in order to achieve optical losses of 100 dB/km should not exceed 10 ppb wt.

1. O.A. Zamyatin, M.F. Churbanov, V.G. Plotnichenko, A.A. Sibirkin, I.G. Goreva. Specific absorption coefficient of nickel in $(TeO_2)_{0.80}(MoO_3)_{0.20}$ glass // Inorganic Materials.-2015.- V.51. # 3.-P. 278-282.
2. O.A. Zamyatin. Specific absorption coefficient of cobalt(II) in $(TeO_2)_{0.80}(MoO_3)_{0.20}$ glass / O.A. Zamyatin , M.F. Churbanov, V.G. Plotnichenko, A.V. Kharakhordin, A.A. Sibirkin, I.G. Fedotova // Inorganic Materials.-2015.- V.51. #6.-P. 631-634.
3. O.A. Zamyatin. Specific absorption coefficient of copper in $(TeO_2)_{0.80}(MoO_3)_{0.20}$ glass / O.A. Zamyatin, M.F. Churbanov, V.G. Plotnichenko, A.A. Sibirkin, I.G. Fedotova, S.A. Gavrin // Inorganic Materials.-2015.- V.51. # 12.-P. 1283-1287.

---

P28

# Electrical, dielectric, and optical properties of $PbO-Ga_2O_3-Bi_2O_3$ glasses

Kostka P. [1], Trnovcová V. [2], Bošák O.[3], Labaš V. [3], Bašinová N.[1], Kubliha M.[3]
[1] Institute of Rock Structure and Mechanics AS CR, V Holesovickach 41, 182 00 Prague, Czech Republic
[2] Faculty of Natural Sciences, Constantine the Philosopher University, Tr. A. Hlinku 1, 94974 Nitra, Slovakia
[3] Faculty of Materials Science and Technology, Slovak University of Technology, Paulínska 16, 917 24 Trnava, Slovakia

Influence of the crucible (Pt, $Al_2O_3$), chemical composition of glasses, and chemical form of one constituent (PbO, $Pb_3O_4$) on ac and dc conductivities, static permittivity, dielectric relaxation, short wavelength optical edge, and infrared (IR) absorption of binary and ternary glasses of the system $PbO-Ga_2O_3-Bi_2O_3$ is presented and discussed.

Temperature dependences of the dc conductivity are Arrhenius-like, all of them having very close conduction activation energies (1.20±0.05 eV). All binary glasses $PbO-Ga_2O_3$ and the ternary glass $PbO-Ga_2O_3-Bi_2O_3$ with a low concentration of $Bi_2O_3$ have almost the same dc conductivity. At a high concentration of $Bi_2O_3$, the dc conductivity of ternary glasses $PbO-Ga_2O_3-Bi_2O_3$ is about 100 times higher. The type of the crucible and the chemical form of Pb-oxide has only a negligible influence on the dc conductivity. At 300 °C, the static relative permittivity of glasses prepared in Pt crucibles ranges from 22.5 up to 26.2. Binary glasses and the ternary glass $PbO-Ga_2O_3-Bi_2O_3$ with a low concentration of $Bi_2O_3$ are stable up to 300 °C, with a softening temperature of 330 °C. Ternary glasses, with the high content of Bi oxide, change their properties irreversibly at 270 °C.

IR absorption of all glasses prepared in Pt crucibles is almost the same, showing vibrational bands of $OH^-$ and the absorption edge near 6.5-7 μm. Melting procedure in $Al_2O_3$ crucibles results in a low transmittance of glasses due to scattering losses. Preparation in Pt crucibles shifts the short wavelength absorption edge to a longer wavelength significantly.

P29

# Planar waveguides based on tungsten-tellurite glass

O.N. Gorshkov[1], I.A. Grishin[1], A.P. Kasatkin[1], S.V. Smetanin[2], M.F. Churbanov[2], A.N. Shushunov[1]
[1]Research Institute for Physics and Technology University of Nizhni Novgorod (Nizhny Novgorod, 603600,
Nizhny Novgorod, etc. Gagarin, 23, building 3, E-mail:.. Gorshkov@nifti.unn.ru)
[2]G.G. Devyatykh Institute of Chemistry of High-Purity Substances of RAS, Nizhny Novgorod (603950
603950 Nizhny Novgorod, St. Tropinin, 49 The, E-mail: Smetanin@ihps.nnov.ru)

The creation of planar waveguides based on tungsten-tellurite glasses (TTG) doped with erbium and ytterbium ions $Er^{3+}$ and $Yb^{3+}$ and research results of their optical properties are discussed in the report. Tellurite glasses are multifunctional material for fiber and integrated optics [1]. It should be emphasized that these glasses have a wider luminescence band of erbium $Er^{3+}$ than, for example, a phosphate glass. Thus the glasses can provide a wider range of wavelengths for work of optically active devices. In present paper, planar waveguides with a superimposed strip based on tungsten tellurite glasses undoped and doped with rare earths were formed on substrates of thermally oxidized silicon [2] by methods of RF magnetron sputtering and lithography. Conditions of formation of thin-film structures, in which the parameters of the photoluminescence (PL) in them (the lifetime of the PL intensity) were similar to the corresponding parameters of the PL in bulk glasses [3], have been found. Optical losses in the test strip waveguides with a width of 5 microns are ~ 2 dB/cm at a wavelength of 1.5 microns. In case of the strip width of 100 microns (that used for waveguides pumped via the multimode semiconductor laser [4]), the loss at the wave length of 1.5 microns constituted ~ 0.4 dB/cm. The obtained values of the losses are close at order of magnitude to the losses that observed in planar waveguides based, for example, on phosphate glasses that are used for creation of planar optical amplifiers and lasers [5]. Taking into account the experimental values of the optical losses the spectral dependencies of waveguide gain for different values of the relative populations of the metastable energy level of ions $Er^{3+}$ were constructed. The dependence of the gain of the optical signal at a wavelength of 1.5 microns on the pump power for different lengths of waveguide was investigated.

