Preparation, Properties and Applications of Chalcogenide Glasses

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My Research Work

- Non-oxide glasses: chalcogenide and chalcohalide glasses, their IR optical properties;
- Oxide glasses: scintillating glasses, luminescence glasses for LED lighting, quantum cutting effects;
- Radiation induced effects on glasses etc..

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References

1. A. Feltz, Amorphous Inorganic Materials and Glasses, VCH, 1993
2. W. Vogel, Glass Chemistry, Springer-Verlag, 1992
Outline

- Generality
- Preparation
- Structure and properties
- Thermal treatment
- Main applications in passive and active infrared optics
1. Generality

The chalcogenide glasses (ChG)

- Named after the chalcogen elements including sulfur, selenium and tellurium.
- To be combined with various others, such as germanium and arsenic, to form stable glasses.
Element Periodic Table
Tracing Back

1870’s  As$_2$S$_3$ glass formed
1950’s  ChG discovered as semiconductor
1960’s  ChG used as IR transmitting materials (passive applications)
1990’s  Active applications - interest for IR photonic technologies
Passive Optics

The passive applications utilize chalcogenide fibers as a light conduit from one location to another without changing the optical properties.

Active applications of chalcogenide glass fibers are where the initial light propagating through the fiber is modified by a process.

2. Preparation

Vacuum sealing (10^{-3} \text{ Pa})

Melting process

Quartz glass ampoule with batch

Rocking furnace
Purification

Purification in order to remove impurities containing O, H and C

- Etching ampoule in hydrofluoric acid
- Distillations by heating the batch components in situ under vacuum
- Addition of oxygen getter for examples, Zr, Al, Mg, Ca, Gd)
IR transmission spectra of As-Ge-Se-Te system glass under different purification conditions

1 Unpurified
2 Se purified
3 As, Se purified
4 As, Se, Te purified
5 Glass (3) distillated
6 Glass (4) distillated

# Purification virus $O_2$ content

<table>
<thead>
<tr>
<th>Purification conditions</th>
<th>Abs. coefficient $\alpha$ (cm$^{-1}$ at 10.6 $\mu$m)</th>
<th>Estimated $O_2$ content (ppm wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge-As-Se system</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Unpurified</td>
<td>0.2030</td>
<td>144.2</td>
</tr>
<tr>
<td>2 As, Se purified</td>
<td>0.0991</td>
<td>3.1</td>
</tr>
<tr>
<td>3 Glass distillated</td>
<td>0.0454</td>
<td>1.3</td>
</tr>
<tr>
<td>Ge-As-Se-Te system</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Unpurified</td>
<td>0.1814</td>
<td>103.4</td>
</tr>
<tr>
<td>2 Se purified</td>
<td>0.1160</td>
<td>66.7</td>
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<tr>
<td>3 As, Se purified</td>
<td>0.0893</td>
<td>17.4</td>
</tr>
<tr>
<td>4 As, Se, Te purified</td>
<td>0.0308</td>
<td>5.6</td>
</tr>
<tr>
<td>5 Glass (3) distillated</td>
<td>0.0209</td>
<td>0.8</td>
</tr>
<tr>
<td>6 Glass (4) distillated</td>
<td>0.0071</td>
<td>0.6</td>
</tr>
</tbody>
</table>
3 Thermal Treatment

- Shortcoming of ChG: weak bond strength

\[ \nu = 2\pi \sqrt{\frac{\kappa}{\mu}} \]

\[ \nu = \text{vibration frequency} \]
\[ \kappa = \text{force constant} \]
\[ \mu = \text{reduced mass of the vibrating ions} \]
\[ (\mu = m_cm_o/(m_c+m_o)) \]
Controlled crystallization

Key points:

• Glass composition

• Thermal treatment conditions
An example of the glass forming region of the novel Ge$_2$S$_2$-Sb$_2$S$_3$-PbS system.

Crystallization ability

- VSG region where glasses with larger $\Delta T (> 170^\circ C, T_c - T_g$), or no exothermal peak in DSC unable crystallized even for long time (>100 h) heating.

- Glasses near the border of glass forming region not thermally stable and tended to crystallize but very difficult to control crystal growth thus affecting IR transmission of materials.
Controlled crystallization

- Compositions suitable for controlled crystallization fall into dark shadow area which is classified as sub-stable glasses (SSG) region.

