Production(?) of chalcogenide glass optics :

motivation, current status and future development

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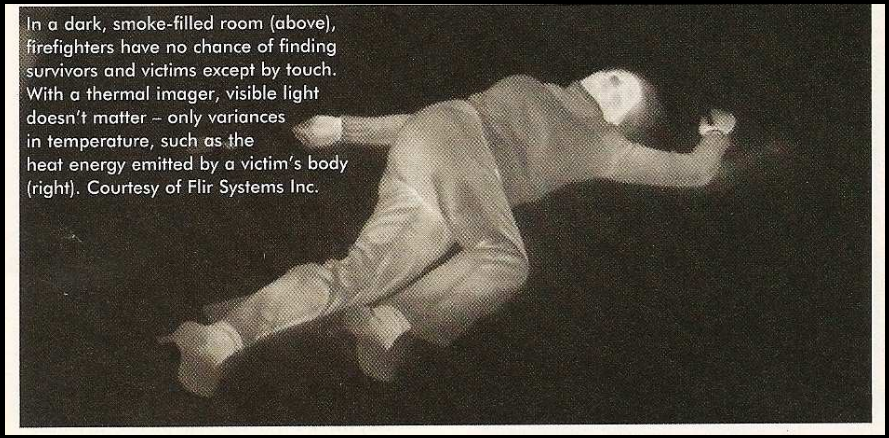
Outline

- 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

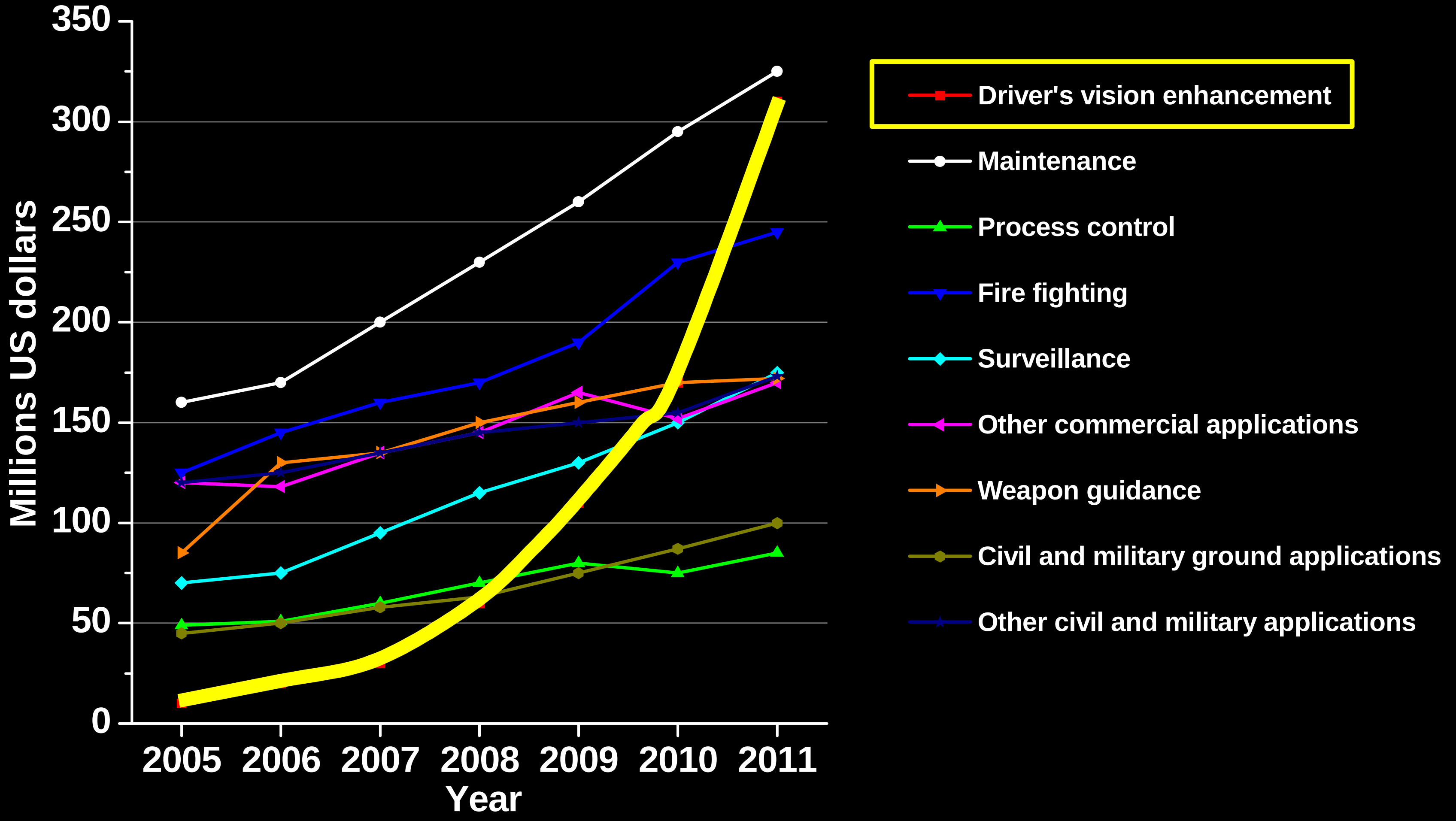
with more and more commercial applications



In a dark, smoke-filled room (above), firefighters have no chance of finding survivors and victims except by touch. With a thermal imager, visible light doesn't matter – only variances in temperature, such as the heat energy emitted by a victim's body (right). Courtesy of Flir Systems Inc.

Why infrared is interesting for driving assistance

Thermal Imaging – A growing market

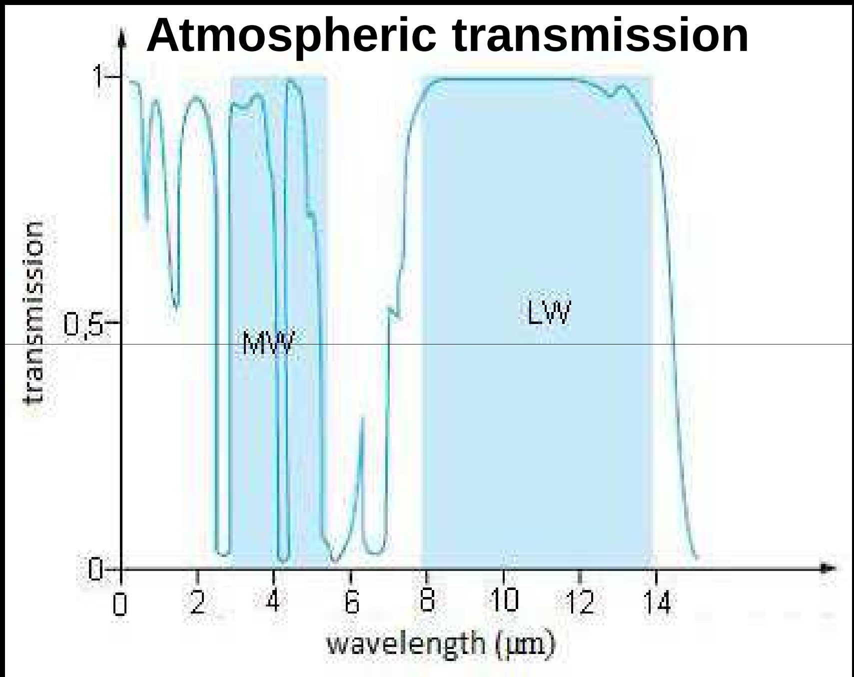


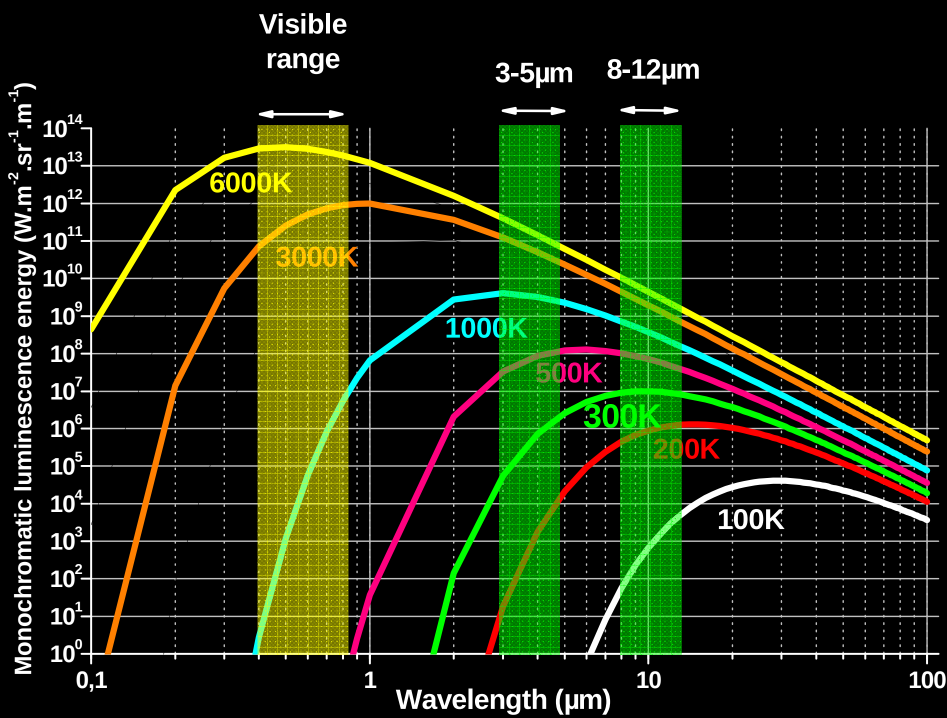
Great progress achieved in uncooled infrared detectors

Constant need for cheaper, more efficient materials

Thermal Imaging : how it works

Based on the detection of the radiations emitted by hot bodies

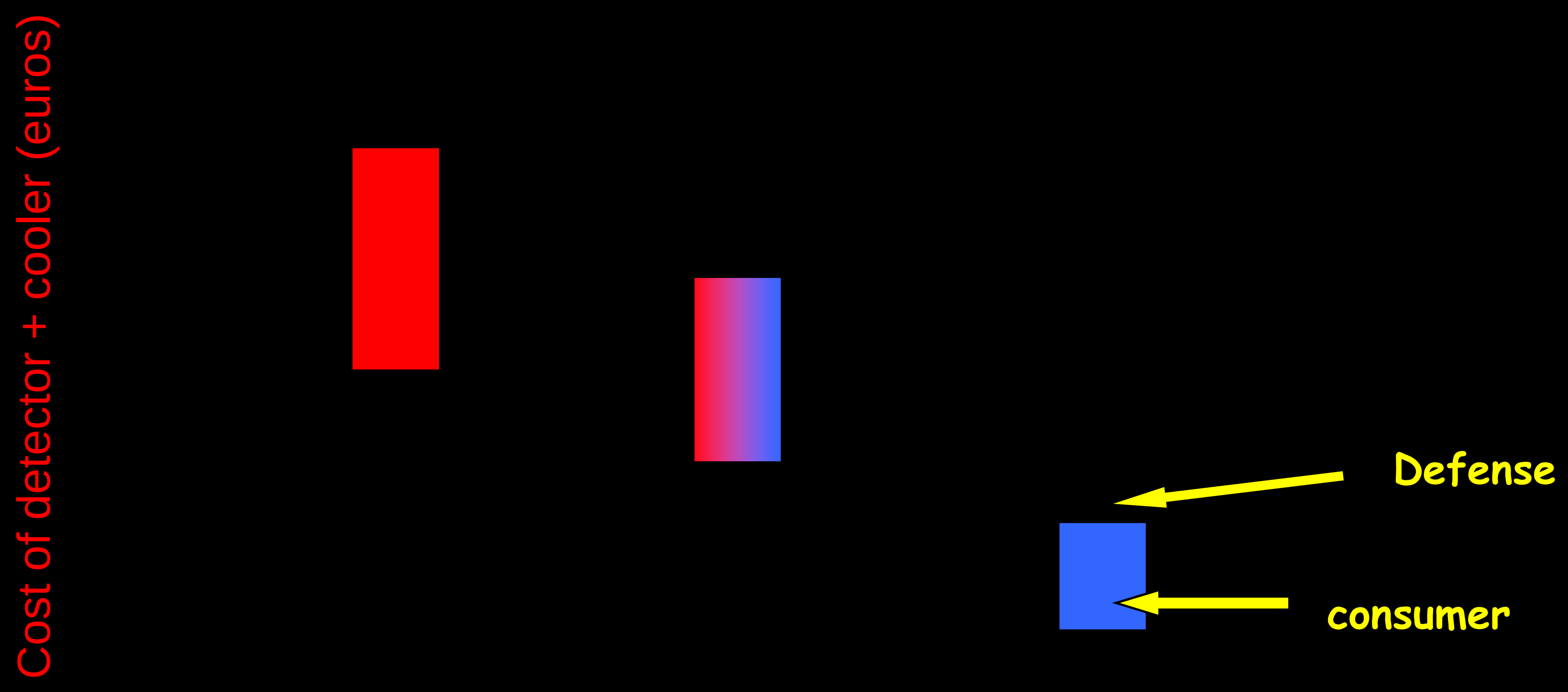




- 2nd atmospheric window (MWIR) : **3-5 µm**
- 3rd atmospheric window (LWIR) : **8-12 µm**