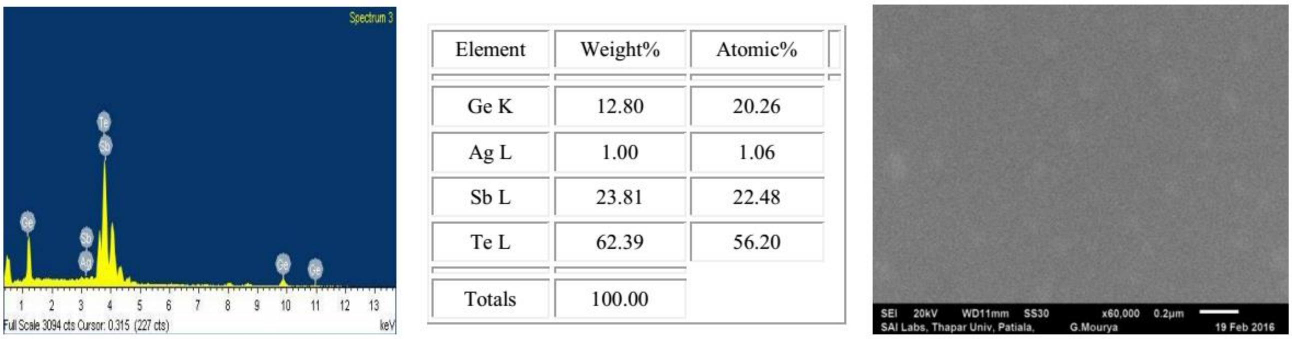
1. Churbanov M.F., Snopatin G.E. Zorin E.V., Smetanin S.V. et. al. J. Optoelectron. Adv. Mater. 2005. Vol.7. №4. P.1765.
2. Gorshkov O.N., Dianov E.M., Churbanov M.F., Vasiliev S.A. at al. Vestnik of UNN. Part FTT 2006. №. 1 (9). P.243.
3. Intyushin E.B., Chigirinskii Y.I. Glass Physics and Chemistry. 2005. V. 31. № 2. P. 219.
4. Madasamy P., Honkanen S., Peyghambarian N. Appl. Phys. Lett. 2003. V. 82. №9. P. 1332.
5. Yan Y.C., Faber A.J., Waal H., Kik P.G. et.al. Appl. Phys. Lett. 1997. V.71. №20. P.2922.

P30

# Effect of visible light on Ag doped GST thin films

P. Singh[1, 2], R. Kaur[1, 2], P. Sharma[3], V. Sharma[3], A. Thakur[2]
[1]Department of Physics, Punjabi University Patiala, 147002, Punjab, India
[2]Advanced Materials Laboratory, Department of Basic and Applied Sciences, Punjabi University Patiala, 147002, Punjab, India
[3]Department of Physics, Jaypee University of Information Technology, Waknaghat, Solan 173234, HP, India
Corresponding author: dranupthakur@gmail.com

Among various phase change materials, $Ge_2Sb_2Te_5$ (GST) is the best phase change material [1-2]. Doping of different elements [3-8] in GST has been done to optimize its properties before to use it practically. Ag doping in GST [9] motivates present authors for its detailed study. Bulk samples $(Ge_2Sb_2Te_5)_{100-x}Ag_x$ ($x = 0, 1, 3$) are prepared using conventional melt quenching technique. Energy dispersive X-ray florescence technique used to confirm stoichiometry of prepared bulk samples and result revealed the desired stoichiometry (fig. 1 (a), (b)). Thin films were deposited on well cleaned glass substrate using thermal evaporation technique under base pressure $4 \times 10^{-6}$ mbar at room temperature. Absence of sharp peaks in Xray diffraction pattern confirms the amorphous nature of deposited thin films. Scanning electron microscope image (fig. 1 (c)) shows uniformly deposited thin films. Energy dispersive X-ray florescence measurement on deposited thin films revealed that there is less than 2 % change in stoichiometry than bulk samples. Deposited thin films were exposed with visible light of known intensity for different time. Transmission spectrum of as deposited thin films and exposed with visible light have been taken using UV-VIS-NIR spectrophotometer at normal incidence. Optical parameters were calculated using transmission spectra. Effect of visible light on these parameters has been studied. Change in optical parameters is because of change in local structure of deposited thin films.



| Element | Weight% | Atomic% |
|---|---|---|
| Ge K | 12.80 | 20.26 |
| Ag L | 1.00 | 1.06 |
| Sb L | 23.81 | 22.48 |
| Te L | 62.39 | 56.20 |
| Totals | 100.00 | |

(a) (b) (c)

Figure 1. (a) Composition spectrum (b) Table for content of constituent elements of $(Ge_2Sb_2Te_5)_{99}Ag_1$ bulk respectively (c) SEM image of as deposited thin film of $Ge_2Sb_2Te_5$.

1. H.F. Harmann, M. O'Boyle, Y.C. Martin, M. Rooks and H. K. Wickramasinghe, Nature Materials 5 (2006) 383-387.
2. Y.J. Park, J.Y. Lee and Y.T. Kim, Applied Physics Letters 88 (2006) 201905.
3. E. Cho, Y. Youn, and S. Han, Applied Physics Letters 99 (2011) 183501.
4. K. Darmawikarta, S. Raoux, P. Tchoulfian, T. Li, J. R. Abelson and S.G. Bishop, Journal of Applied Physics 112 (2012) 124907.
5. J. Fu, X. Shen, Q. Nie, G. Wang, L. Wu, S. Dai, T. Xu and R.P. Wang, Applied Surface Science 264 (2013) 269–272.
6. Q. Wang, B. Liu, Y. Xia, Y. Zheng, R. Huo, Q. Zhang, S. Song, Y. Cheng, Z. Song and S. Feng, Applied Physics Letters 107 (2015). 222101.
7. Y. Zhu, Z. Zhang, S. Song, H. Xie, Z. Song, X. Li, L. Shen, L. Li, L. Wu, B. Liu, Materials Research Bulletin 64 (2015). 333–336.
8. G. Wang, Q. Nie, X. Shen, R. P. Wang, L. Wu, J. Fu, T. Xu and S. Dai, Applied Physics Letters 101 (2012) 051906.
9. K.H. Song, S.W. Kim, J.H. Seo, and H.Y. Lee, Journal of Applied Physics 104, (2008) 103516.

P31

# Hot pressing of transparent ceramics of $Tb_2O_3$-$Y_2O_3$ solid solutions

D.A. Permin [1,3], I.L. Snetkov [2], S.S. Balabanov [1,3], E.M. Gavrishchuk [1,3], O.N. Klyusik [3], D.D. Kuznetsov [3]
[1] G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences
[2] Institute of Applied Physics of the Russian Academy of Sciences
[3] N.I. Lobachevski Nizhny Novgorod State University
permin@ihps.nnov.ru

Faraday isolators and rotators are important optical elements of laser systems. At present, terbium gallium garnet (TGG) is the most widely used magneto-active material due to high value of the Verdet constant (37 rad/(T·m) at $\lambda$=1 μm) and high thermo-optical properties. However, there are magneto-active materials with a higher value of Verdet constant, for example, terbium aluminum garnet ceramics TAG, Ce:TAG. From this point of view terbium oxide and its solid solutions with rare-earth oxides (Y, Sc, Lu) attract great interest due to the possibility to control magneto- and thermooptical properties by varying the material composition [1]. The report concerns fabrication of the $(Tb_xY_{1-x})_2O_3$ (where $x$ is 0.1, 0.2, 0.3 and 1) solid solution transparent ceramics by hot pressing of nanodisperse powders.