- With these glasses under proper annealing conditions, IR transmitting glass ceramics with improved properties can be obtained.
SEM results

(a) P9 at 330°C for 163 h,
(b) P7 at 300°C for 5 h,
(c) P5 at 340°C for 15 h,
(d) P5 at 310°C for 15 h,
(e) P5 at 310°C for 32 h,
(f) P5 at 310°C for 85 h.

P5: 51GeS$_2$-9Sb$_2$S$_3$-40PbS
P7: 30GeS$_2$-35Sb$_2$S$_3$-35PbS
P9: 55GeS$_2$-30Sb$_2$S$_3$-15PbS

Crystal size: < 100 nm
IR transmittance

IR transmission of glass-ceramic beyond 2µm is nearly the same as the glass matrix.
Resistance to fracture

Glass-ceramics derived from SSG possess higher fracture toughness and lower thermal expansion coefficients.
Controlled crystallization of \( \text{GeSe}_2-\text{Ga}_2\text{Se}_3-\text{CsI} \) ChGs during molding: (left) IR transmission spectra; (right) Resistance to crack propagation of (a) the base glass and (b) glass-ceramic

4 Structure and Properties

A comparison of glassy-like $A_2B_3$ structure with crystalline one after Zachariasen

Crystalline

Glassy

Feature of glass network:
Short-range in order, long-range disorder
ChG: Structural models

ChG can be classified by reference to dimensionality

- 1D spaghetti-type, such as Se glass made of infinite chains

- 2D distorted planar glasses such as As$_2$S$_3$ made from connections of 2 coordinated S atoms and 3 coordinated As atoms

- 3D glasses, such as GeSe$_2$ being result of GeSe$_4$ tetrahedra connections
Properties

Different from oxide glasses

• Narrower bandgap (1-3 eV)
  – semi-conducting

• Lower phonon energy (<350 cm\(^{-1}\))
  – IR transmittance

• Photo-induced effects
**Optical transmission**

Absorption due to electronic transitions between VB and CB

**Absorption of light due to vibration modes between atoms:**
- **Silica:** $\text{Si–O} : 1100 \text{ cm}^{-1}$
- **Fluorozirconates:** $\text{Zr–F} : 580 \text{ cm}^{-1}$
- **Sulphides:** $\text{Ge–S} : 350 \text{ cm}^{-1}$
- **Selenides, Tellurides:** $< 300 \text{ cm}^{-1}$
An example

Evolution of the bandgap energy for GeSe$_2$-Ga$_2$Se$_3$-CsCl glasses with 0, 10, 20, 30, and 40 mol% CsCl.

Grains homogeneous (ca. 100 nm) with uninfluenced FIR transmittance and the same $\alpha$, and almost doubled toughness from 0.227 to 0.425.
Tellurium based glasses have excellent transmission in 3-20 μm. Especially, Ge-As-Te system exhibits the best stability, more amenable for larger scale production.

Photo-induced (PI) effects

- PI dissolution (doping)
- PI refractive index (RI) change
- PI phase change
- PI bandgap energy change (darkening or bleaching)
- PI contraction
- .......
Changes of RIs of GeGaS (a) and GeGaS-AgI (b) before and after laser exposing. The red curves are obtained 24 h and 2 h later after the laser exposing

$\Delta n > 6\%$


Schema of photo-induced phase change material $\text{KSB}_5\text{S}_8$
Variation of absorption coefficient ($\Delta \alpha$) vs. Ge content in Ge$_x$As$_{45-x}$Se$_{55}$ system

Effect of intensity on PI volume change in GeAsSe$_{13}$ glass. The annealed glass (black) shows PE, the quenched (red) PC. For large intensity, the latter eventually expands.

