Engineering Novel Materials for Infrared Photonics

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When we think of glass......

Courtesy of: National Geographic, J. Jones – Imperial College and MoSci Corp.
When we think of *infrared* glass....

Ref: D. Hewak, ACerS Bulletin, Umicore Corp., and IRradiance Glass
FUTURE OPTICAL SYSTEMS → MULTI-FUNCTIONAL MATERIALS and the PROCESSING required for their INTEGRATION – our TOOLBOX

Material Chemistry spectral range of use

Environmental stability

Design

Material/device rad-hard stability

Form-specific property variation

Next generation products

Next generation production methods

Material integration know-how

Scale-up compatibility

Novel fabrication strategies

Multi-material mismatch
Infrared materials – design options

For IR applications, there are far fewer total materials (glass + crystals) than available for visible systems (oxide glasses, polymers or crystals)

1 – Semiconductors (Si, Ge)
2 – Chalcogenides
3 – II-VI crystals (ZnSe, ZnS)
4 – Flourides, Tellurides

(6) commercially available ‘flavors’ of chalcogenide glass (ChG)

From N. Carlie, SCHOTT
Chalcogenide glasses (ChGs):

- Amorphous compounds of chalcogens (S, Se and Te) covalently bonded to other elements
- \( \text{As}_2\text{S}_3, \text{As}_2\text{Se}_3, \text{GeSbS}, \text{GaLaS}, \text{GeSbTe} \) (phase change)
- **Oxygen–free** for good infrared transmission
Optical designers must have complete spectral information on new materials for inclusion in next-generation optical designs.

In the infrared (IR), this includes:
- **thermo-optic** properties which dictate how systems can be designed to be “athermal”
- **thermo-mechanical** properties which define how to FABRICATE and COAT

Compatibility with well established crystalline design candidates is essential.

_J.M. Hoffman, W.L. Wolfe, Cryogenic refractive indices of ZnSe, Ge, and Si at 10.6 μm, Appl. Opt. 30 (1991) 4014-4016._
Engineering ChG chemistry for key property optimization

Compositionally tunable optical nanocomposites: MWIR/LWIR glass and glass ceramic

Compositional tuning of multicomponent chalcogenides increases the number of glasses available for optical designers

*M-GRIN: Innovative Design and Manufacturing of Gradient-Index-Based Transformation Optics Components*
T. Mayer, D. Werner, C. Rivero-Baleine, K. Richardson, Research grant # 4970-UCF-AFRL-7225
ChG GRIN Physical Properties: GAP-Se

<table>
<thead>
<tr>
<th>Property</th>
<th>As$_2$Se$_3^*$</th>
<th>GRIN</th>
<th>GRIN + thermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission Window (µm)</td>
<td>1.0-12</td>
<td>1.1-16</td>
<td>2.0-16</td>
</tr>
<tr>
<td>Refractive Index (at 4 µm)</td>
<td>2.7946</td>
<td>2.9565</td>
<td>3.2968</td>
</tr>
<tr>
<td>dn/dT (x 10^-6 °C^-1) (at λ, µm)</td>
<td>36.1-32.7</td>
<td>47 (3.39)</td>
<td>--</td>
</tr>
<tr>
<td>Glass transition temperature, Tg (°C)</td>
<td>185</td>
<td>189</td>
<td>189</td>
</tr>
<tr>
<td>Softening point, (°C)</td>
<td>--</td>
<td>213</td>
<td>--</td>
</tr>
<tr>
<td>Crystallization Temp, T_x, (°C)</td>
<td>--</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>Upper Use temperature (°C)</td>
<td>--</td>
<td>162</td>
<td>163</td>
</tr>
<tr>
<td>Dispersion value (3-5 µm)</td>
<td>--</td>
<td>69</td>
<td>41</td>
</tr>
<tr>
<td>Thermal expansion (ppm/°C)</td>
<td>20.8</td>
<td>18.82</td>
<td>19.31</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>4.63</td>
<td>5.5677</td>
<td>5.5394</td>
</tr>
<tr>
<td>Micro-hardness (GPa)</td>
<td>1.04</td>
<td>1.657</td>
<td>1.785</td>
</tr>
</tbody>
</table>

*from: SCHOTT IR Materials data sheets – IRG 26 (May 2013)

Engineered chemistry and morphology enables novel optical materials with manufacturability comparable to existing deployed materials.
ChG films for enhanced PV light capture

Low-Symmetry Grating (LSG) design

LSG design achieves 2-fold enhancement compared to the Lambertian limit

Solution-derived chalcogenide glass (ChGs) films/gratings offer integration flexibility compatible with other additive methods