Need for materials transparent in these windows

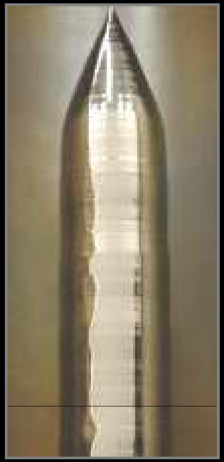
Cost of Infrared detectors

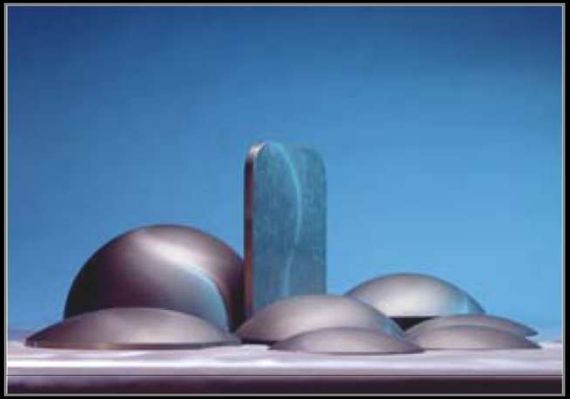


Typical IR Optics

Materials for thermal imaging optics

Single Crystalline Germanium



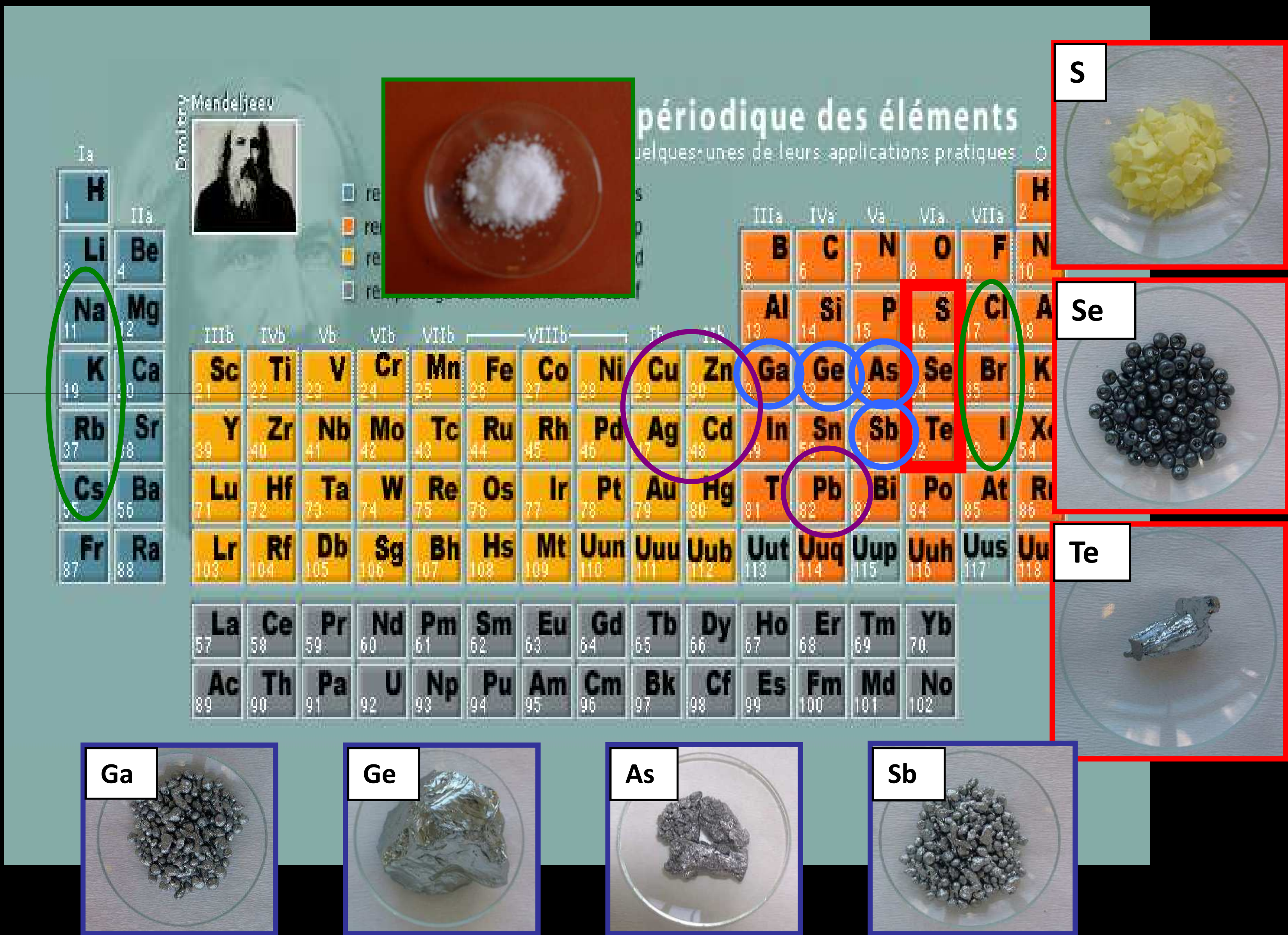


- Expensive
- Single point diamond turning

Polycrystalline Zinc Selenide (ZnSe)

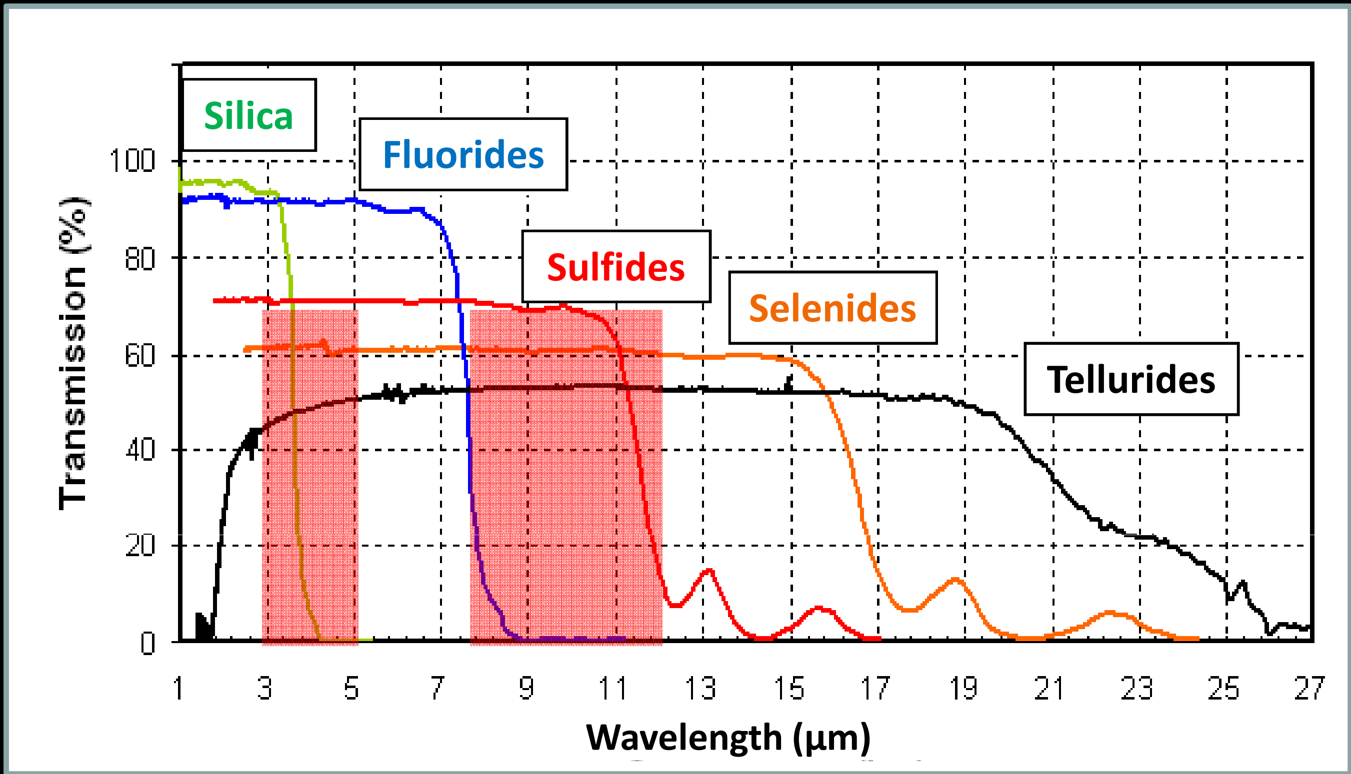
- Synthesized by CVD
- Single point diamond turning

