Microcrystallization and
Active Applications of some Novel Glasses

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Passive and Active Applications

Passive applications
Without changing the optical properties, other than that due to scattering, absorption and end face reflection losses, etc.

Active applications:
The initial light propagating being modified by a process. Examples include fiber lasers, amplifiers, all-optical devices, etc.
Passive and Active Applications
14 Schools

- Pharmacy
- Biotechnology
- Chemical Engineering
- Chemistry and Pharmaceuties
- Materials Science and Engineering
- Resources and Environmental Engineering
- Information Science and Engineering
- Mechanical and Power Engineering
- Science (Maths and Physics)
- Culture and Arts
- Foreign Languages
- Philosophy and Politics
- Business and Economics
- Public & Social Administration

3500 employees
1000 professors
15000 undergraduates
4000 graduates

52 B.Sc.
72 M.Sc.
12 Eng. M.
26 Ph. D.
5 Postdoc.
Novel Functional Glasses

**Oxide Glasses**
- Rare earth doped
- ZnO-activated

**Chalcogenide Glasses**
- Micro-crystallization
- IR luminescence
- Non-linearity
- Irradiation induced effects
Oxide Glasses

Rare earth doping for scintillation and white LED
ZnO activating for fast scintillation

Internationally Collaborated with
A good alternative candidate as higher energy irradiation detector for dosimetry system due to:

- A low barrier of information bleaching temperature (<350 °C)
- The higher energy irradiation detection (> 5MGy)
Optical properties of Ce$^{3+}$ doped glasses

Transmitting and emission spectra of Ce$^{3+}$ doped oxide glasses with different optical basicity - the electron donor power of the oxides

• Fast decay time of 20–50 ns suitable for scintillation

• Advantages of glasses: good matrix for rare earths, lower cost, stable properties etc.

• Disadvantages: Non-shielded 5d orbit sensitive to matrix; lower quantum efficiency

Energy levels diagram of Ce$^{3+}$ 4f-5d electrons transitions
Transmittance and emission spectra of Ce$^{3+}$ doped oxide glasses with different alkali content


Enhanced emissions due to energy transfer from Gd$^{3+}$ or partitioning role of La$^{3+}$


Enhanced emissions due to energy transfer from Gd$^{3+}$ or partitioning role of La$^{3+}$
Luminescent Glasses for White LED Lighting

Emission spectra of Dy$^{3+}$ doped (left above), Tb$^{3+}$/Eu co-doped (left below) and Ce$^{3+}$/Tb$^{3+}$/Eu co-doped glasses excited at UV wavelength

*J. Lum.* doi:10.1016/j
Luminescent Glasses for White LED Lighting

![Graph showing intensity vs. wavelength for luminescent glasses.](image)

*J. Lum.* doi:10.1016/j
White-Light-Emitting diodes (W-LEDs)

An important class of lighting devices for replacement of conventional lighting sources of incandescent and fluorescent lamps.

Advantage: long lifetime, lower energy consumption, and environmentally-friendly characteristics.

Glasses: lower production cost, simpler manufacture procedure, free of halo effect, etc, feasible to replace phosphors for W-LED.
Color coordinate diagram of luminescence glasses

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>X</th>
<th>Y</th>
</tr>
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<tbody>
<tr>
<td>SCB-4</td>
<td>0.3731</td>
<td>0.3828</td>
</tr>
<tr>
<td>SCB-5</td>
<td>0.4137</td>
<td>0.3684</td>
</tr>
<tr>
<td>PSB-1</td>
<td>0.4241</td>
<td>0.3578</td>
</tr>
</tbody>
</table>

37CaO-13BaO-40SiO₂-10B₂O₃:0.5Ce,0.25Tb,1.5Eu
37CaO-13BaO-50SiO₂:2Dy
20SrO-15BaO-5B₂O₃-60P₂O₅:1Eu,1Tb

*Color coordinate diagram of luminescence glasses*

[J. Lum. doi:10.1016/j]
Emission spectra of Eu-doped glasses with different B$_2$O$_3$ (above) and different type of alkaline earth oxides

Submit to J. Am. Ceram. Soc.
ZnO-Activated Oxide Glasses for Scintillation

Absorption spectra of glasses with different compositions (left), different ZnO/BaO ratios (middle) and different thermal treating conditions.