Preparation of initial nanopowders was carried out by self-propagating high temperature synthesis (SHS) from acetate-nitrate complex precursors. This approach involves dissolving metal oxide in the mixture of acetic and nitric acids. When heated such precursor is ignited as a result of nitrate and acetic ligands (which serve as an oxidizer and a fuel) reaction [2]. At the end of combustion the solid foam consisting of nanodisperse oxide particles is formed. Since the starting terbium oxide powder $Tb_4O_7$ does not dissolved in acetic acid, it was previously reduced to $Tb_2O_3$ by calcining in alcohol vapor stream at a temperature of 600-700°C. By the data of electron microscopy and BET methods, the dispersity of the product is defined by the synthesis parameters, and average particle size does not exceed 100 nm.

The nanopowders were compacted by uniaxial pressing with a pressure of 200 MPa to samples 13 mm in diameter and 2 mm thick. The formed compacts were hot pressed in a vacuum furnace in a graphite mold at a temperature of 1500-1550°C with a pressure of 50 MPa for 1 hour. After sintering, the ceramic samples were subjected to optical processing.

With increasing $Tb^{3+}$ ion concentration, the Verdet constant of $Tb^{3+}$:$Y_2O_3$ increases linearly and at a concentration of 30 % is comparable to the Verdet constant of a TGG single crystal ($V_{TGG}$) containing 37.5 % of $Tb^{3+}$ ion. Terbium sesquioxide $Tb_2O_3$ (100 % $Tb^{3+}$:$Y_2O_3$) demonstrated the highest value of the Verdet constant by more than 3 times higher than that of the TGG material over the 380-1750 nm transparency range of the material. The approximation of the Verdet constant dependence on wavelength in the range of 380 nm – 1750 nm was obtained for the first time for all investigated ceramic samples and the approximation for $Tb_2O_3$ material was predicted. As compared to the recently studied magneto-active materials, $Tb_2O_3$ has a substantially higher value of Verdet constant, which makes it very promising for Faraday devices and further investigation of its properties is of great interest.

The developing of terbium oxide powders synthesis technique was supported by RFBR, research project No. 16-03-00595 A and investigation of ceramics magnetooptical properties was supported by the mega-grant of the Government of the Russian Federation No. 14.B25.31.0024

1. S. Makikawa, A. Yahagi, and A. Ikesue, Patent No. EP2687500 A1 (16.03.2011 2014); T. Shimada, Patent No. US9052415 B2 (16.03.2011 2015)
2. S.S. Balabanov, E.M., Gavrishchuk, A.M., Kut'in, D.A. Permin, Self-propagating high-temperature synthesis of $Y_2O_3$ powders from $Y(NO_3)_{3x}(CH_3COO)_{3(1-X)}$•$nH_2O$, Inorganic Materials, 47 [5] (2011) 484-488

P32

# Effect of CoO addition on the structure and optical properties of transparent glass-ceramics based on ZnO and $Zn_2SiO_4$ nanocrystals

I. Alekseeva[1], O. Dymshits[1], A. Zhilin[1], D. Shemchuk[1], S. Zapalova[1], M. Tsenter[1], V. Golubkov[2], P. Loiko[3], N. Skoptsov[3], A. Malyarevich[3], K. Yumashev[3], K. Bogdanov[4], V. Vitkin[4]
[1]NITIOM Vavilov State Optical Institute, Saint Petersburg, Russia
[2]I.V. Grebenschikov Institute of Silicate Chemistry, Russian Academy of Science, Saint Petersburg, Russia
[3]Center for Optical Materials and Technologies, Belarusian National Technical University, Minsk, Belarus
[4]National Research University of Information Technologies, Mechanics and Optics, Saint Petersburg, Russia
e-mail: vodym@goi.ru, vodym1959@gmail.com

Glasses 200 g in weight with the composition (mol %) 12 $K_2O$, 28 ZnO, 12 $Al_2O_3$, 48 $SiO_2$ without any dopant and doped with 0.01 – 3.0 wt % CoO were prepared by a conventional melt-quenching technique in platinum crucibles at 1580 °C for 5 h with stirring followed by controlled crystallization via secondary heat-treatments ranged from 680 to 1000 °C; the heat-treatment durations were 2 - 100 h. The structure of the initial glasses and its transformation with the heat-treatments were characterized by Small Angle X-ray Scattering (SAXS), X-ray diffraction (XRD) analysis, differential thermal analysis, Raman spectroscopy, absorption and luminescence spectroscopy. Nonlinear properties of transparent cobalt-doped glass-ceramics were evaluated. According to SAXS findings, inhomogeneous regions are formed during the glass cooling and annealing. The introduction of CoO influences the liquid phase separation that precedes the crystallization and changes the nature of crystalline phases and kinetics of their crystallization. According to XRD study, depending on the heat-treatment schedule and the CoO concentration, glass-ceramics contained either ZnO nanocrystals, or a mixture of nanosized crystals of β-willemite and zinc oxide, or nanosized crystals of β-willemite solely. Heat-treatments at 950 °C and above resulted in crystallization of α-willemite, the material became opaque. Raman spectroscopy data proved these findings.

From the analysis of absorption spectra it is evident that $Co^{2+}$ ions enter into the structure of the zinc oxide and the β-willemite nanosize crystals. They take positions of the $Zn^{2+}$ ions in undistorted tetrahedral sites in the ZnO crystals. The increase of the absorption intensity of the tetrahedrally coordinated cobalt ions correlates with the increase of the fraction of crystallized ZnO. With the precipitation of the $\beta$-$Zn_2SiO_4$ crystals, $Co^{2+}$ ions enter into their structure in a distorted tetrahedral coordination in the positions of $Zn^{2+}$ ions.

Passive Q-switching of a diode side-pumped Er,Yb:glass laser was realized with the developed cobalt-doped glass-ceramics. The red-shift of the IR spectral band as compared with conventional Co-doped spinel saturable absorbers allows one to use these materials as saturable absorbers for Er glass lasers, as well as Er crystalline lasers [1].

This work was partly supported by the RFBR (Grant 13-03-01289 A).

1. P.A. Loiko, O.S. Dymshits, V.V. Vitkin, N.A. Skoptsov, A.A. Zhilin, D.V. Shemchuk, M.Ya. Tsenter, K.V. Bogdanov, A.M. Malyarevich, I.V. Glazunov, X. Mateos, K.V. Yumashev, Structure and nonlinear optical properties of novel transparent glass-ceramics based on $Co^{2+}$:ZnO nanocrystals, Laser Phys. Lett., 2016, accepted for publication.

P33

# Evanescent wave analysis of a multimode chalcogenide fiber embedded into a crude oil

S.V.Korsakova[1], E.A.Romanova[1], V.S.Shiryaev[2], A.A.Pushkin[2], A.P.Velmuzhov[2]
[1]Saratov State University, Saratov, Russia
[2]Institute of Chemistry of High Purity Substances of RAS, Nizhny Novgorod, Russia

The mid-infrared (IR) spectroscopy has the advantages of fast, real-time, *in situ*, selective, nondestructive and safe detection. It has been successfully employed for studies of solid-liquid interfaces, chemical reaction rates, complex material curing, liquid and gas detection and monitoring, biological applications [1].