Chalcogenide glasses - Definition



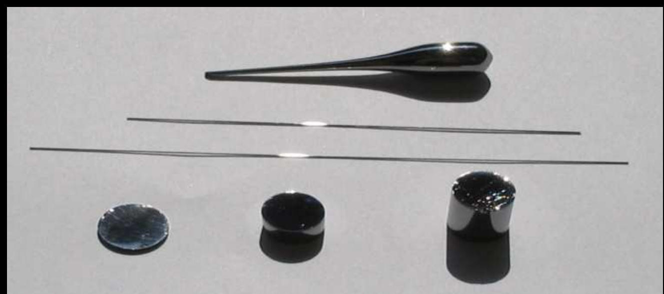
Chalcogenide glasses - Properties

Large transparency in the Infrared



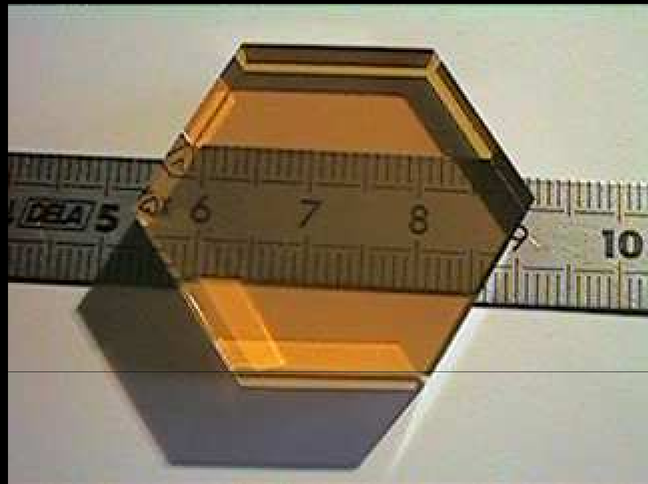
moldable

Low dn/dT

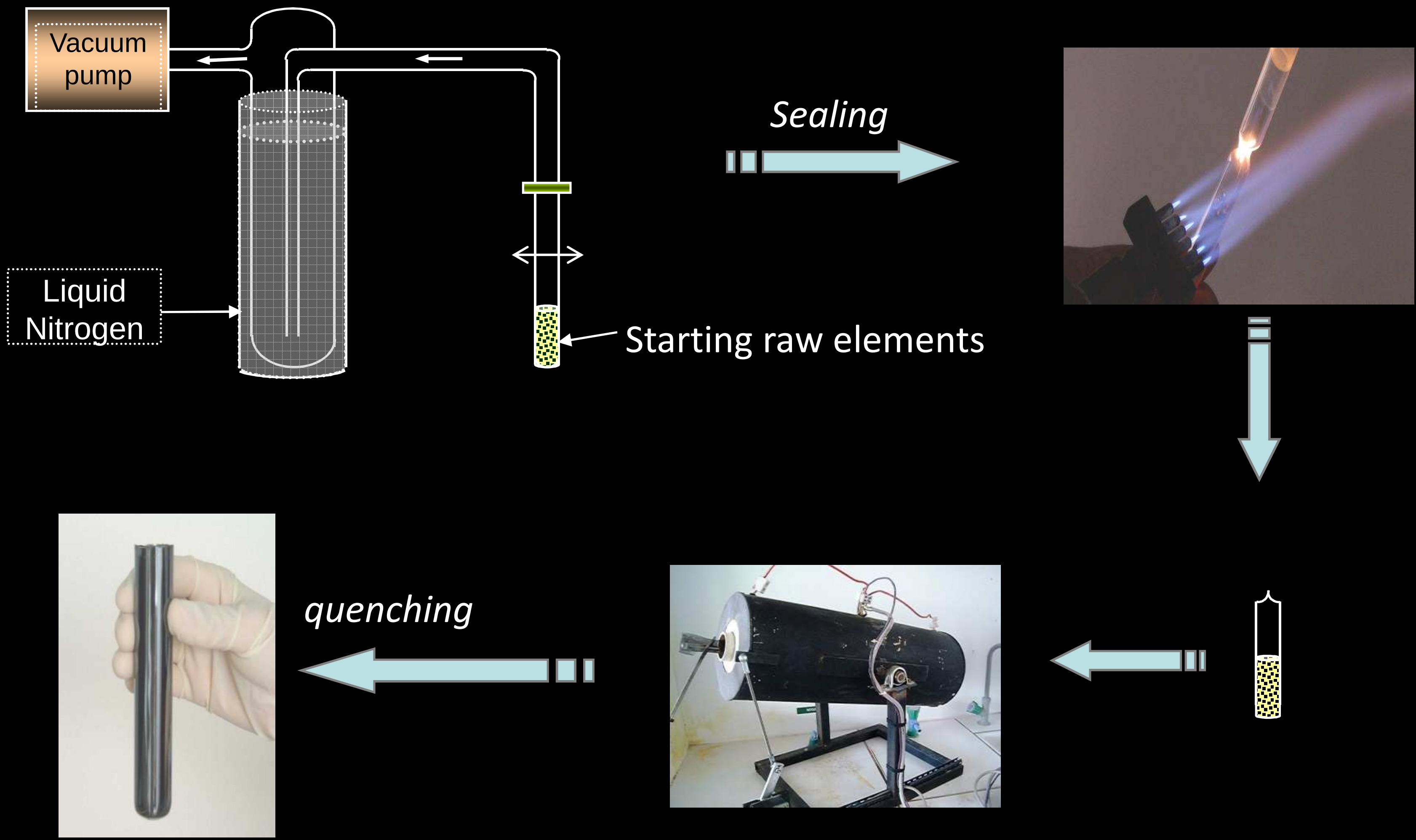

Bulk / Fibers


Lenses

Chalcogenide glass samples

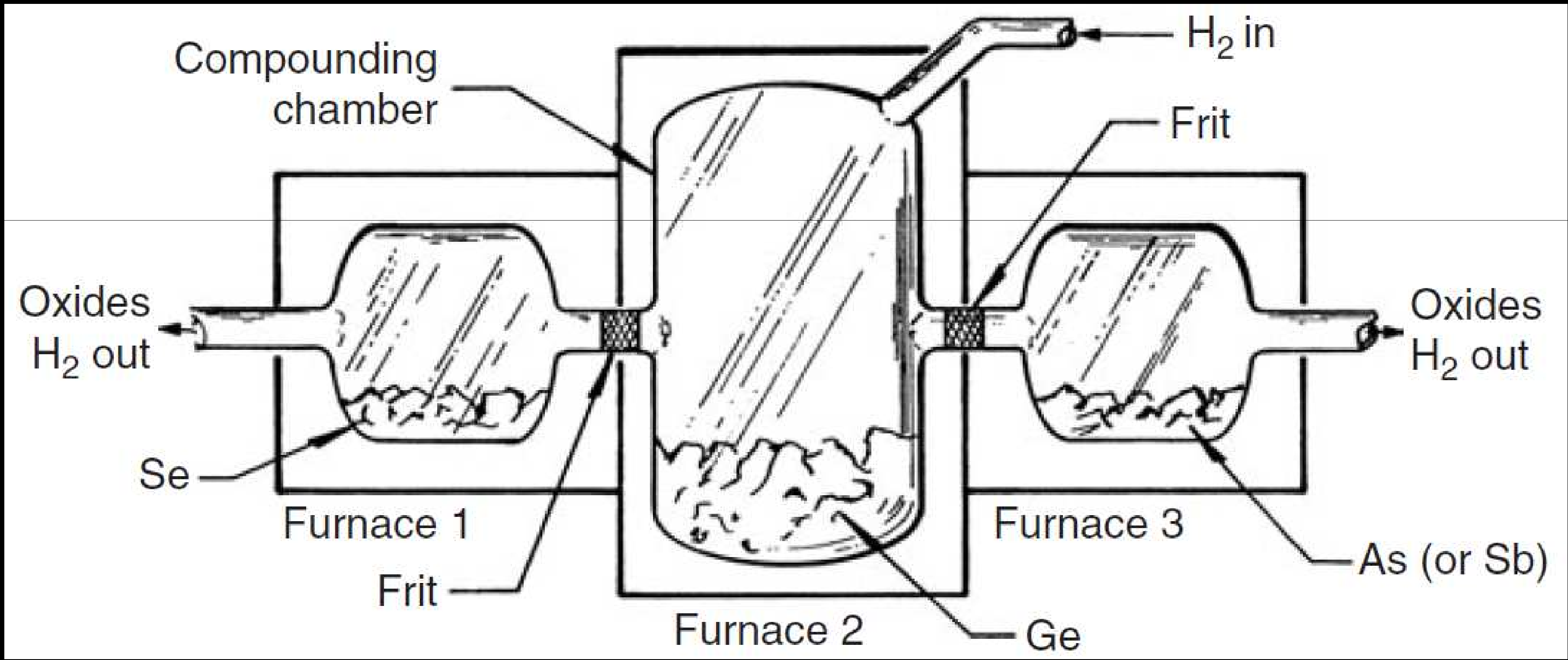


Chalcogenide glass synthesis



Industrial fabrication of chalcogenide glass Ge-As-Se

Dr. A. Ray Hilton, Sr. *Amorphous Materials, Inc.*
Garland, Texas



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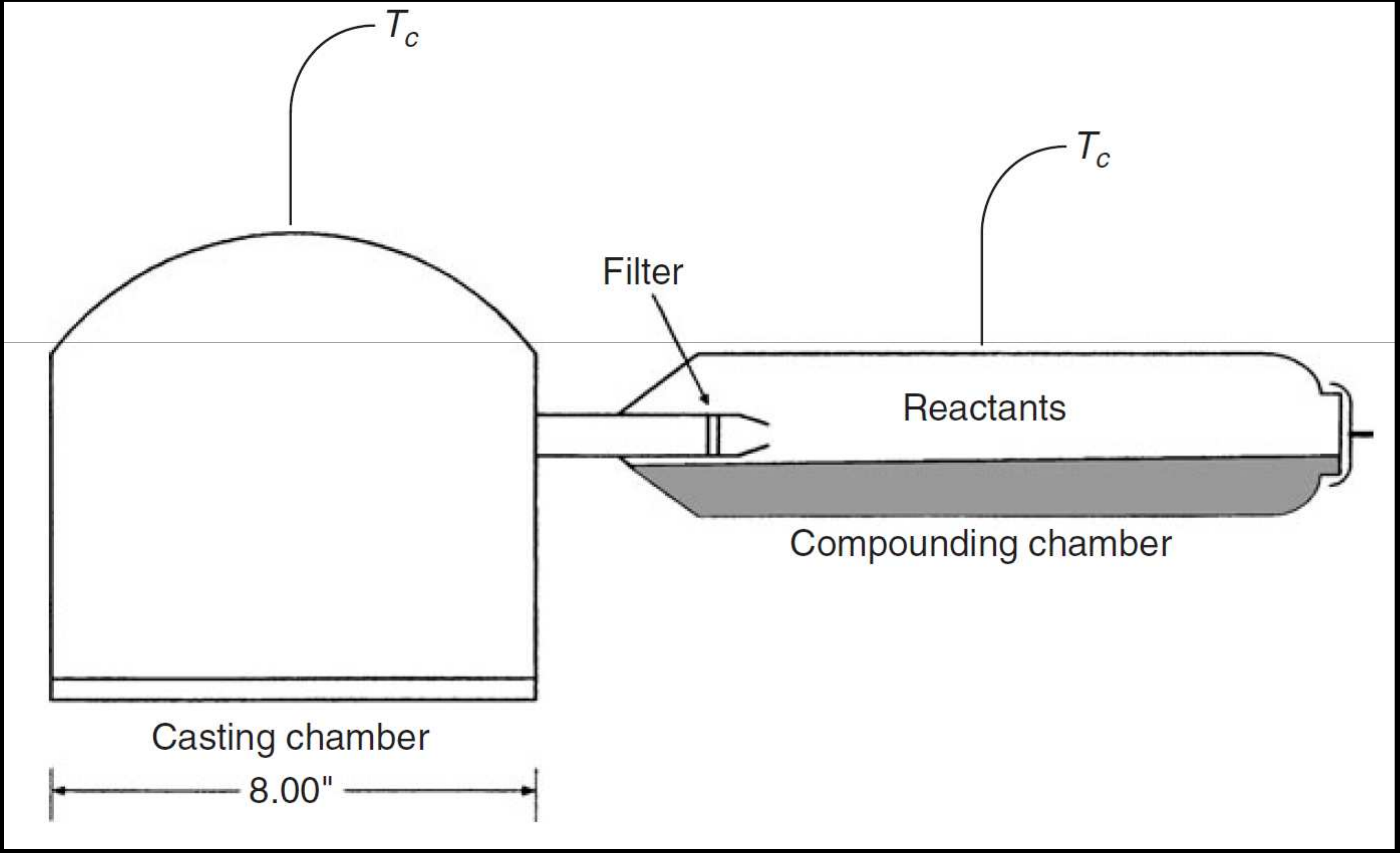
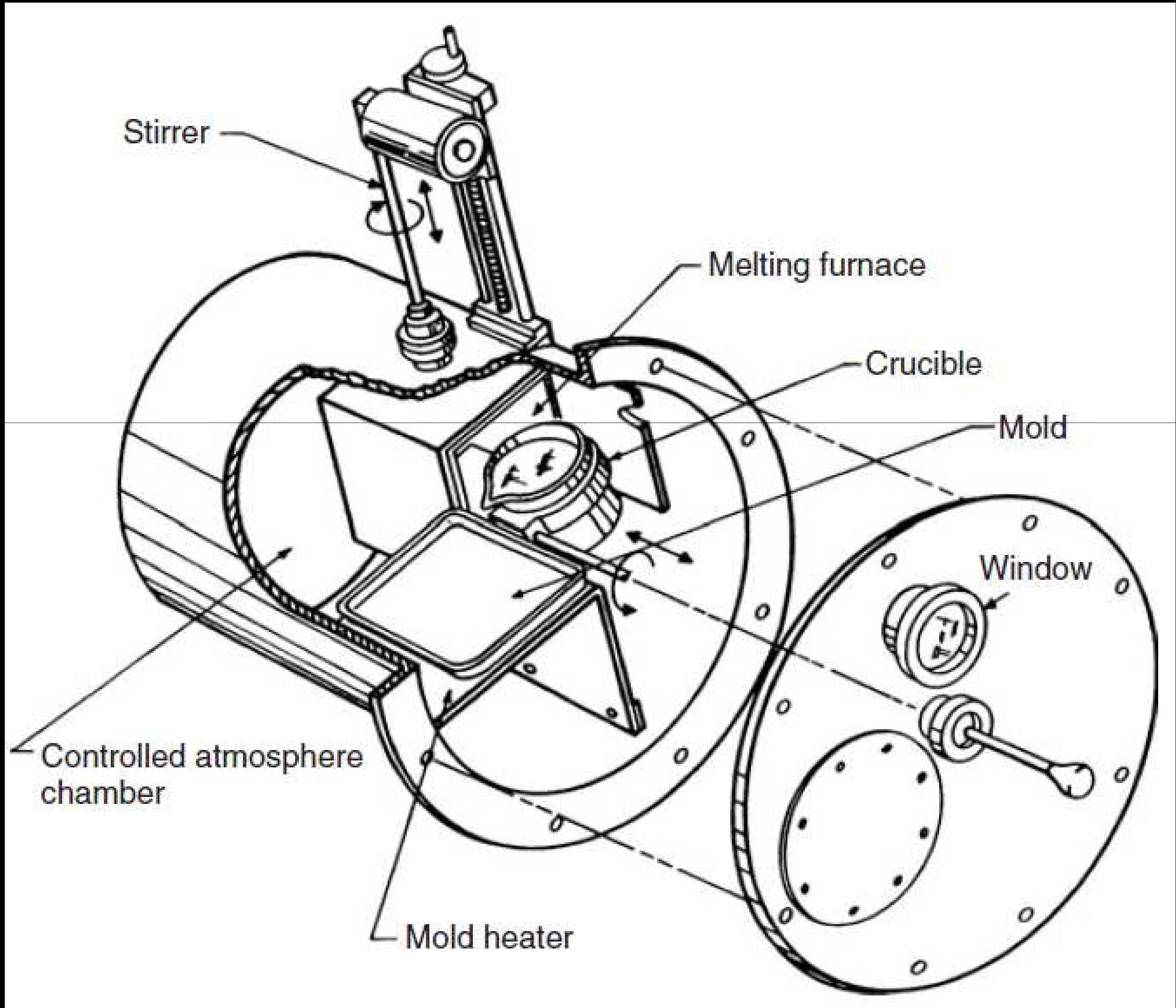
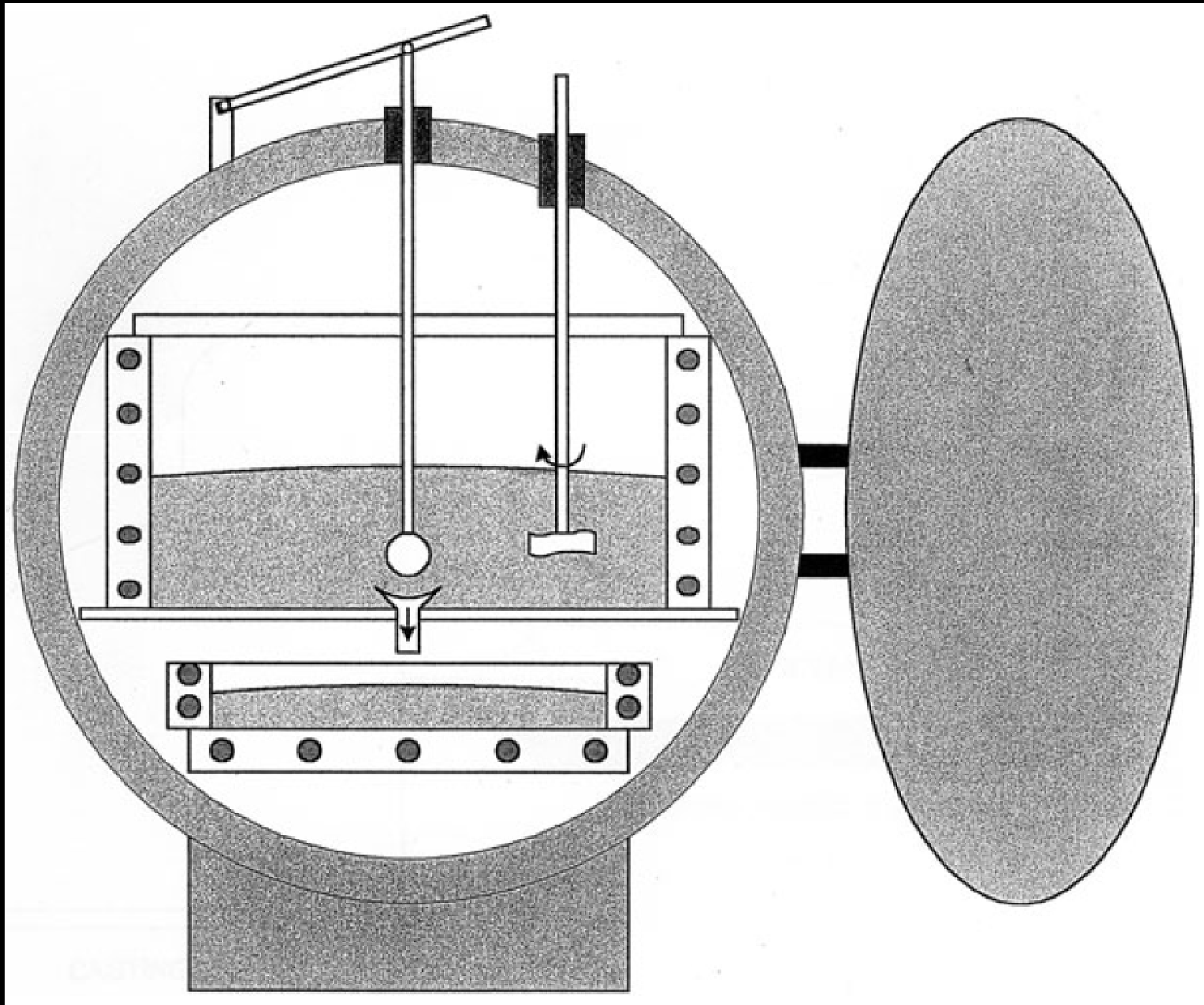