J. Am. Ceram. Soc. (accepted)
ZnO-Activated Oxide Glasses for Scintillation
Luminescence \( \text{ZnO} \)

Applications in optoelectronic devices: vacuum fluorescent and field emission displays, blue and ultraviolet emitters and detectors.

Near band-gap excitonic emission from \( \text{ZnO} \) at around 380 nm with the subnanosecond lifetime.

It appears of interest for developing novel superfast scintillating materials with \( \text{ZnO} \) as activator.
Photoluminescence

Emission spectra of glasses annealed at different temperatures (left) and decay curve of glasses with different compositions

Emission spectra (below) and Raman spectra (right) of glasses with and without F⁻ ions

Si-O-Zn → Si-O-Si

*J. Phys. Chem. Solids,* under review
Chalcogenide Glasses (ChG)

- Novel systems for crystallization
- IR luminescence
- Second Harmonic Generation (SHG)
- $\gamma$-irradiation induced effects

Internationally Collaborated with

- ENEA
- Centro Ricerche Casaccia
- UNIVERSITE DE RENNES I
Typical Chemical Elements used in chalcogenide glass

|   | C   | N   | O   | F   | Si  | P   | S   | Cl  | Ge  | As  | Se  | Br  | Sn  | Sb  | Te  | I   | Pb  | Bi  | Po  | At  |
|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|

Se-Ge-As chalcogenide glass systems

Optical transmission spectra of chalcogenide glasses
Sample Preparation

Vacuum Sealing

Sealed Tube

Prepared Samples

Melting in Rocking Furnace

Melting time (hours)

Temperature (°C)

Sample Preparation

Vacuum Sealing

Sealed Tube

Prepared Samples

Melting in Rocking Furnace

Melting time (hours)

Temperature (°C)
Novel Chalcogenide Glass Systems

Novel glass forming regions:
GeSe$_2$-As$_2$S$_3$-CdSe (below),
GeS$_2$-Sb$_2$S$_3$-PbS (right above)
GeSe$_2$-As$_2$Se$_3$-PbSe

Properties of some glasses in the (1-x) (0.85GeS₂+0.15Sb₂S₃)-xPbS Group

<table>
<thead>
<tr>
<th>Sample code</th>
<th>ρ (kg/m³)</th>
<th>Molar Volume (cm³/mol)</th>
<th>Hᵥ (kg/mm²)</th>
<th>Kᵥ (MPa. m¹/²)</th>
<th>Tₔ (°C)</th>
<th>Tᵥ (°C)</th>
<th>ΔT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>3.1299</td>
<td>53.42</td>
<td>185.2</td>
<td>0.2379</td>
<td>336</td>
<td>537</td>
<td>201</td>
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<tr>
<td>P2</td>
<td>3.6110</td>
<td>48.30</td>
<td>184.2</td>
<td>0.2090</td>
<td>312</td>
<td>505</td>
<td>193</td>
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<tr>
<td>P3</td>
<td>3.8481</td>
<td>47.19</td>
<td>166.6</td>
<td>0.1937</td>
<td>293</td>
<td>467</td>
<td>174</td>
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<tr>
<td>P4</td>
<td>4.2197</td>
<td>44.75</td>
<td>169.6</td>
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<td>293</td>
<td>458</td>
<td>165</td>
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<td>P5</td>
<td>4.4352</td>
<td>44.20</td>
<td>169.6</td>
<td>0.1913</td>
<td>295</td>
<td>437</td>
<td>142</td>
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</table>