The mid-IR spectroscopy in the range of wavelengths 3 – 25 μm provides a universal tool for quantitative detection and real-time remote monitoring of molecular species in gaseous or liquid form, because inorganic and organic molecular substances exhibit strong fundamental absorption bands in the mid- IR spectral range.

In this work, we investigate transmission of a multimode fiber made of chalcogenide glass $GeSe_4$ – 5 %I embedded into a crude oil. We have used two kinds of oil. One sample is from a Baltic oilfield and another one is from a Yakut oilfield. Absorption spectra of the oil samples are shown in Fig. 1. For these samples, characteristic absorption bands and corresponding chemical groups have been identified.

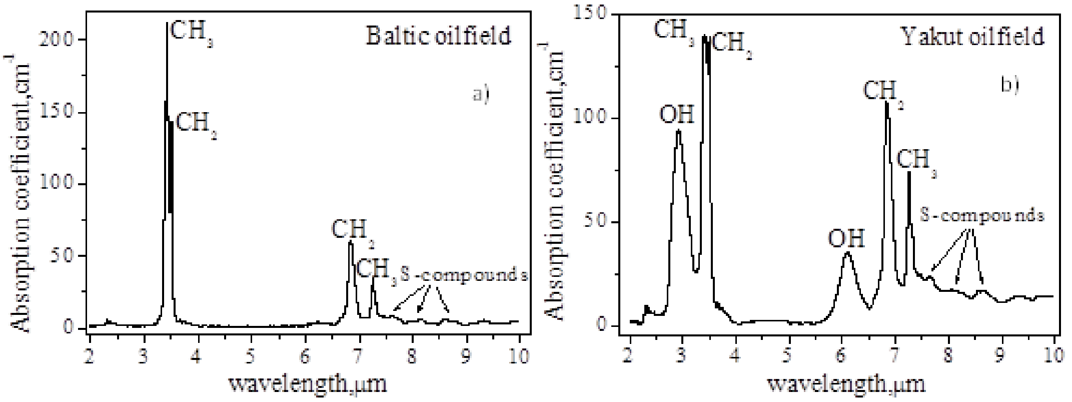


Figure 1.

At first, transmittance $T_0$ of the fiber piece placed into an empty glass was measured. Then some amount of oil was poured into the tube and transmittance $T_1$ was measured. Spectral dependence of $T_1/\ T_0$ has been plotted for each oil sample.

In a numerical model of the mid-IR radiation propagation in the fiber, attenuation coefficients of evanescent waves corresponding to different fiber modes have been calculated. The attenuation coefficients increase with the mode radial order. Output characteristics of the sensor can be optimised by filtering the fiber modes in order to enhance the higher-order modes amplitudes and reduce the lower modes amplitudes.

The total attenuation coefficient for the sum of fiber mode has been evaluated in assumption that the powers of the modes are equal. The attenuation coefficient has been calculated over the entire transmission spectrum and compared with the results of measurements.

This work was supported by the Russian Science Foundation (Russia, Grant No. 16-13-10251).

1. A. Messica, A. Greenstein, and A. Katzir., "Theory of fiber-optic, evanescent-wave spectroscopy and sensors" Applied Optics 35, p. 2274-2284(1996).

P34

# Whispering gallery modes of optical microresonators made of chalcogenide glass

D. S. Zhivotkov, E. A. Romanova
Saratov State University, Saratov, Russia
E-mail: jun_danich_92@mail.ru

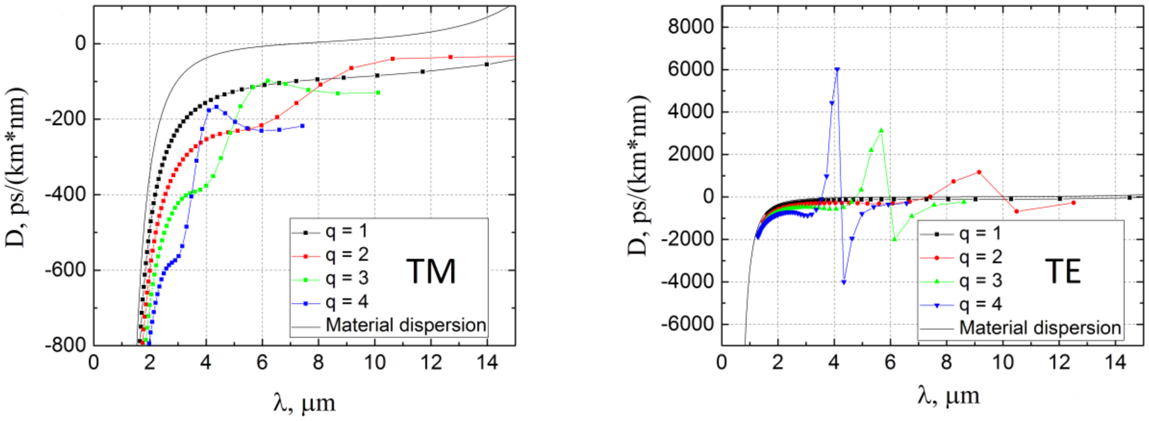
Chalcogenide optical microresonators can be used as functional elements of fiber sensors for the mid-infrared (IR) spectroscopy of liquids and gases. Large optical nonlinearity of chalcogenide glasses is a base for broadband frequency combs generation in the mid-IR spectral range. Kerr constant and group velocity dispersion (GVD) are basic parameters, which govern a spectrum broadening. Geometrical dispersion of the whispering gallery modes of optical microresonators can be used to manage sign and magnitude of GVD.

In this work, we evaluate the GVD coefficients of 2*D* circular microresonators made of $As_2Se_3$ glass by using a model of infinitely long dielectric cylinder. Frequencies of TE and TM modes of such microresonators are not equidistant because of the material dispersion (refractive index of the glass $n = n(\omega)$) and geometrical dispersion of the modes [1].

Resonance frequencies $\nu_l$ of the TE and TM whispering gallery modes of the microresonator with the radius $R$ = 5 μm have been calculated by numerical solution of their characteristic equations with $n(\omega)$ of $As_2Se_3$ given by a Zellmeyer formula. The GVD coefficients have been calculated as [1]:

$$D = \frac{n_l^2}{2pcR} \square \frac{\mathrm{D}(\mathrm{D}n_l)}{(\mathrm{D}n_l)^3} \qquad (1)$$

where *c* is the light velocity in vacuum. Wavelength dependencies of *D* are shown in Fig.1.



a) b)

Figure 1.