Casting of chalcogenide glass

Dr. A. Ray Hilton, Sr. *Amorphous Materials, Inc.*

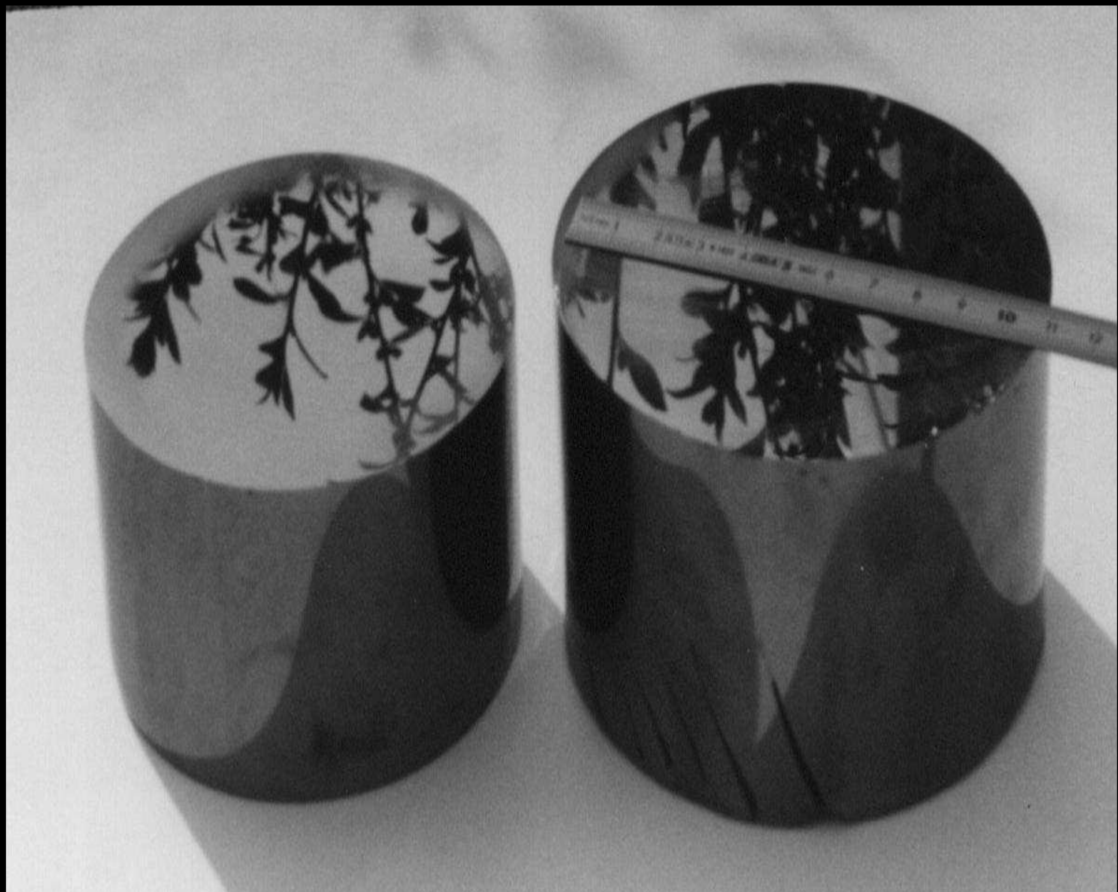


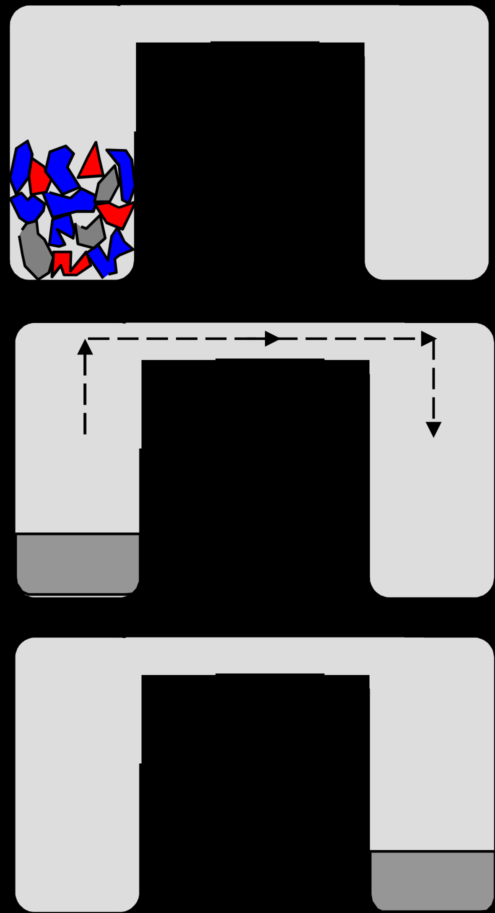
Casting of chalcogenide glass



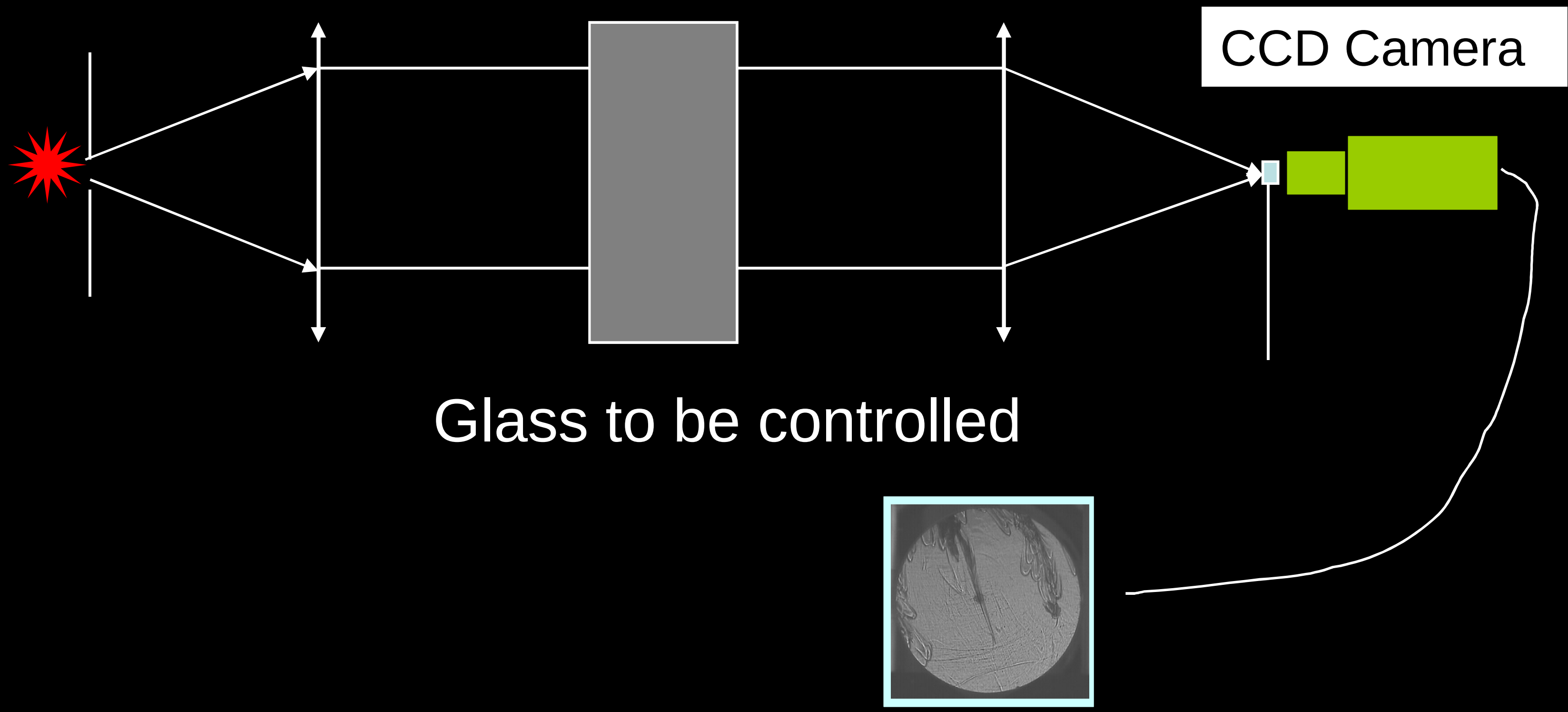
Different steps of Chalcogenide glass production