Main applications

- Passive optics
  - Laser transmission
  - Thermal imaging
- Active optics
  - Non-linear optics
  - IR amplifier
Laser power delivery

(a) CO laser transmission, (b) CO$_2$ laser transmission and (c) pulsed high energy laser transmission in the 2-5 μm region (±0.01 mW)

Thermal imaging

- Silica
- Fluorides
- Chalcogenides

Transmission (%)

Wavelength (µm)

- Vis
- Telecom (1.55 µm)

- Transparency of atmosphere
- Maximum emission of black bodies at RT

IR optics for thermal imaging
Advantage of ChG

- Lower cost production by moulding compared with single-point diamond turning process for crystalline materials, e.g. Ge
New 2006 BMW Series equipped with IR night-vision system with molded chalcogenide glass optics
Crystal size: ~ 10 nm

IR transmission of GCs compared with \( \text{Ga}_5\text{Sb}_{10}\text{Ge}_{25}\text{Se}_{60} \) glass

Molded lens

A molded GC lens (D=30 mm)

Molding precision: form defect of molded lenses by comparing the designed profile and the measured profile of the lens is < 0.5 μm.
Amplifier for telecommunication

A close look at the amplifying application
Matrix material is a key

Comparison of emission spectra between Ge-Ga-S glass and oxide glass doped with Pr$^{3+}$ ions

Pr$^{3+}$1.32 μm emission
**Multiphonon relaxations (MPR)**

- **Total probability of de-excitation:**
  \[ W_{\text{tot}} = W_{\text{rad}} + W_{\text{MP}} + W_{\text{ET}} + \ldots \]

  Radiative  Multiphonon  Energy Transfer

- **Quantum efficiency:**
  \[ \eta = \frac{W_{\text{rad}}}{W_{\text{rad}} + W_{\text{MP}} + W_{\text{ET}}} \]

  \[ W_{\text{MP}} \uparrow \text{ with } \uparrow \text{phonon energy of the host} \]

  \[ W_{\text{mp}} \downarrow 1/1000 \]

  Higher quantum efficiency in chalcogenide glasses
Emission Spectra of Ge-Ga-S (dashed) and Ge-Ga-S-CsBr glasses doped with Dy$^{3+}$ ions

Addition of CsBr resulted in a new low-phonon band at 245 cm\(^{-1}\), associated with the Ga–Br bonds vibration, a major phonon mode determining the MPR process.
Broad NIR emission from Er$^{3+}$-Tm$^{3+}$ co-doped 70GeS$_2$-20In$_2$S$_3$-10CsI glasses

Emission spectra of Bi-Dy co-doped 70GeS$_2$-9.5Ga$_2$S$_3$-20KBr chalcohalide glasses melted at the different temperature

Shanghai Institute of Optics and Fine Mechanics, China
Zhejiang University, China

Emission spectra of Bi-doped 80GeS$_2$-20Ga$_2$S$_3$ chalcogenide glasses

FWHM ~ 200 nm

All-optical device (AOD)

All-optical dual core coupler (A) setup, (B) schematic dual core SiO₂ fiber, (C) two single-mode cores as waveguides.

Intensity of incoming light controls coupling from one core to the other.
Optical nonlinearity

Plot of $n_2$ versus the term containing the normalized photon energy

With the higher susceptibility $\chi^{(3)}$ and SHG $\chi^{(2)}$, ChG photonic chips allow all-optical signal processing.

MF patterns of thermal poled Ge-Sb-S samples recorded for three temperatures: (a) 170°C and (b) 230°C (full line) and 310°C (dashed lines)

$n^{(2)} = 8.0 \text{ pm/V}$

A Maker fringe of 60GeS$_2$-20Ga$_2$S$_3$-20KBr glass with higher alkali content after thermal poling

$n^{(2)} = 7.0$ pm/V

Maker fringe patterns of the $\beta$-GeS$_2$ crystallized glasses without poling treatment

$n^{(2)} = 5.36$-$7.3$ pm/V

XRD and Raman spectra
Fudan University, China
ECUST, China


$\chi^3 = 10.07 \times 10^{12}$ esu

Optical Kerr Effect
Signal of GeSe$_2$-In$_2$Se$_3$-CsI glasses
Raman spectra

[GeSe₄] at 200 cm⁻¹ and [InSe₄] at 154 cm⁻¹ are the main structural units while the increasing CsI does not cause clear structural
Fudan University, China
ECUST, China

Optical Kerr Effect Signal of As$_2$S$_3$ glass before and after laser radiation

Laser radiation induced enhancement of $\chi^3$ on As$_2$S$_3$ glass

Summary

- Purification is an important procedure for synthesis of high purity ChGs.

- Controlled crystallization is an effective way to improve mechanical and thermal properties of ChGs.

- Different from oxide glasses, ChGs have narrower bandgap, lower phonon energy, and are photosensitive.

- ChGs are potential for applications in active optics due to unique IR optical properties.
Thank You for Your Attention