We have found that a zero of the total GVD coefficient of a TM mode is located at a greater wavelength than a zero of the material GVD (Fig.1a). The less the microresonator radius, the greater the wavelength of the total GVD zero. Geometrical dispersion of the TE modes has more complicated spectral dependence (Fig. 1b). A unique zero of GVD can be located at greater or less wavelength with respect to the zero of material GVD. A remarkable feature is existence of a range of $D > 0$. Quality factor of the microresonator modes increases with azimuthal order. Modes with high azimuthal orders have giant Q-factors up to $10^{21}$.

1. Pascal Del'Haye, Optical frequency comb generation in monolithic microresonators, Dissertation an der Fakult at fur Physik der Ludwig-Maximilians-Universitat Munchen, 2011.

P35

# Chalcogenide fused fiber couplers development and characterization

O.V. Benderov[2], I.V. Skripachev[1], G.E. Snopatin[1], A.A. Pushkin[1], V.V. Gerasimenko[1], B.S. Stepanov[1]
[1]Institute of Chemistry of High-Purity Substances of RAS, 49 Troponina St., Nizhny Novgorod 603950
[2]Moscow Institute of Physics and Technology, 9 Institutskiy per., Dolgoprudny, Moscow Region, 141700
Corresponding author: oleg.benderov@gmail.com

MIR fiber application is still very limited due to absence of commercially available MIR fiber based devices like couplers, WDM, ring resonators. However, in past few years significant progress in developing of chalcogenide and fluoride fiber based devices has been shown [1]. In this work, theoretical model for chalcogenide fused fiber couplers and experimental setup for its fabrication and characterization are presented. Optimal geometrical parameters for achieving required coupling ratio were studied with computer simulation. A custom workstation with NiCr electric heater to reach temperature of 100 – 350 °C in heated region was developed. Argon atmosphere was used to prevent oxidization on the surface of fused fibers and losses increasing [2]. Chalcogenide fiber tapers were manufactured and their different geometrical parameters characterized (fig 1.). Constant tension was applied on fiber during heating using calibrated load of 3 g. 1.5 um laser emission coupling of several percent was demonstrated with 6/125 um single mode chalcogenide fiber provided by G.G. Devyatykh Institute of Chemistry of High-Purity Substances [3]. Various difficulties of chalcogenide fused fiber couplers manufacturing are discussed.

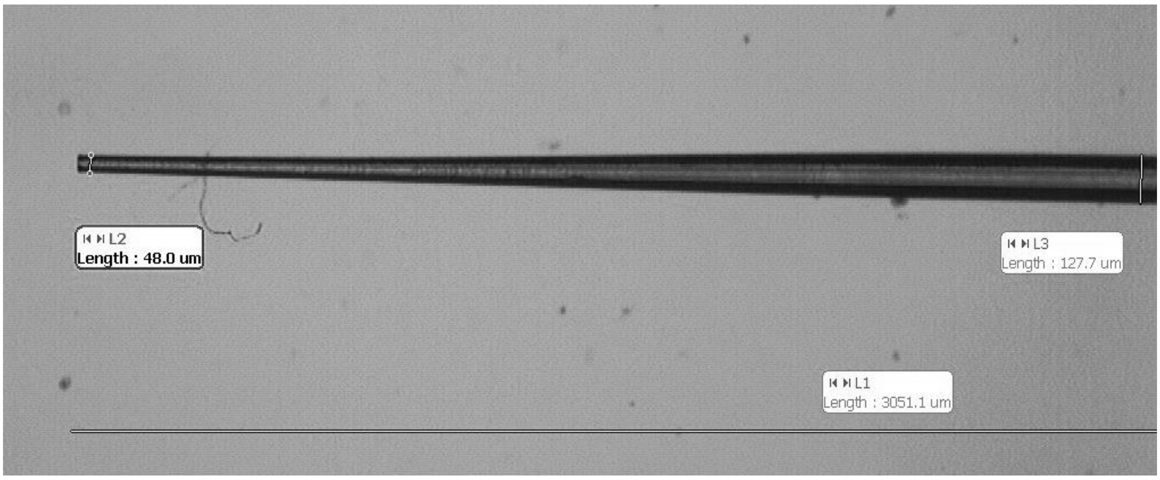


Figure 1. Image of chalcogenide fiber taper with waist diameter of about 50 um.

This research is supported by Russian Science Foundation (RSF), project № 15-12-20040.

1. G. Stevens, T. Woodbridge, SPIE Vol. 9730 973007-1, (2016)
2. D. T. Schaafsma, J. A. Moon, J. S. Sanghera, and I. D. Aggarwal, Jornal of Lightwave Technology, vol. 15, №. 12, (1997)
3. Е.М. Дианов, М.Ф. Чурбанов и др., Неорганические Материалы, том 39, №6, с.741-745, (2003)

P36

# On the possibility of mid-IR supercontinuum generation in dispersion engineered chalcogenide fibers with all-fiber femtosecond pump source

E.A. Anashkina[1,]*, V.S. Shiryaev[2], G.E. Snopatin[2], A.V. Kim[1]
[1]Institute of Applied Physics of the Russian Academy of Sciences, Nizhny Novgorod, Russia
[2]Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, Nizhny Novgorod, Russia
*elena.anashkina@gmail.com

Mid-IR supercontinuum (SC) light has a lot of applications in both fundamental science and industry. The promising way of developing such laser sources is based on using chalcogenide fibers [1]. Due to very large nonlinearity (200-1000 times higher than that for silica), it is possible to obtain mid-IR SC with using standard near-IR femtosecond (fs) lasers even with pulse energies of order tens of pJ [2]. In this case, dispersion engineering is of great importance, because fibers with two (or three) zero dispersion wavelengths (ZDW) allows to extend SC boundary due to red-shifted dispersive wave generation [3]. Even though, ZDW for chalcogenide glasses is typically beyond 4.5 μm, it is possible to develop chalcogenide fibers with anomalous dispersion in the near-IR due to high waveguide contribution. It can be done for microstructured and photonic crystal fibers as well as for all-solid step-index fibers with large index difference between thin core and cladding. Here we study the latter case.

We synthesized high-purity $As_{39.4}Se_{55.3}Te_{5.3}$ glass for core and $As_{39.4}S_{60.6}$ glass for cladding and manufactured low-loss fibers (see Fig. 1(a)). The glass compositions were optimized to obtain large refractive index difference between core and cladding of about $\Delta n = 0.5\text{-}0.7$. It allows obtaining two ZDWs in the range of interest. For fiber optimization, the standard procedure of finding electric and magnetic field components and the propagation constant of the lowest hybrid waveguide modes $HE_{11}$ and $EH_{11}$ as the exact solution of Maxwell's equation for step index fiber profiles was applied. For numerically optimized diameter of 1.8 μm we have obtained three octave-spanning SC generation in the 1-8 μm range. Based on this modeling we have manufactured fibers with core diameters of 1.5-1.8 μm. To simulate fs pulse propagation therein, we solved the unidirectional nonlinear field propagation equation using the split-step Fourier method with taken into account calculated dispersion profile, Kerr and Raman nonlinearities, loss, effective mode area dependence on frequency [4]. Simulated spectral evolution of 50-pJ 150-fs pulses at 2 μm is shown in Fig. 1(b). Such kind of pump pulses can be easily produced with our previously developed hybrid Er/Tm fiber laser system [5]. This result may be useful for the design and development of very simple mid-IR laser system based on step-index chalcogenide fiber and all-fiber fs laser source at 2 μm.