Maximum size : 200 mm

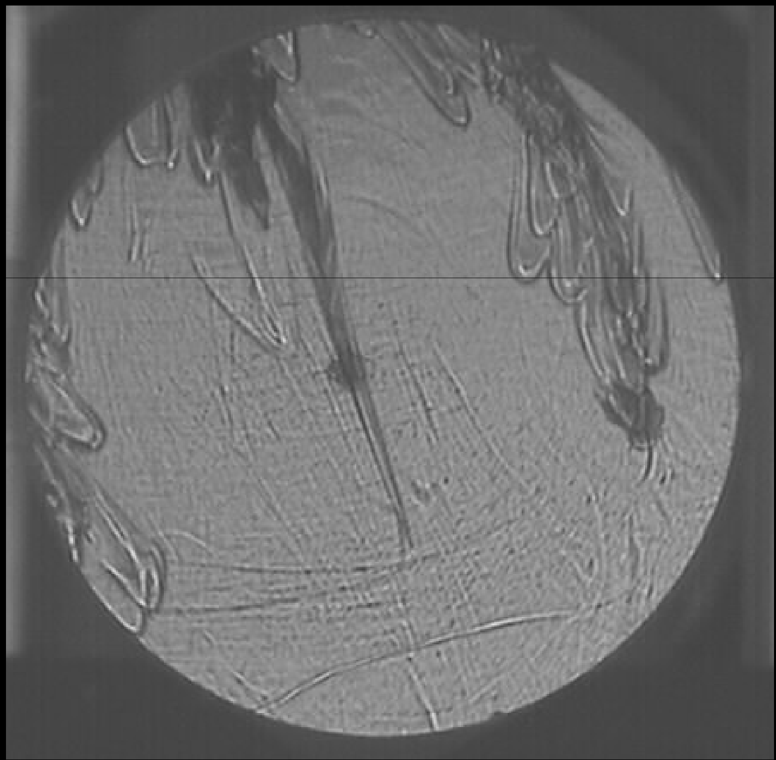


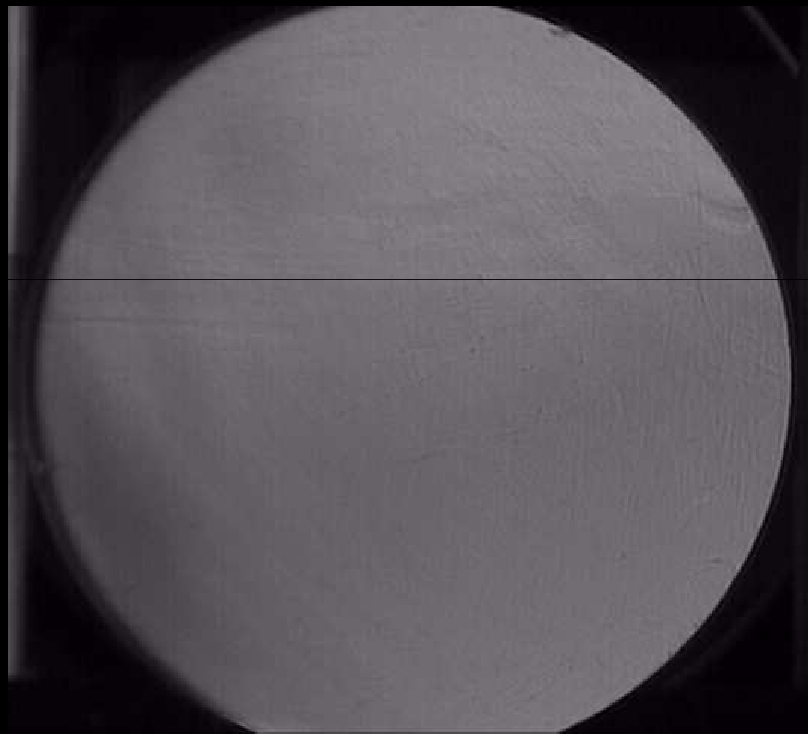


Homogeneity control



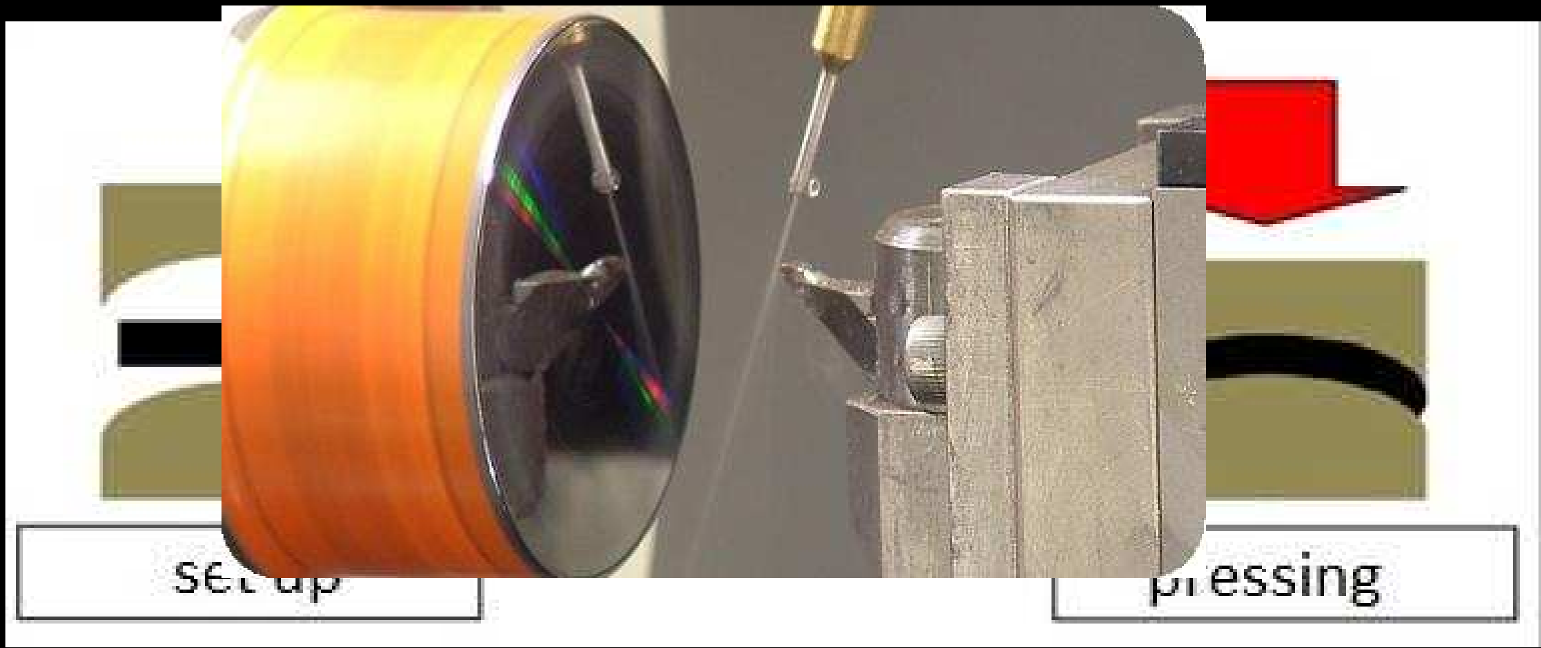
Homogeneity control





Fabrication of optical lenses

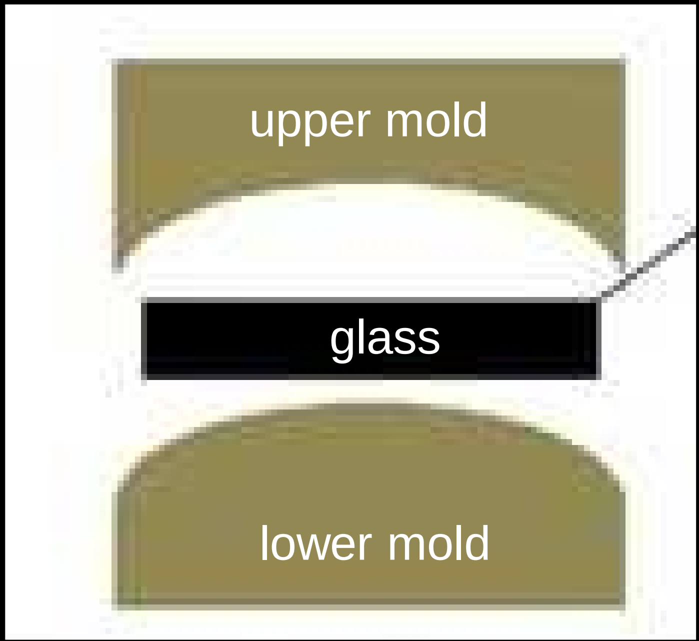
- Grinding/polishing : spherical surfaces
- Single point diamond turning
- Molding



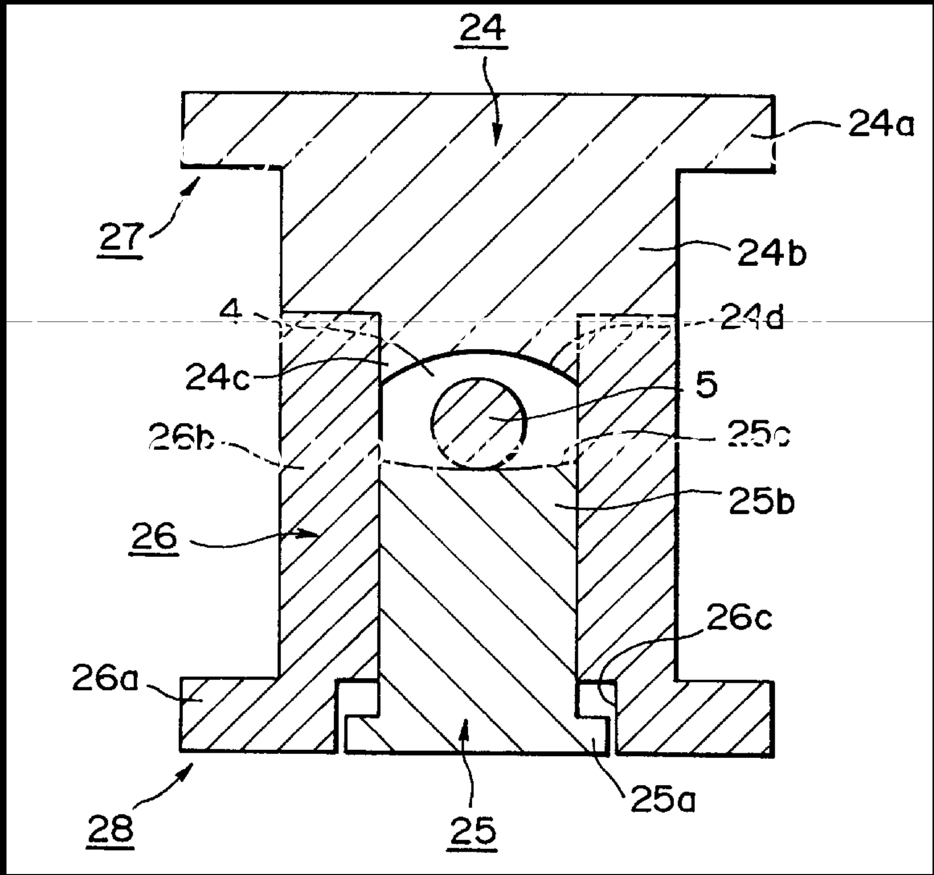
Molding of chalcogenid glass lenses

Examples of molded chalcogenide glass optics

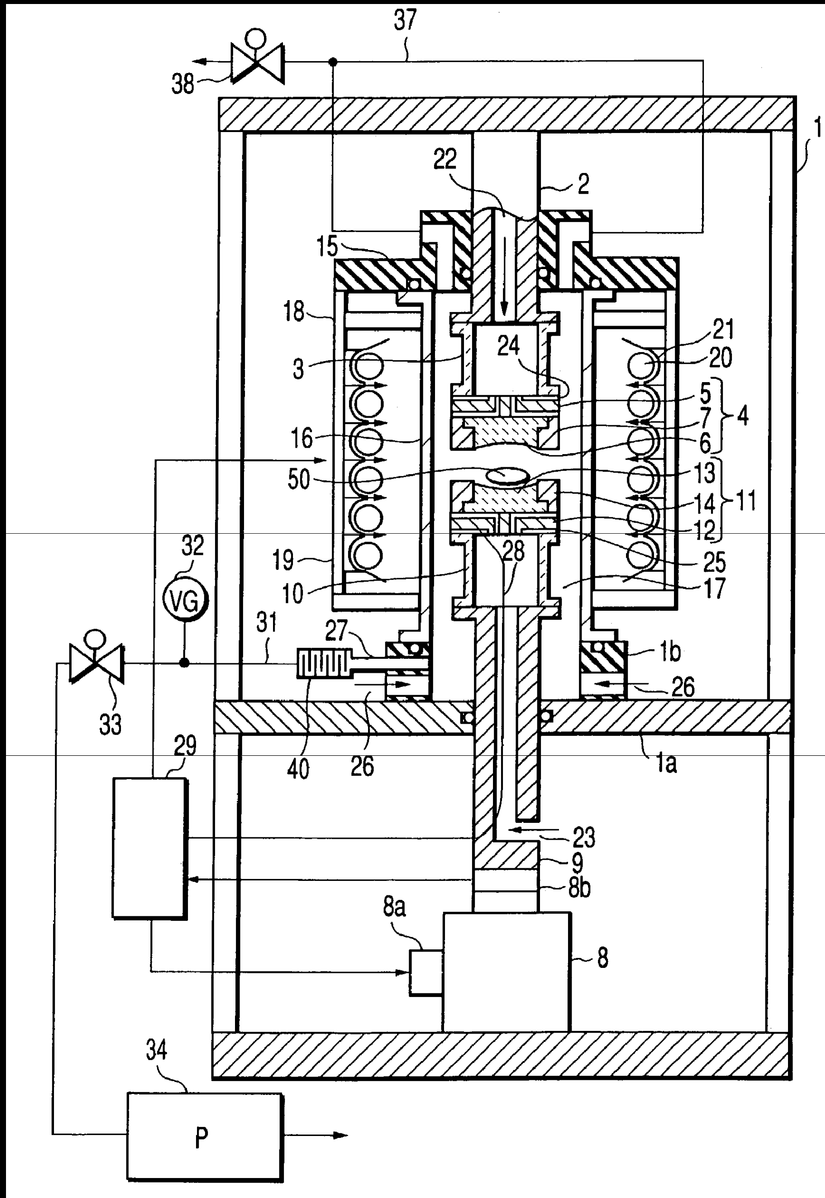
Challenges for chalcogenide glass molding