70 µm bifacial Si device performance

<table>
<thead>
<tr>
<th></th>
<th>VOC (mV)</th>
<th>J_sc (mA/cm²)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top illumination</td>
<td>690</td>
<td>26.2</td>
<td>65.3</td>
<td>11.8</td>
</tr>
<tr>
<td>Bottom illumination</td>
<td>690</td>
<td>27.1</td>
<td>65.9</td>
<td>12.3</td>
</tr>
</tbody>
</table>

ChG-GRIN: Motivation

• Need for new materials to support advances in SWIR/MWIR/LWIR optical system applications
  ✓ Crystalline materials available (Si and Ge); chalcogenide glasses – ChG and heavy metal oxides (HMOs)
  ✓ Well-characterized chemistry/structure/property know-how needed
    - input for optical designers (absorption, refractive index, dispersion, thermo-optic properties, nonlinear optical behavior)
  ✓ Component/device manufacturing compatibility or flexibility
    - bulk, thin film and fiber-based materials
    - focus on SWaP: size, weight and power
  ✓ MGRIN - Low loss, manufacturable mid-infrared glass and glass ceramic materials with tailored and graded refractive indices
Our M-GRIN solution uses a multicomponent chalcogenide nanocrystal composite material.

Develop compositionally agile, highly transmissive ChG-based material system with extraordinary $\Delta n \geq 0.5$ throughout the infrared spectral range.

Controlled nucleation and growth of monosized nanocrystals within a ChG glass matrix to form tailorable GRIN profiles in both the radial and axial directions.
Multicomponent ChG Nanocomposite GRIN System

Key attributes for MWIR glass ceramic (GC) nanocomposite GRIN elements:

✓ All phases (glass and crystal) have **low MWIR absorption loss**

✓ Nanocrystals ($n_{\text{crystal}}$) have **high refractive index** relative to base glass ($n_{\text{glass}}$)

✓ **Low scatter loss** with sub-100 nm diameter crystals

✓ Nanocrystal-to-glass filling fraction ($V_{\text{crystal}} : V_{\text{glass}}$) is **tailorable** knowing nucleation (I) and growth (U) rates of desired crystal phase(s)

**TARGET:** ($n_{\text{eff:GC}}$) - ($n_{\text{glass}}$) = $\Delta n_{\text{max}} > 0.1$
Chalcogenide Glass GRIN System

MWIR transparent glass with tailorable refractive index

Large 400g melts have uniform optical properties

Refractive index of base glass can be tuned by varying composition.

MWIR transparent glass with tailorable refractive index
Controlled crystallization (nucleation and growth) is required to precipitate high index crystal phase with mono-size distribution within a low index glass matrix.

Glass’ unique thermal analysis signature yields distinct, composition-specific nucleation (I) and growth (U) rate curves.
Thermally Driven High-Index Nanocrystal Formation

Melt: GAP-Se base ChG glass

Anneal: stress relieved

Nucleation: phase separation → number density of crystals defined

Growth: nanocrystals formed → volume fraction defined

Thermal processing results in controlled phase separation and growth of high-index nanocrystals within multicomponent ChG glass
Using I-U curve for thermal GRIN

1D Thermal-Thermal Gradient

A 5-cm long GAP-Se rod was thermally treated (nucleated) and then placed in a gradient furnace with a linear (growth) temperature profile that varied from 225°C to 260°C ($n_{glass} = 2.7946$ @ 4µm)

1D GRIN profile with $\Delta n \sim 0.17$ introduced by enforcing a 1D thermal gradient across a 5 cm long GAP-Se rod; infrared index and dispersion quantified with morphology

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda$ = 3 µm</th>
<th>$\lambda$ = 4 µm</th>
<th>$\lambda$ = 5 µm</th>
<th>Abbe number</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-3</td>
<td>2.83</td>
<td>2.81</td>
<td>2.81</td>
<td>103.7</td>
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<tr>
<td>2-6</td>
<td>2.90</td>
<td>2.89</td>
<td>2.88</td>
<td>99.8</td>
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<tr>
<td>2-8</td>
<td>2.95</td>
<td>2.94</td>
<td>2.93</td>
<td>115.6</td>
</tr>
<tr>
<td>2-10</td>
<td>2.99</td>
<td>2.98</td>
<td>2.98</td>
<td>129.4</td>
</tr>
</tbody>
</table>
Process to Create Spatially-Controlled GRIN Profile

*Controlled* crystallization (nucleation and growth) is required to precipitate high index crystal phase with mono-size distribution within a low index glass matrix

1. Spatially varying laser exposure - **nucleation**

   - Laser exposure is used to locally engineer $n_{\text{eff}}$ by controlling the spatially defined concentration of nuclei and high-index nanocrystals

2. Thermal treatment – **growth**

   - $n_{\text{eff}} \sim (n_{\text{glass}} \times V_{\text{glass}}) + (n_{\text{crystal}} \times V_{\text{crystal}})$
TEM on base glass and \textit{laser irradiated} bulk samples - \textit{bright field microscopy}