This work was supported by the Russian Science Foundation (Russia, Grant No. 16-13-10251).

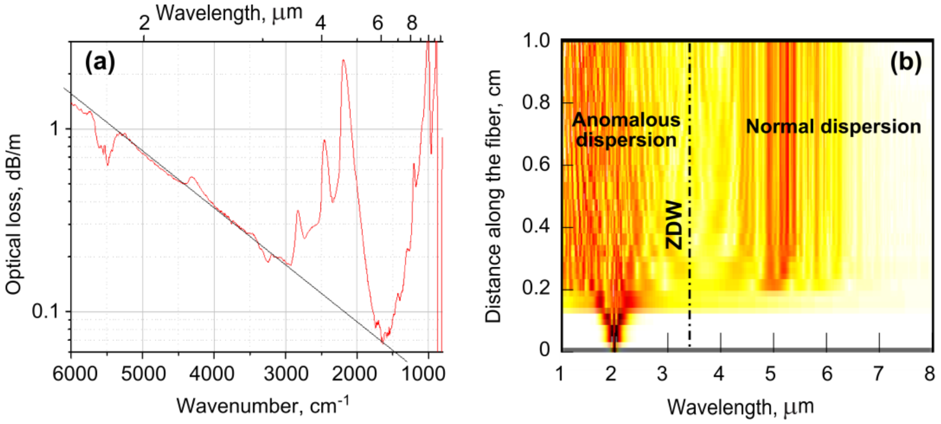


Fig. 1. (a) Measured optical loss in multimode $As_{39.4}Se_{55.3}Te_{5.3}$ core and $As_{38}S_{62}$ cladding fiber. (b) Simulated spectral evolution of 50-pJ 150-fs pulses at 2 μm in the fiber with core diameter of 1.8 μm.

1. C.R. Petersen et.al., Nature Photonics 8, 830 (2014).
2. N. Granzow et.al., Opt. Express 21, 10969 (2013).
3. T. Cheng et.al., Applied Physics Express 9, 022502 (2016).
4. E.A. Anashkina et.al., IEEE Journal of Selected Topics in Quantum Electronics 20, 643 (2014).
5. M.Yu. Koptev et.al., Optics Letters 39, 2008 (2014).

---

# Fractal structure of polycrystalline zinc selenide surface defects

Kolesnikov A.N.
G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences.
49 Troponina St., Nizhny Novgorod 603950
kolesnikov@ihps.nnov.ru

The article [1] reported about developed software to identify the characteristics of the surface of polished zinc selenide optical elements in its series of micro photo, including the number and size of defects, density of scratches, etc.

In the study of large series of specimens received approximately the same conditions, it was observed that photographs taken at various magnifications, similar to each other. This suggests that the distribution of defects on the surface corresponds to some fractal structure, because this structures are self-similarity properties when are studied in different scales.

On the basis of the well-known formula for the calculation of fractal dimension

$$D = \lim_{\varepsilon \to 0} \frac{\ln N}{\ln\left(\frac{1}{\varepsilon}\right)}$$

where $N$ is the number of objects in a certain segment of space, ε – the characteristic size of the object, it was received an equation applicable for this case

$$D = \frac{\ln n + 2\ln U}{\ln U + A}, \qquad A = \frac{\ln n_0 \ln U_1 - \ln n_1 \ln U_0}{\ln\left(\frac{n_1}{n_0}\right) + 2\ln\left(\frac{U_1}{U_0}\right)} \tag{1}$$

where $n$ – number of defects per photo, $U$ – microscope magnification. Indexes 0 and 1 correspond to the supporting image and photos that are used for the calculation of fractal dimension $D$. Calculations made by the formula (1) indicated that the fractal dimension slightly more than 1. This is confirmed by the fractal dimension value obtained for dependencies of the logarithm of the number of objects from the logarithm of their size. They were close to linear for both point defects and scratches. This confirms the fractal nature of the observable structure defects. It was established that fractal dimension in the process of polishing is slightly reduced.

1. Gavrishchuk E.M., Vilkova E.Yu., Kolesnikov A.N., Timofeeva O.V. Investigating the polished surfaces of zinc chalcogenides by computer recognition of defects on micrographs. Journal of Optical Technology. 2010. V. 77. № 1. P. 67-73.

# Author Index

Technopark-Mordovia

# Technopark of the Republic of Mordovia - a driver of development of fiber optic branch of the region

*V.V. Yakuba, General Director of the Autonomous institution «Technopark-Mordovia»*

«Technopark-Mordovia» - the territory of favorable conditions for development and commercialization of innovations where the scientific organizations, educational institutions and manufacturing enterprises are integrated. The main task of the technopark is creation of the developed infrastructure and favorable conditions for implementation of the knowledge-intensive projects in the following fields: fiber optics and optoelectronics, electronic instrument making, nanotechnologies and composite materials, energy saving lighting engineering, information technologies, biotechnologies.

In accordance with Social and Economic Strategy of Russia for the period until 2020 the technopark is directly involved in forming of the new markets of high-technology products and services in the Russian Federation. First of all, it belongs to products of photonics – a scientific and technical industry of the modern high-technology industry connected with use of light radiation in optical elements, devices and systems. In the region was created of an industrial cluster "Fiber Optics and Optoelectronics", which is directed to forming in Russia the market of unique products of photonics in relation to various segments of the market: optical fiber, including special application, laser equipment, solar power, LED-based lighting, equipment for security systems, medical equipment.

Key objects of the created cluster are destined to become the Engineering Center of Fiber Optics (hereinafter referred to as ECFO) and the Design Center of Innovations (hereinafter referred to as DCI) of the Autonomous institution «Technopark-Mordovia». Use of technological capabilities of ECFO and DCI by enterprises of the cluster will allow to create competitive high-technology products and, finally, to carve out their niche of the photonics market.

**The Engineering Center of Fiber Optics** is an interregional technological platform for development of process and manufacturing engineering of special fiber light guides with pre-designed properties for industrial enterprises working in the field of photonics.

While executing the ECFO project it was succeeded to integrate the leading schools of sciences in the field of special fiber, and also to get support of world famous scientists and foreign partners.

Areas of activities of the ECFO:

- carrying out research and development for implementation in mass production of new types of special fiber light guides;
- production of special fiber light guides and devices based on them;
- provision of a manufacturing area for small innovative enterprises;
- training of specialists in the field of production of fiber light guides and optoelectronic devices.