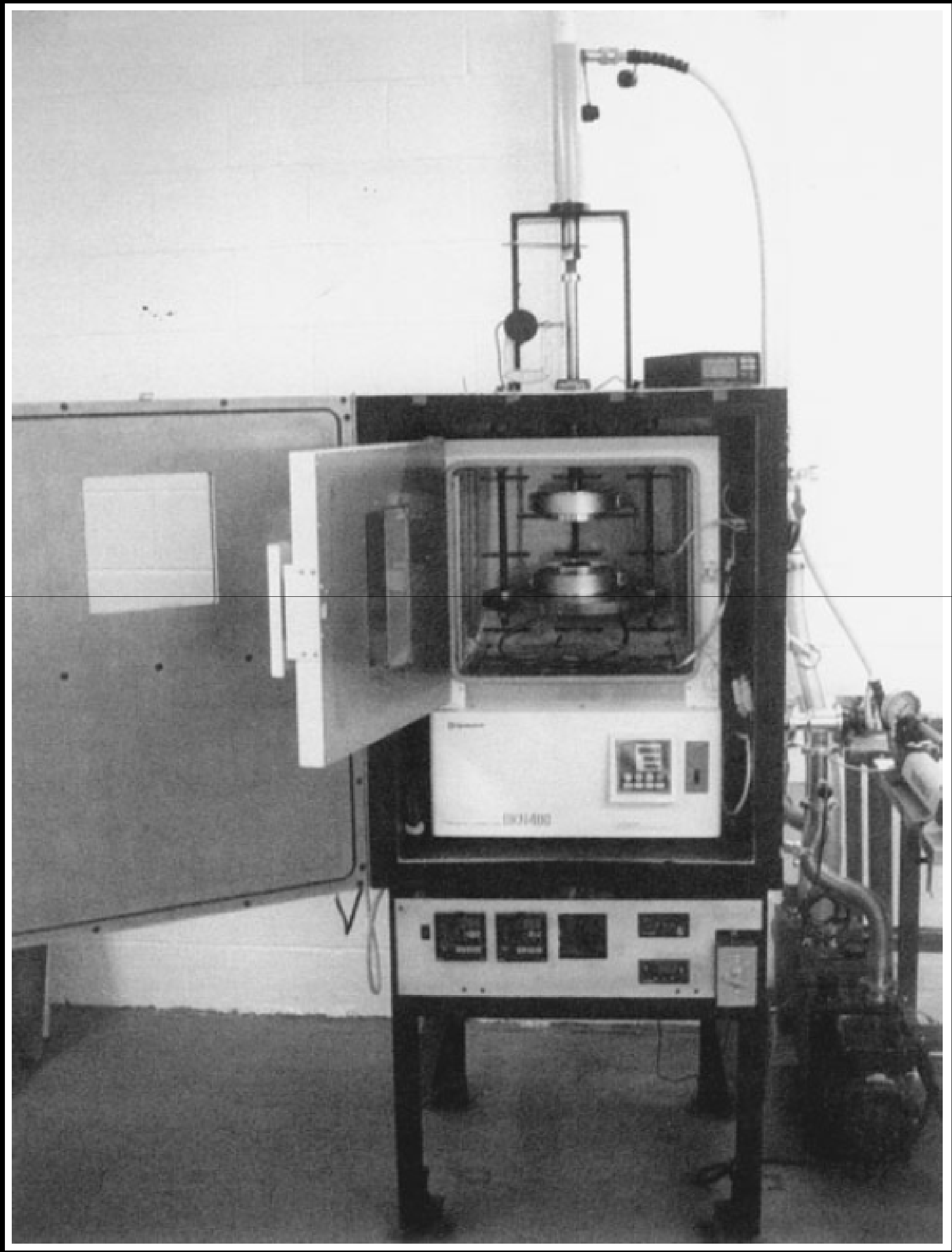
Sumitomo patent



Toshiba patented molding machine



Amorphous Materials Inc molding machine



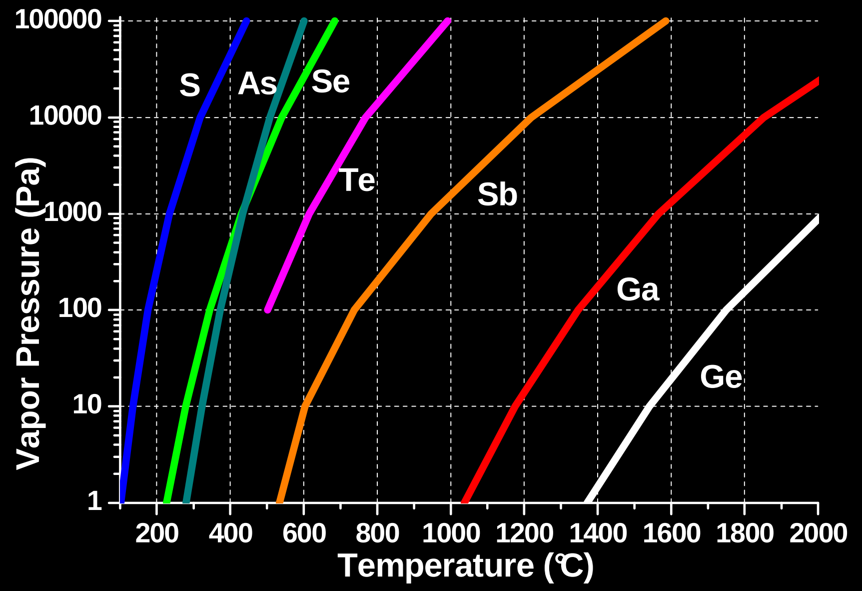
Challenges and future trends

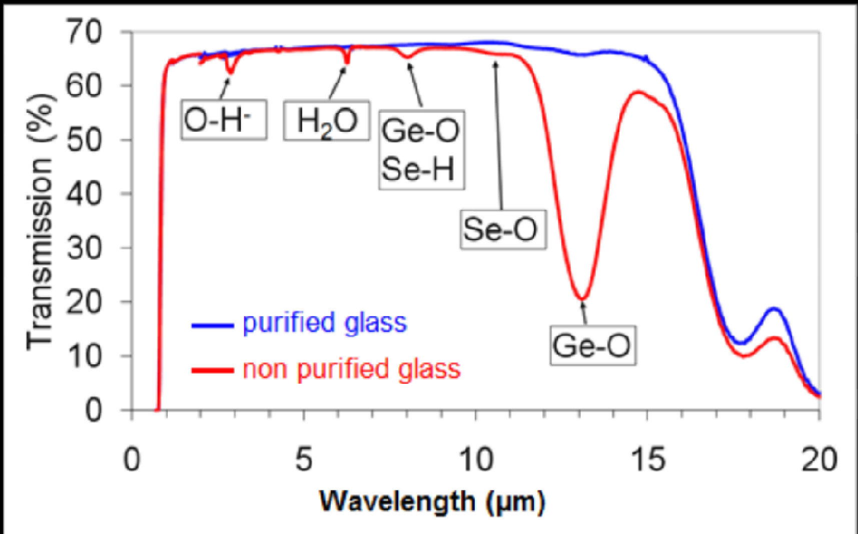
for chalcogenide glass and lens fabrication

Synthesis of chalcogenide glasses

Important difference in vapor pressures for the different elements

Closed systems

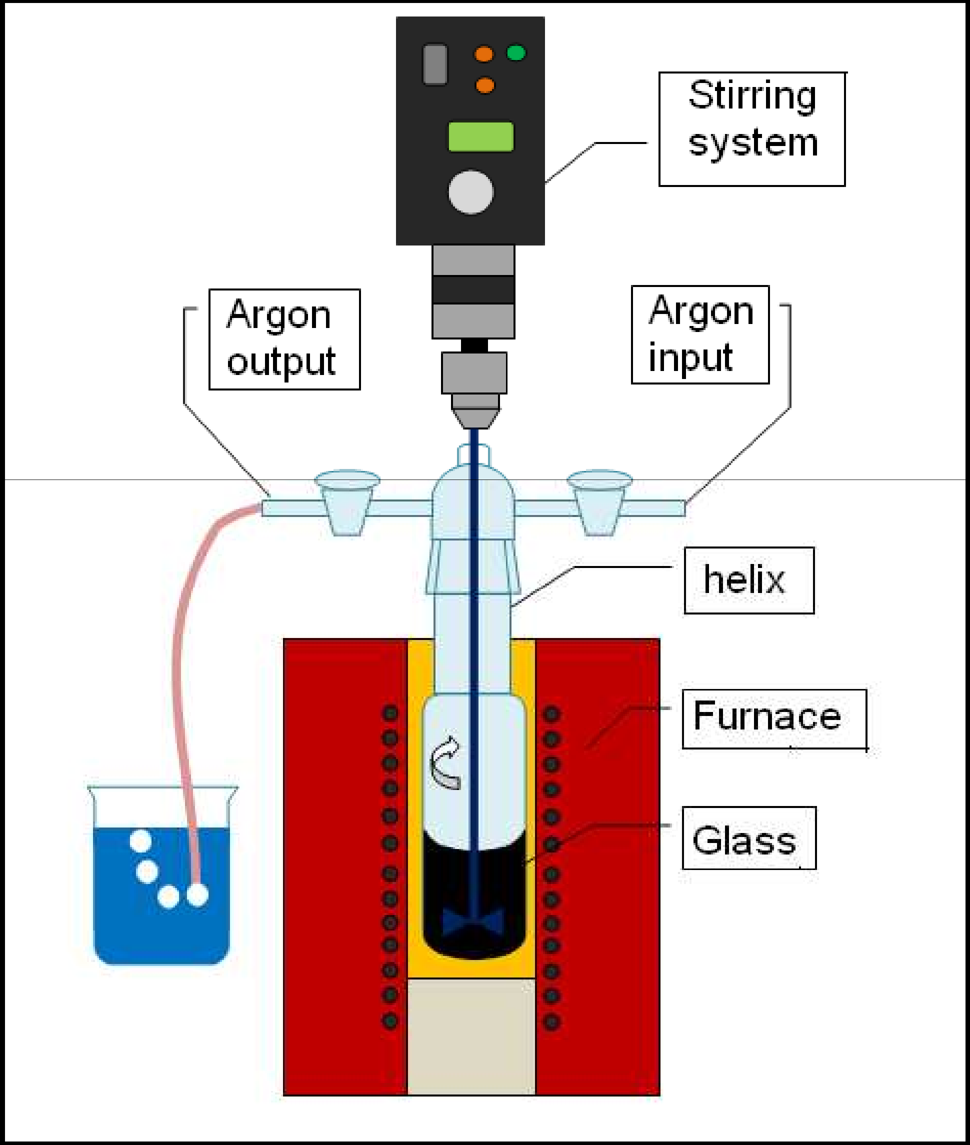




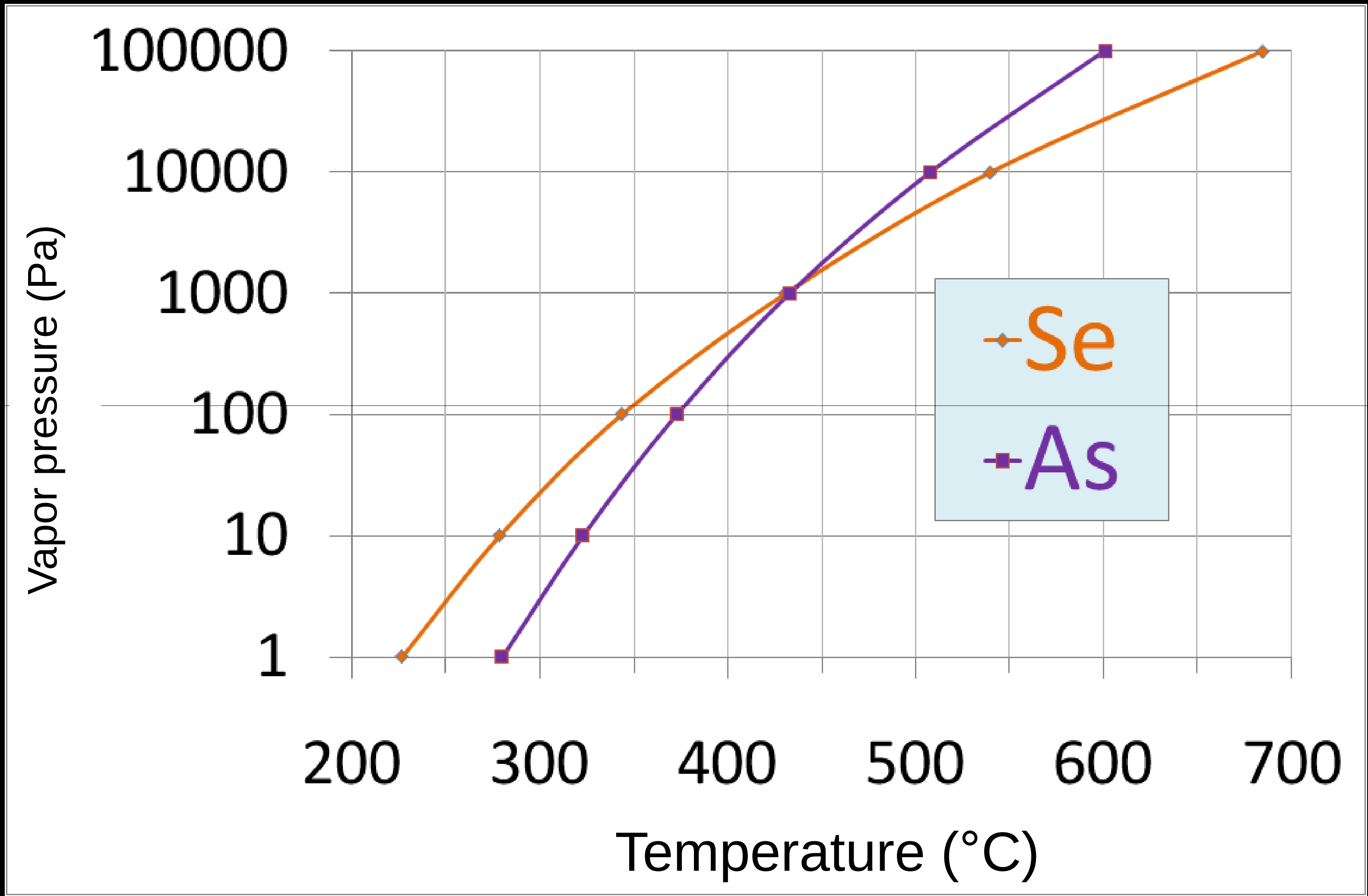
Highly sensitive to contamination by oxygen

Controlled atmosphere

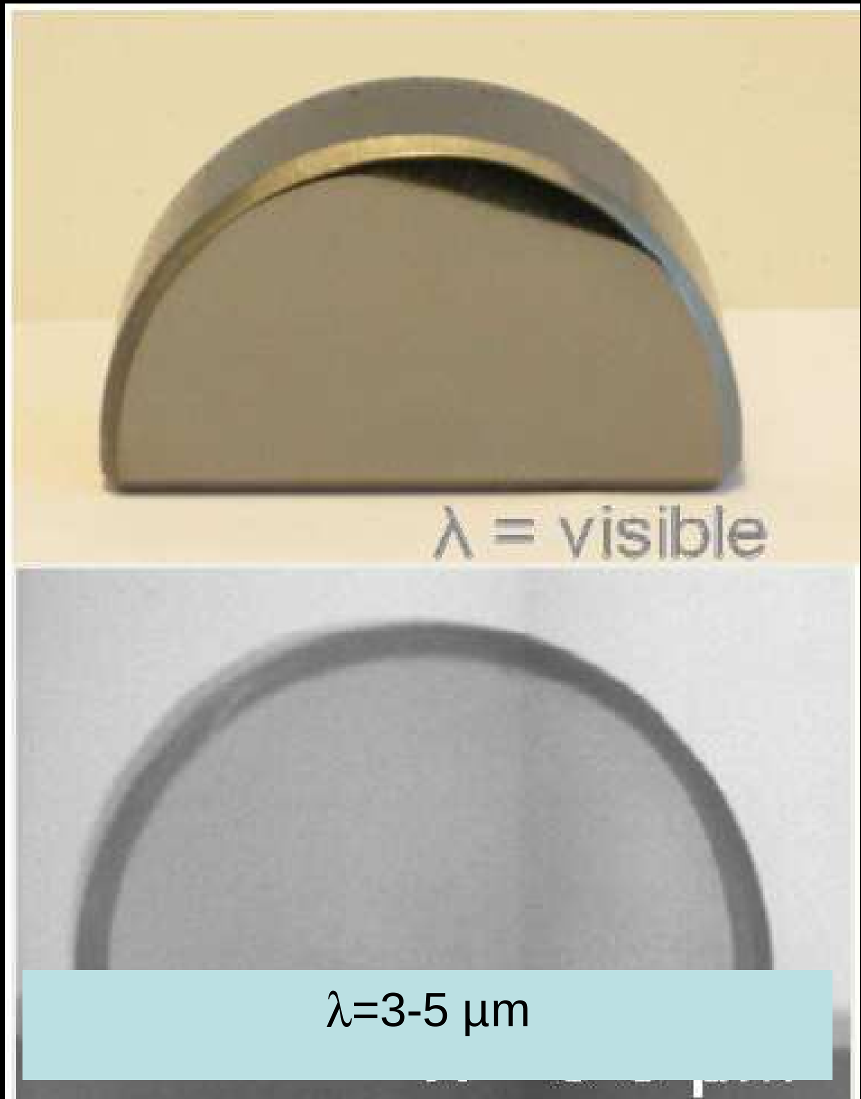
Set-up for chalcogenide glass synthesis in argon