- Initial base glass has nanoscale phase separation $\rightarrow$ low stability phase
- 1064 nm laser exposure on bulk glass imparts optical absorption, leading to \textit{laser-thermal crystal nucleation}; post processed with furnace growth

\begin{itemize}
  \item \textbf{Control}
  \begin{itemize}
    \item BASE GLASS
      \begin{itemize}
        \item Phase separation represented by dark (Pb-rich) matrix and bright (Pb-deficient) droplet regions (100 nm)
      \end{itemize}
  \end{itemize}

  \begin{itemize}
    \item \textbf{Laser Exposed}
      \begin{itemize}
        \item Phase Separation represented by dark and bright regions (100 nm)
        \item Size of each phase-separated region $\sim$ 50 nm (20 nm)
        \item The fringed dark Pb-rich crystalline phase; Bright region: Pb-deficient glass matrix (5 nm)
        \item Spotty patterns (crystalline) + a diffuse ring (amorphous)
      \end{itemize}
  \end{itemize}
\end{itemize}
XEDS can chemically assess phase separation and species segregation - **dark field**

- Pb atoms are segregated by melt/quench protocol into Pb-deficient droplets.
- Pb distribution matches well with the **dark region** in the BASE TEM image.
- Laser-induced Pb segregation is maintained during laser irradiation.
- Pb-rich matrix regions subsequently (preferentially) crystallize with further thermal treatment.
MWIR Color-Corrected Afocal Telescope Design

GOAL: SWaP reduction

EXAMPLE: 2 Ge-Si doublets = 4 elements

High density crystalline optics

Can we reduce the number of elements and their weight by converting system to GRIN-based glass/glass ceramic using known processing parameters and material inputs?
The Si-GRIN spherical singlet design provides a thickness reduction of 3:1 and a weight reduction of 2.5:1 over the traditional Ge/Si aspheric doublet design.
Layered GRIN films on homogeneous bulk MWIR Glass

Cross-section of GRIN layer on CTE-matched MWIR glass component (*Class 4 – IRG*)

Homogeneous post-deposition thermal processing introduces uniform distribution of high-index nanocrystals giving a maximum index change of $\Delta n_{\text{eff}} \sim 0.2$
Index Change versus laser irradiance and fluence

Treatment Details:
- 1.4 μm GAP-Se films with SiO$_x$ AR layer on fused silica substrate
- Constant 190°C for 30 min thermal treatment
- Higher index changes are expected with higher fluence exposures

Identified laser exposure and thermal treatment conditions that give controlled and reproducible index change
Index change versus thermal treatment time below 45 mins, and then saturates → defines process window

Index Change at 4 μm

Time (min)

Treatment Details:
- 1.4 μm GAP-Se films with SiOₓ AR layer on fused silica substrate
- Sequential thermal treatment at constant 190°C for 30 min
Layered GRIN films on homogeneous bulk MWIR Glass

- Laser exposure induces controlled phase separation in amorphous film
- Thermal treatment creates sub-60 nm high-index nanocrystals
- Nanocrystal concentration varies with laser exposure and post-exposure thermal treatment conditions → spatial control of dose yields spatial GRIN
- Knowing laser + HT process window, what is the spatial resolution of the GRIN?
Laser Exposure through Grating Mask

Top view
- Metal pattern
  - Width: 1.02 µm
  - Thickness: 185 nm
- Layer surface
  - Width: 2.45 µm

Cross-sectional view
- i beam-deposited C
- e beam-deposited C
- metal pattern
- layer
- SiO_x AR layer
- fused silica substrate
Laser Exposure through Grating Mask

Following *laser exposure only*:

- 1.4 μm layers with SiO$_x$ AR layer on fused silica substrate
- Benchmark fluence prior to thermal treatment
- Microstructure in exposed areas are consistent with broad area experiments, while unexposed areas remain unchanged
- High spatial resolution of < 100 nm

High spatial resolution indicates a photonic driven laser-induced phase separation process with superb *spatial control of nucleated microstructure*
Heat treatment yields uniform nanocrystal formation throughout the thickness of the deposited layer – fill fraction variation yields $\Delta n_z$ in glass below transparent regions of the mask.
GPCL team’s awareness of chemistry-structure-property relationships in (infrared) glass and glass ceramic media yield:

✓ Novel materials with *engineered* properties

✓ New knowledge in the link between *material processing and device integration* → allows creation of new optical functions suitable for existing and next-generation component and system solutions

INTERDISCIPLINARITY IS KEY: Glass science, optical design, manufacturing and metrology know-how is required to ensure materials exhibit desired optical properties *WITH* environmentally-robust performance
Thank you

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