*Fig. 1. Engineering Center of Fiber Optics*

At the present time the technopark together with the leading Russian and foreign centers carry out a number of educational programs for training of process engineers of production of special fiber light guides and optoelectronic devices.

In plans of the technopark - to carry out the training of necessary specialists in the field of photonics based on ECFO. For accomplishment of the objective an active work on creation in the technopark of the following basic departments is carried out: "Fiber-Optic Sensors" (together with ITMO University) and "Advanced Technologies and Engineering" (together with the St. Petersburg State Polytechnic University). Basic departments will form a basis of the Training Center of ECFO where theoretical and practical training of specialists will be carried out.

For the quickest possible implementation of process of development and production of an innovative product the work of the Engineering Center of Fiber Optics will be carried out in close cooperation with the Design Center of Innovations.

**The Design Center of Innovations** is intended to accomplishment of a full range of services from development of mathematical models and drawings of new products of electronic and optoelectronic instrument making, software to production of prototypes products, their testing and certification. In DCI the engineering procedure of prototyping of innovations, at the input of which - result of scientific developments, and at the output - a prototype of a competitive product with wide opportunities for commercialization, is carried out. Structurally the DCI consists of CAD-center, SOFT- center, the Center of Subcontracting and the Scientific and Test Center.

*Fig.2. Design Center of Innovations*

All four centers are interconnected technologically. In the CAD-center on the basis of modern systems of computer modeling and instruments of design automation the drawings of a prototype of an innovative product are developed. Further the project is transferred to the SOFT-center. In the SOFT-center the program systems integrated in the product are developed. At the following stage the project of delivery of nodes and accessories for "screwdriver industries" of a prototype is prepared. These tasks are carried out by the Center of Subcontracting. The final stage of design process of innovations is carried out in the Scientific and Test Center where scientific researches and certification tests of a ready prototype are conducted.

The technology of prototyping carried out in the DCI is an information technology by definition. Computing systems and the software of the CAD-center, the SOFT-center and the Center of Subcontracting are intended to creation of the functional, design and process descriptions of a prototype, and the equipment and the software of laboratories of mechanical, electromagnetic and climatic tests of prototypes of electronic and optoelectronic equipment are necessary for receiving information on their operating characteristics. The basic testing equipment of the DCI is the radio anechoic chamber and TEM-chamber (Transverse Electro-Magnetic), big and medium climatic chambers, vibration stands and benches for stability tests to different kinds of mechanical shocks, the centrifuge for stability tests to the linear accelerations. The equipment allows to combine different types of tests. As a result of production process of the DCI the physical prototype of a product and its digital mockup representing a complex of the electronic documents describing the product, its application and maintenance, are carried out.

Even now in the National Research N.P. Ogarev Mordovia State University the target training of students in the direction of "Program Engineering" is carried out, in the DCI the department of Computer-Aided Design Systems (CAD) of the university is open, an integration of programs of training of experts of the DCI in foreign scientific centers in the directions "Testing and Certification" is conducted.

Technological capabilities of the Engineering Center of Fiber Optics and the Design Center of Innovations offer exciting possibilities for resident companies of the technopark in commercialization of innovations in the field of photonics and in fact put into practice the slogan: Technopark-Mordovia is an infrastructure, competences, brand.

# FORC - Photonics

**LLC "Innovative Enterprise "FORC - Photonics"** was founded in 2005 as an organization specialized in the field of fiber optics. The main profile of society is the development, production, implementation and maintenance of optoelectronic and fiber optic systems for different purposes, using electronic components, microprocessor technology, laser and fiber optics for different sectors of the economy.

Our designers and engineers are collaborating with leading scientific institutions of RAS and Europe. Our own design office deals with development and certification of new types of instruments and equipment on the basis of special optical fiber. Intellectual property of the company has more than 8 patents on the subject of activity.

At the present time the Company is assigned as a project participant in establishment and functioning of "Skolkovo" innovation center. The Company is a participant in the technological platform "Innovative laser, optical and optoelectronic technologies - photonics" and a member of the Russian Laser Association.

LLC IE "FORC-Photonics" conducts work in the framework of the ITER project, the development and implementation of fiber-optic safety control for thermonuclear reactor, from 2008 to the present time.

**The main activities of the company are:**

- **Fiber-optic sensors and devices of their polling** to measure temperature, pressure, displacement, vibration, deformation and other physical quantities.
- **Fiber Bragg gratings (FBG)** as spectrally-selective elements in the systems for measuring physical quantities, in various types of fiber lasers and amplifiers, as well as in fiber-optic communication systems
- **Fiber-optic light sources** as broadband sources of incoherent radiation for measurement of physical quantities, as well as communication systems.
- **Fiber laser systems**. Development and production of continuous wave fiber lasers (wavelength lasing 1.0 ÷ 2.0 μm) on the basis of optical fibers doped with the ions of rare earth elements.
- **Fiber amplifiers** for use in communication systems, as well as **powerful fiber amplifiers**.

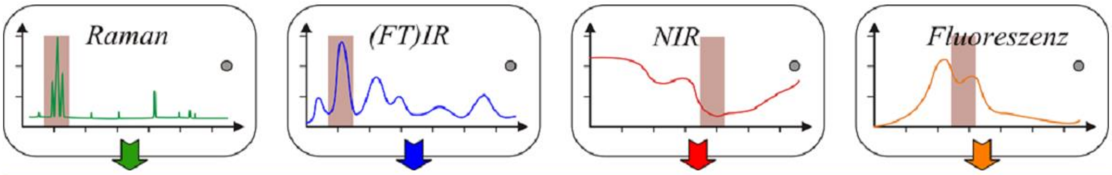
**Contact information:**
**Address: ul. Vavilova, 38, korp. 3, Moscow, 119333, Russia**
**e-mail:** info@forc-photonics.ru
**Sales Department:** sales@forc-photonics.ru
**tel.:** **+7 (495) 589 76 72**
**tel./fax:** **+7 (495) 374 76 34**

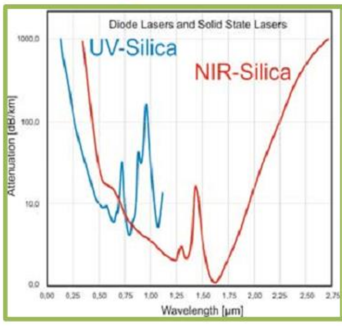
www.forc-photonics.ru

art photonics

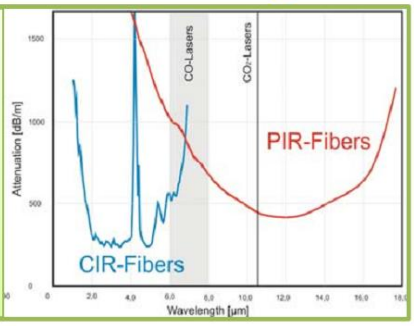
**FlexiSens®**

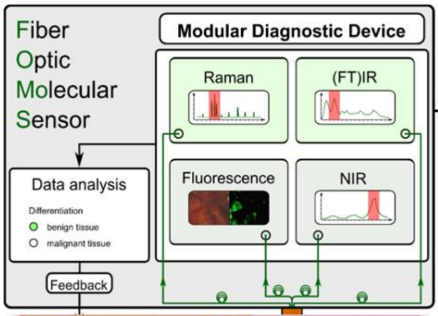
## From Multi-Spectral Fiber Sensing to Fiber Sensors for Process-Control