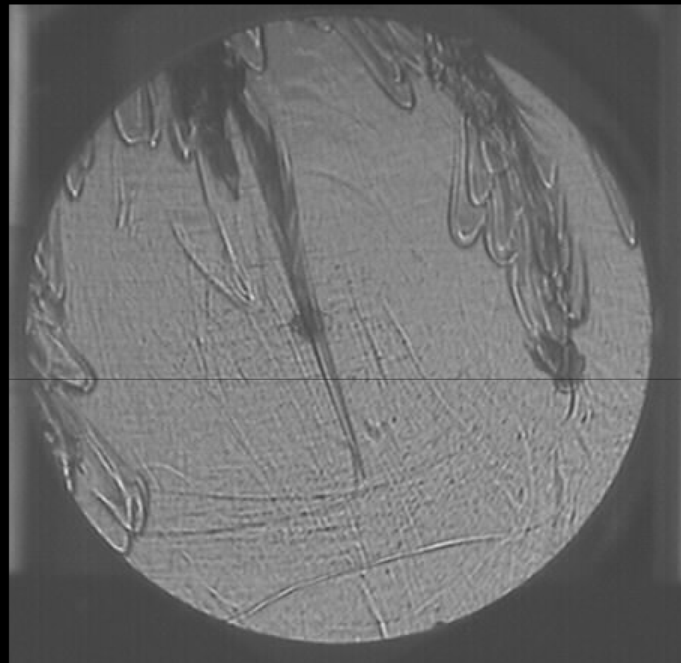


Vapor pressure of As and Se



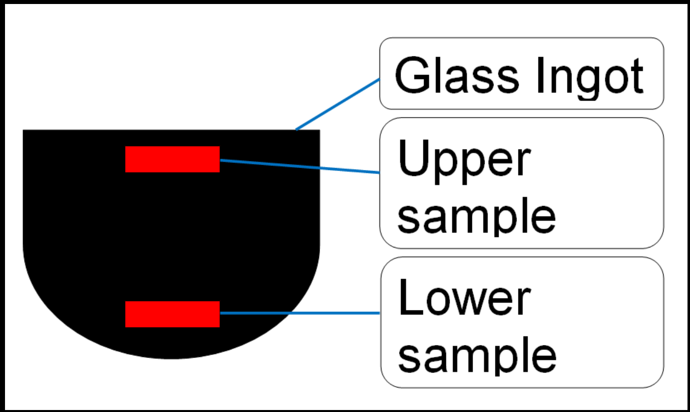
Photos of good sample





Example of glass obtained with sealed silica tube

Index reproducibility



3 glasses tested

Index precision :2.10^{-3}

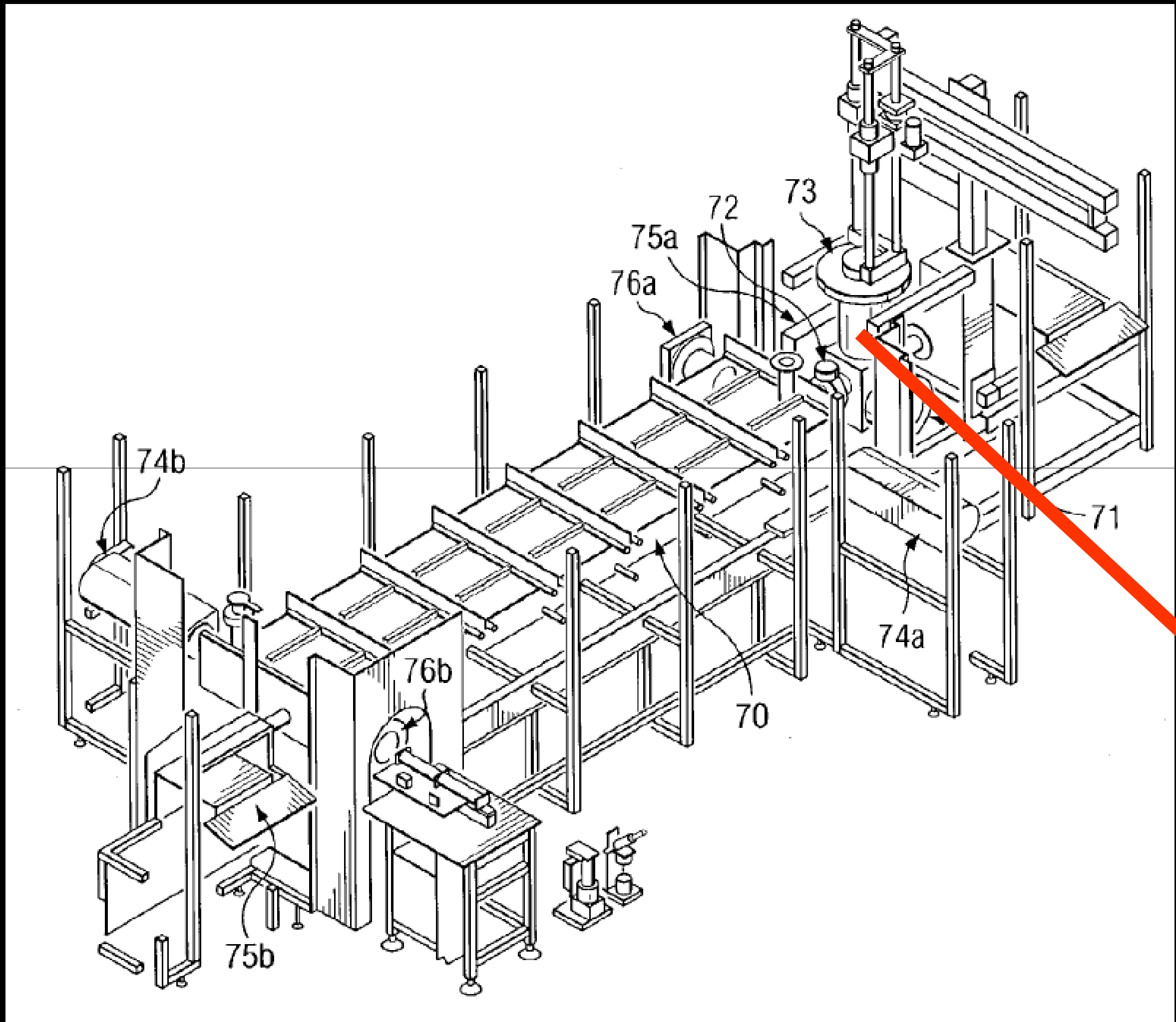
glasses	Index at 1.55 µm		difference
	Lower sample	Upper sample	
A	2.8204	2.8198	$6.\ 10^{-4}$
B	2.8112	2.8120	$-\ 8.\ 10^{-4}$
C	2.8099	2.8104	$-\ 5.\ 10^{-4}$

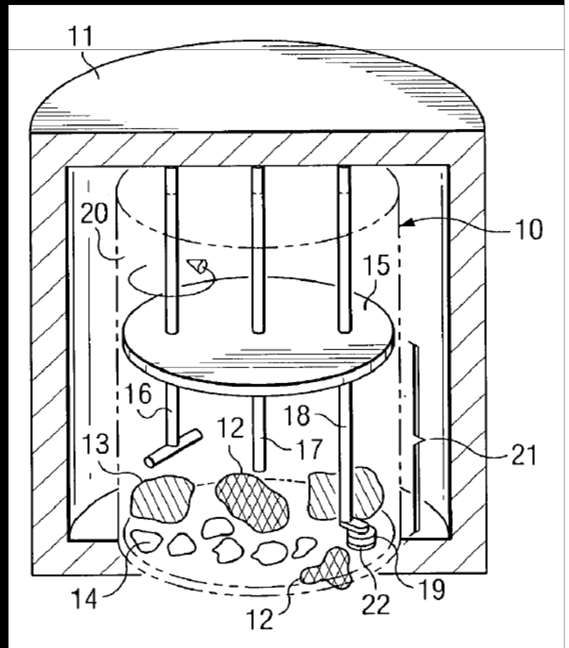
Technique can not be used for synthesizing Germanium containing glass

Difference B-C	$3.\ 10^{-4}$	$1.6.\ 10^{-3}$

Continuous production line

Umicore patent
For IR optics



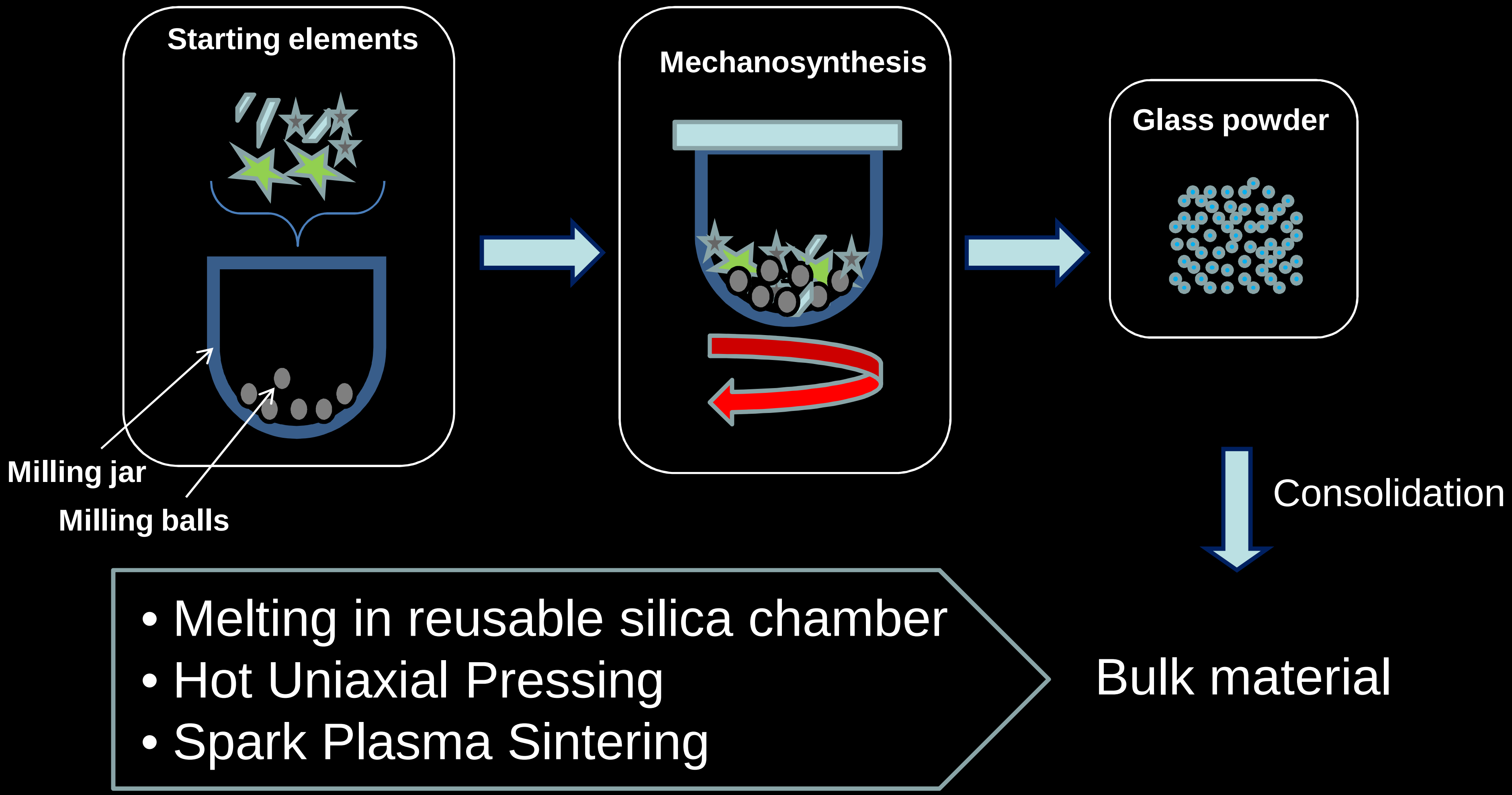


New approach for

chalcogenide glass production

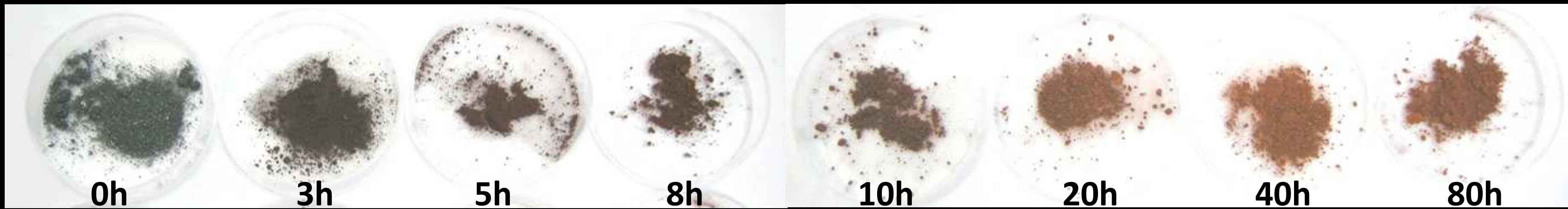
Mechanosynthesis

using mechanical energy instead of thermal energy to induce chemical reaction



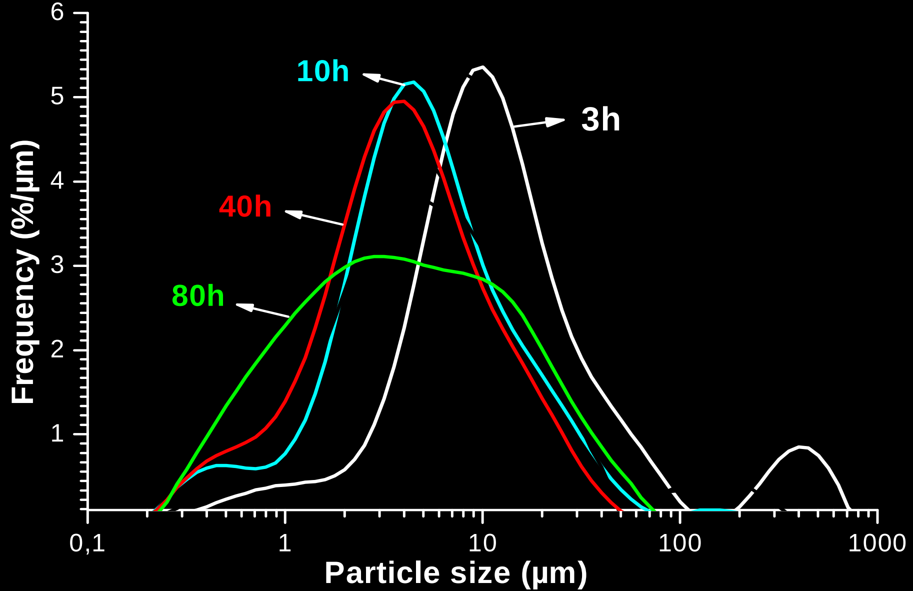
Mechanosynthesis $80GeSe_2$-$20Ga_2Se_3$