DSC curves of GeSe₂-As₂Se₃-CdSe chalcogenide glasses


IR transmitting spectra of P5 (51GeS2-9Sb2S3-40PbS) glass

XRD patterns of (a) P5; (b) P5 after annealing at 340°C for 15h; (c) P7 at 300 °C for 5h; (d) P5 at 310 °C for 85h; (e) P6 at 330 °C for 12h

Thermal Expansion Coefficient (µm/m °C)

Fracture Toughness

Annealing Duration (h)

- Fracture Toughness
- Thermal Expansion
SEM Observations:
(a) P9 at 330°C for 163h,
(b) P7 at 300°C for 5h,
(c) P5 at 340°C for 15h,
(d) P5 at 310°C for 15h,
(e) P5 at 310°C for 32h
(f) P5 at 310°C for 85h
Transmission spectra and XRD patterns of sample 40GeSe$_2$-50As$_2$Se$_3$-10PbSe after different thermal treatments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Base</th>
<th>GC1</th>
<th>GC2</th>
<th>GC3</th>
<th>GC4</th>
<th>GC5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$((\mu\text{m}/\text{m.}^\circ\text{C}))</td>
<td>12.93</td>
<td>12.13</td>
<td>11.94</td>
<td>11.7</td>
<td>9.41</td>
<td>8.79</td>
</tr>
</tbody>
</table>

Submit to J. Am. Ceram. Soc.
SEM observations of sample annealed: (left) 230°C, 20h; (right above) 250°C, 10h; (right below) 270°C, 10h;
IR Luminescence

Average Coordination Number (ACN) >2.67 \( \tau = 440-530 \, \mu s \)

Transmission and emission spectra of Dy\(^{3+}\) doped Ge-Ga-Se glasses

Transmission and emission spectra of Dy\(^{3+}\) doped Ge-Ga-Se glasses

Transmission (%)

Wavelength (nm)

Intensity / a.u.

Wavelength / nm

Background

Amplifying Fiber

Fiber

Distributor

Coupler

isolator

Detector

Pump LD

Control board

Power

Incoming signal

Outgoing signal
Energy Levels of Dy$^{3+}$

1850 cm$^{-1}$

2.86 µm  1.75 µm

1.34 µm

4.38 µm
Transmission and emission spectra of Dy\textsuperscript{3+} doped Ge-Ga-As-Se chalcogenide glasses

Absorption (a) and luminescence (b) spectra of Bi doped GeS$_2$-Ga$_2$S$_3$-KBr chalcohalide glasses at 900°C and 930 °C

*Appl. Phys. Lett.* (under review)
Absorption (a) and luminescence (b) spectra of Bi/Dy co-doped GeS$_2$-Ga$_2$S$_3$-KBr chalcohalide glasses at different temperatures

\[ \text{Bi} \rightarrow \text{Bi}^{++} + \text{Bi}^{2+} \rightarrow \text{Bi}^{3+} \]

*Chem. Mater.* (under review)
Absorption (a) and luminescence (b) spectra of Bi/Dy co-doped GeS$_2$-Ga$_2$S$_3$-KBr chalcohalide glasses at different temperatures
Diagram of modified thermal poling technique (below) for SHG measurement (Maker fringe pattern) of chalcohalide glasses with the higher content of alkali ions

\[ n^{(2)} = 7.0 \text{ pm/V} \]
Optical transmission changes ($\Delta T$)(below) and maximum $\Delta T$ versus the absorbed dose for glass sample 30Ge10As60Se

$\Delta T$ value versus absorbed dose for glass sample 30Ge10As60Se

NIMB, 234(2005) 523-530

SEM observations of glass samples 42As58S (a, b) and 24Ge12As64Se(c, d) before and after irradiation (3.6MGy).

Raman spectra for glasses (1) 30Ge5Ga65Se (3.6MGy), (2) 35Ge5As60Se (14KGy), (3) 40As60S (3.6MGy).

Thank You