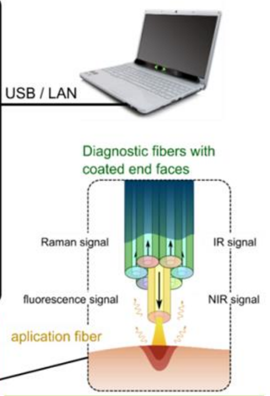




**Combination of different fibers in 0.2-16µm range enable to design multi-spectral fiber probes and to use any spectroscopy method or combine them for remote media analysis and for process control *in-line with* high accuracy**







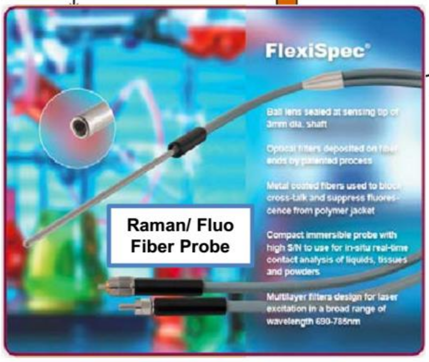
Optimal set of wavelengths to see moisture of media in contact

Customized calibration for high accuracy in fast data acquisition

IP-address to collect data from each sensor by LAN

Trans-Flex or diffuse reflection fiber probes for selected media

### Customized Fiber Sensors



**Raman/ Fluo Fiber Probe**

Ball lens sealed at sensing tip of 3mm dia. shaft

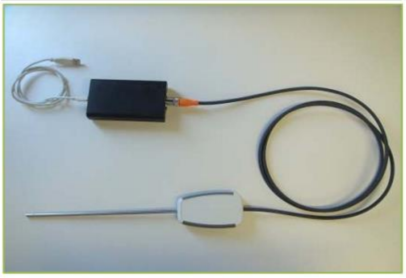
Optical filters deposited on fiber ends by patented process

Metal coated fibers used to block cross-talk and suppress fluorescence from polymer jacket

Compact immersible probe with high S/N to use for in-situ real-time contact analysis of liquids, tissues and powders

Multilayer filters design for laser excitation in a broad range of wavelength 690-785nm

**Combi-probes *may be used for* any method: transmission, ATR-absorption, diffuse reflection, fluorescence, Raman scattering**



**art photonics GmbH**
Rudower Chaussee 46
12489 Berlin Germany

Phone +49 (0)30-677 988 70
sales@artphotonics.com
www.artphotonics.com

QAS Int. - certified
DIN EN ISO 9001:2008
Zertifikat Nr. A1887GER

broad spectra fiber solutions

# FIBER SPECTROSCOPY in broad spectral range - from UV to Mid IR-range

art photonics

**art photonics GmbH** was founded in Berlin in 1998 to develop and produce specialty fiber optics for very broad spectral range – from UV to Mid InfraRed (180nm - 18µm). Today **art photonics** is the world's leading manufacturer of optical fibers, spectroscopy fiber probes & fiber bundles, high power laser cables for industrial and medical applications.

In 2011 **art photonics** launched ***FlexiSpec***® - new family of fiber probes and probe couplers to enable flexible fiber spectroscopy for in-line process-spectroscopyapplications in UV-Vis-NIR and, especially, in Mid IR-range.

***FlexiSpec***® Probes design family enables to measure ATR-absorption, transmission or transflexion spectra, to control diffuse reflection, scattering, fluorescent or multi-spectral analysis – when coupled to any FT-IR, FT-NIR or grating spectrometer; to LED, QCL, MEMS Fabry-Perot, Interference Filter or other spectral sensors, - to be used in-field or in PAT-applications, eliminating the need of time consuming samples collection/ preparation.

***FlexiSpec***® industrial probes of standard 12mm diameter are compatible with process-interfaces required to clean probe optics in contaminating media - in full or semi-automated mode. Probes can comply with ATEX standards when used with SensoGate-FOS or Ceramat-FOS process-interfaces - developed with company KNICK in Berlin. These interfaces allow to retract, clean and calibrate probes during chemical process to secure correct remote analysis of molecular composition for any liquid, gas or solid mixtures under a harsh process conditions.

***FlexiSpec***® industrial probes of 6.3 or 12mm diameters are robust for various applications in a broad temperature range, at very high or low pressure, can withstand vibrations, aggressive or toxic media, while a tiny biomedical probes of small diameter are designed to match demands of biomedical diagnostics and to withstand required sterilization conditions.

**During the APACT 2015 we will demonstrate our new Fiber Probe Coupler – FPC-6M and new Spectral fiber Moisture Sensor.**

FPC-6M provides the highest efficiency coupling of any fiber probe with bench FTIR-spectrometer when it´s installed in its sample chamber. Thus FPC-6M enables to monitor reaction process in-line in lab, while it can be also modified for industrial FTIR to run process-control in with a robust probes terminated with SMA or other customized connectors.

Spectral fiber Moisture Sensor (***MoiSens***) is the 1st product designed for ***FlexiSens***® product line for the task to control moisture in media using its absorption bands in the Near IR-range. ***MoiSens*** concept is based on rapid scan of specific LED wavelengths to illuminate media and collect the signal either in diffuse reflection or transmission mode. Mode selection is defined by media type with correspondent type of fiber probe, while the signals are fast converted by microprocessor in data sent by LAN for remote control.

artphotonics.com

**art photonics GmbH**
Rudower Chaussee 46
12489 Berlin Germany

Phone + 49 (0) 30-6779 887-0
sales@artphotonics.com
www.artphotonics.com

QAS Int. - certified
DIN EN ISO 9001:2008
Zertifikat Nr. A1887GER

ISO 9001
REGISTERED FIRM

# ISNOG 2016

## 20th INTERNATIONAL SYMPOSIUM ON NON-OXIDE AND NEW OPTICAL GLASSES

21-26 of August, 2016 / Nizhny Novgorod, Russia

# Sponsors

Russian Academy of Sciences

RFBR RUSSIAN FOUNDATION FOR BASIC RESEARCH

FORC - Photonics

Technopark-Mordovia

art photonics

ПНППК

Perm Scientific-Industrial Instrument Making Company (PNPPK)