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Lecture 6, Part 1: Preparation, properties and applications of chalcogenide glasses

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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.
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 Pa)

**Melting process**

**Rocking furnace**

**Quartz glass ampoule with batch**

Temperature (°C) vs. Melting time (hours) graph

- Seal
- Raw Materials
- Cold Part
- N₂ Liquid
- Pump

Diagram of a vacuum sealing process with a rocking furnace and a quartz glass ampoule with batch.
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>
</tr>
<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

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

- \( v \) = vibration frequency
- \( \kappa \) = force constant
- \( \mu \) = reduced mass of the vibrating ions
  
  \( (\mu = m_c m_o/(m_c + m_o)) \)
Controlled crystallization

Key points:

• Glass composition
• Thermal treatment conditions
Glass forming region of the novel GeS$_2$-Sb$_2$S$_3$-PbS system

Crystallization ability

• VSG region where glasses with larger ΔT (> 170°C, T<sub>c</sub> - T<sub>g</sub>), 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 330ºC for 163 h,
(b) P7 at 300ºC for 5 h,
(c) P5 at 340ºC for 15 h,
(d) P5 at 310ºC for 15 h,
(e) P5 at 310ºC for 32 h,
(f) P5 at 310ºC 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 GeSe$_2$-Ga$_2$Se$_3$-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 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
Absorption due to electronic transitions between VB and CB

Optical transmission

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

An example: PI bandgap change

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 expansion.

5 Main applications

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

(a) CO laser transmission, (b) CO\textsubscript{2} laser transmission and (c) pulsed high energy laser transmission in the 2-5 \(\mu\)m region (\(\pm 0.01\) mW)

Thermal imaging

![Graph showing transmission vs wavelength for silica, fluorides, and chalcogenides.

- **Vis (1.55 µm)**
- **Telecom (1.55 µm)**
- **Transparency of atmosphere**
- **Maximum emission of black bodies at RT**
- **IR optics for thermal imaging**

Wavelength (µm)

- **Silica**
- **Fluorides**
- **Chalcogenides**

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
Night-vision car

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 $< 0.5 \, \mu m$. 
Amplifier for telecommunication

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

Pr^{3+} 1.32 μm emission

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

\[ \eta = \frac{W_{\text{rad}}}{W_{\text{rad}} + W_{\text{MP}} + W_{\text{ET}}} \]

\[ W_{\text{MP}} \uparrow \] 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

Raman spectra

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

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 SiO$_2$ fiber, (C) two single-mode cores as waveguides.

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

Optical nonlinearity

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

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

Université de Rennes 1, France

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

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)


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

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

Kyoto University, Japan
ECUST, China
Maker fringe patterns of the β-GeS₂ crystallized glasses without poling treatment

\[ n^{(2)} = 5.36-7.3 \text{ pm/V} \]

XRD and Raman spectra
Optical Kerr effect

Signal of GeSe$_2$-In$_2$Se$_3$-CsI glasses

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

Raman spectra

[GeSe$_4$] at 200 cm$^{-1}$ and [InSe$_4$] at 154 cm$^{-1}$ are the main structural units while the increasing CsI does not cause clear structural
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