Production(?) of chalcogenide glass optics: motivation, current status and future development

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Outline

- Background and motivations
- Current technique for chalcogenide glass fabrication
- Challenges and future trends for chalcogenide glass and lens fabrication
- Summary
Thermal imaging was developed for defense application with more and more commercial applications.
Why infrared is interesting for driving assistance
Great progress achieved in uncooled infrared detectors

Constant need for cheaper, more efficient materials
Thermal Imaging: how it works

Based on the detection of the radiations emitted by hot bodies

- 2nd atmospheric window (MWIR): 3-5 µm
- 3rd atmospheric window (LWIR): 8-12 µm

Need for materials transparent in these windows
Cost of Infrared detectors

Cost of detector + cooler (euros)

Defense

consumer
Typical IR Optics
Materials for thermal imaging optics

**Single Crystalline Germanium**
- Expensive
- Single point diamond turning

**Polycrystalline Zinc Selenide (ZnSe)**
- Synthesized by CVD
- Single point diamond turning
Chalcogenide glasses - Definition

- S
- Se
- Te
- Ge
- As
- Sb
- Ga
Chalcogenide glasses - Properties

Large transparency in the Infrared

moldable

Low dn/dT

Bulk / Fibers  Lenses
Chalcogenide glass samples
Chalcogenide glass synthesis

- Vacuum pump
- Liquid Nitrogen
- Starting raw elements
- Sealing
- quenching
Industrial fabrication of chalcogenide glass Ge-As-Se

Dr. A. Ray Hilton, Sr. Amorphous Materials, Inc.
Garland, Texas
Industrial fabrication of chalcogenide glass Ge-As-Se

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Casting of chalcogenide glass

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Casting of chalcogenide glass
Different steps of Chalcogenide glass production

Maximum size: 200 mm
Homogeneity control

Glass to be controlled

CCD Camera
Homogeneity control
Fabrication of optical lenses

- Grinding/polishing: spherical surfaces
- Single point diamond turning
- Molding

Molding of chalcogenid glass lenses
Examples of molded chalcogenide glass optics
Challenges for chalcogenide glass molding

Sumitomo patent

Inert gas or in vacuum to avoid oxidation

Necessity to prepare preform before molding
Toshiba patented molding machine
Challenges and future trends for chalcogenide glass and lens fabrication
Synthesis of chalcogenide glasses

Important difference in vapor pressures for the different elements

Closed systems

Highly sensitive to contamination by oxygen

Controlled atmosphere
Set-up for chalcogenide glass synthesis in argon
Vapor pressure of As and Se

![Graph showing vapor pressure of As and Se vs. temperature.](image)
Photos of good sample

Example of glass obtained with sealed silica tube
Index reproducibility

3 glasses tested

Index precision : $2.10^{-3}$

<table>
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<th>glasses</th>
<th>Index at 1.55 µm</th>
<th>difference</th>
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<td>Lower sample</td>
<td>Upper sample</td>
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<tr>
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Difference B-C $3.10^{-4}$ 1.6 $10^{-3}$

Technique can not be used for synthesizing Germanium containing glass
Continuous production line

Umicore patent
For IR optics
New approach for chalcogenide glass production
Mechanosynthesis

using mechanical energy instead of thermal energy to induce chemical reaction

- Melting in reusable silica chamber
- Hot Uniaxial Pressing
- Spark Plasma Sintering
Mechanosynthesis $80\text{GeSe}_2-20\text{Ga}_2\text{Se}_3$

Evolution of powder coloration with milling duration

Progressive reaction between the elements and lowering of particle size

Particle size distribution

XRD Spectra
Mechanosynthesis

- Synthesis of micrometric glass powder
- Thermal properties close to that of glasses prepared in sealed silica ampoule

To produce bulk glasses or optics

Melting and casting → Sintering
Melting of the powders/casting

In closed silica chamber under argon atmosphere.

The powders already possess the desired composition.

Reduced risks of evaporation of selenium.

Experimental set-up:
- Argon entrance
- Argon exit
- Furnace
- Glass
- Rotating Helix
**Bulk glass/lenses fabrication by hot pressing**

**Principle:** sintering of the powder at a temperature above the glass transition temperature \((T_g)\) but below the melting temperature \((T_m)\)

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**Hot Uniaxial Pressing (HUP)**

- **Pressure control**
- **Die**
- **Powder**
- **Protective plate**
- **Furnace**
- **Pistons**

**Spark Plasma Sintering (SPS)**

- **Pressure control**
- **Vacuum chamber**
- **Powder**
- **Power supply**

**Faster temperature ramps reached with SPS**
Conventional hot pressing needs stable glasses

80GeSe$_2$-20Ga$_2$Se$_3$ composition: $\Delta T<100^\circ$C

Materials obtained:

- Inhomogeneous sintering (thermal profile of the press)
- Uncontrolled crystallization
- No optical transmission

Crystallization due to prolonged stages at $T>T_g$

Need to reduce sintering process duration => SPS
Fast sintering of $80\text{GeSe}_2-20\text{Ga}_2\text{Se}_3$ powder with SPS

Dr Synter 505 Syntex SPS machine

Experimental conditions
- Under vacuum
- Thermal treatment

Total duration: 10 min (more than 2h for HUP)
glass bulks sintered at different dwell temperatures (50 MPa, 2-min)

G. Delaizir et al

Fast sintered $80\text{GeSe}_2-20\text{Ga}_2\text{Se}_3$ glass discs

Powder sintered **2 minutes at 390°C** (Tg+40°C), 50MPa

Densification > 99%

Transparent bulk samples $\varnothing = 8$ mm, 20 mm et 36 mm

Maximum diameter obtained using silica tubes = 9 mm
Fast sintered $80\text{GeSe}_2-20\text{Ga}_2\text{Se}_3$ Glass-Ceramics

Sintering at 390°C for longer durations

Progressive controllable crystallization (crystals < 100 nm)

Glass-ceramics transparent in the infrared range

Important pollution by oxygen (transmission cut-off at 12 µm)

Glass prepared in silica tube and ground

Cooperation with LARMAUR
Summary

- Chalcogenide glasses are fabricated batch by batch in sealed silica tube
  - Discontinued process
  - Expensive single use silica ampoules
  - Only for highly stable glasses

- Fabrication in controlled atmosphere
  - Highly homogenous glasses
  - Only for Ge-free glasses

- Mechano-synthesis + Spark plasma Sintering
  - Possibility of continuous process
  - Wide choice of glass composition
  - Large size glass ceramic optics

We need process revolution