Evolution of powder coloration with milling duration

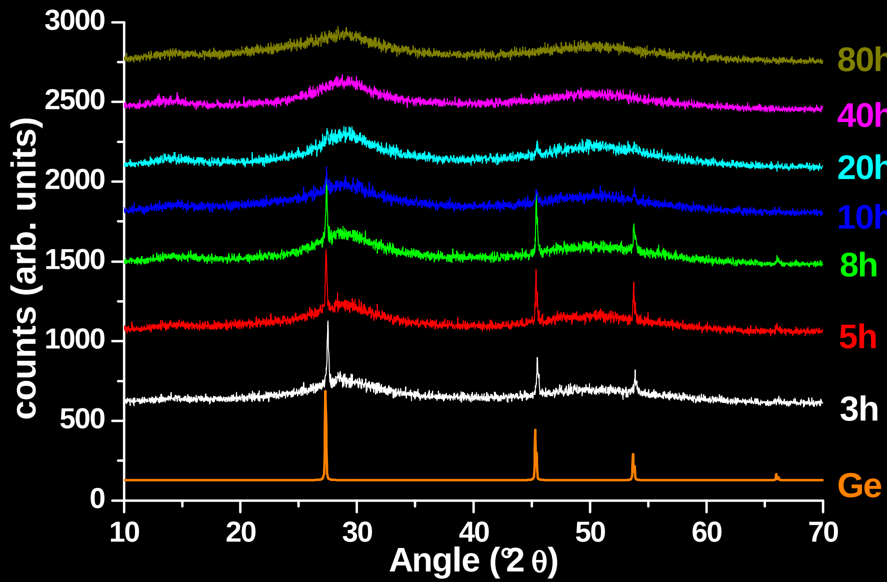


Progressive reaction between the elements and lowering of particle size

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

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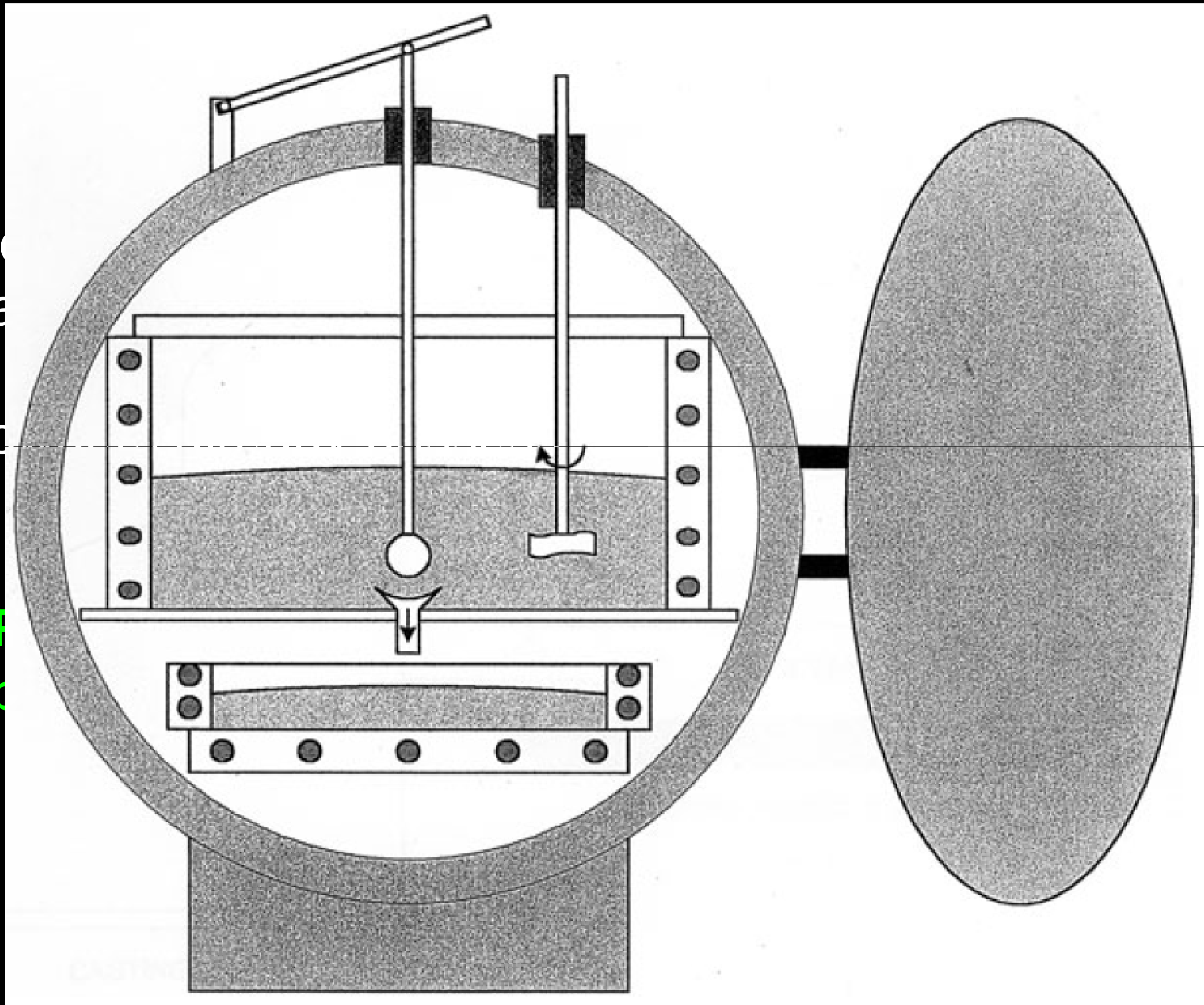

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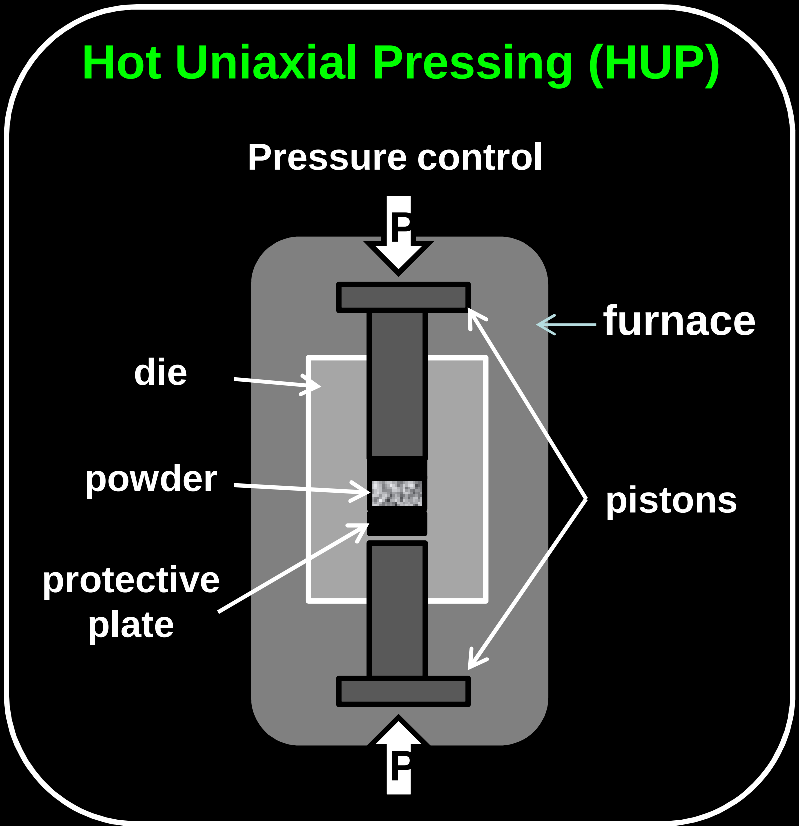
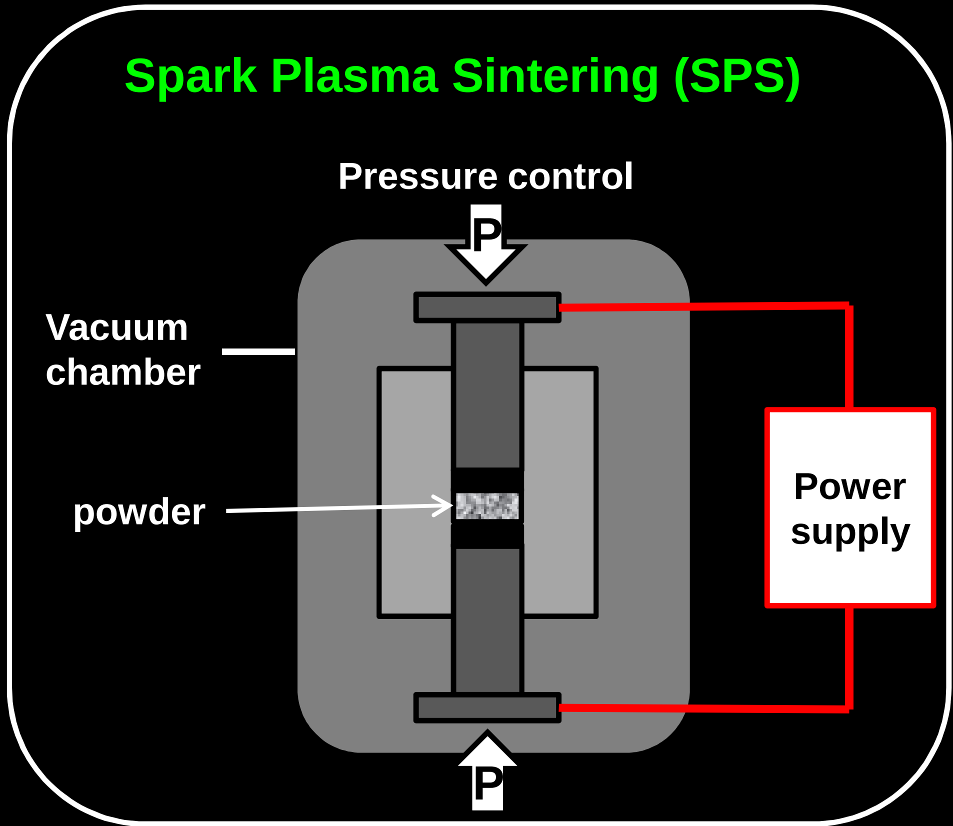
Bulk glass/lenses fabrication by hot pressing

Principle: sintering of the powder at a temperature above the glass transition temperature (Tg) but below the melting temperature (Tm)





Faster temperature ramps reached with SPS

Conventional hot pressing needs stable glasses

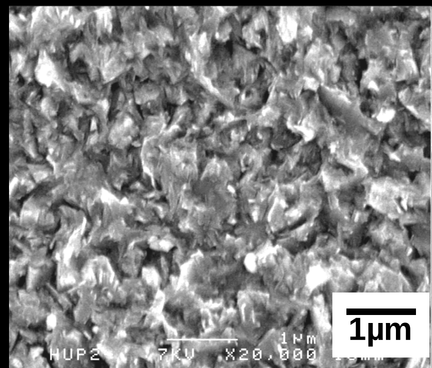
80$GeSe_2$-20Ga_2Se_3 composition: $\Delta T<100°C$

Materials obtained:

- Inhomogeneous sintering (thermal profile of the press)

- Uncontrolled crystallization

- No optical transmission



Crystallization due to prolonged stages at T>Tg

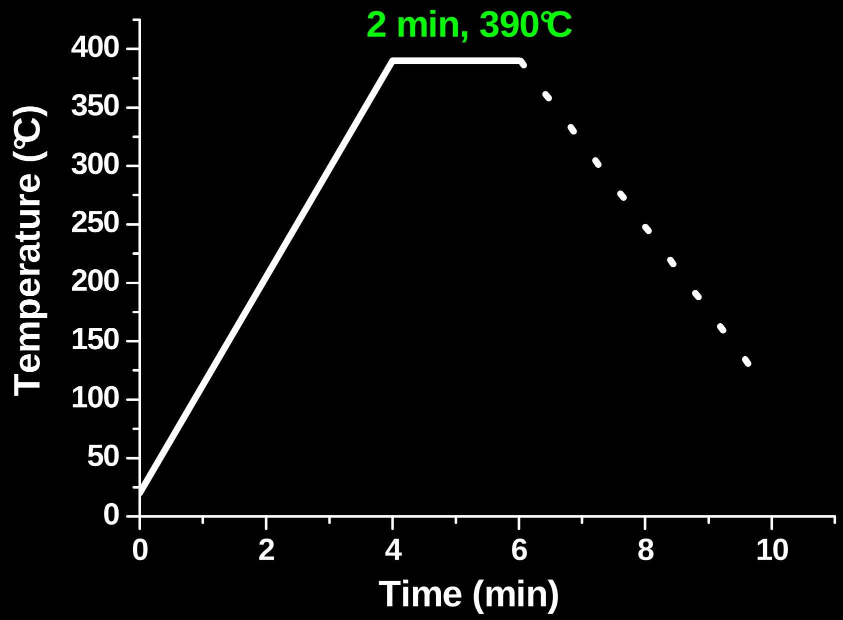
Need to reduce sintering process duration => SPS

Fast sintering of $80GeSe_2$-$20Ga_2Se_3$ powder with SPS

Dr Synter 505 Syntex SPS machine

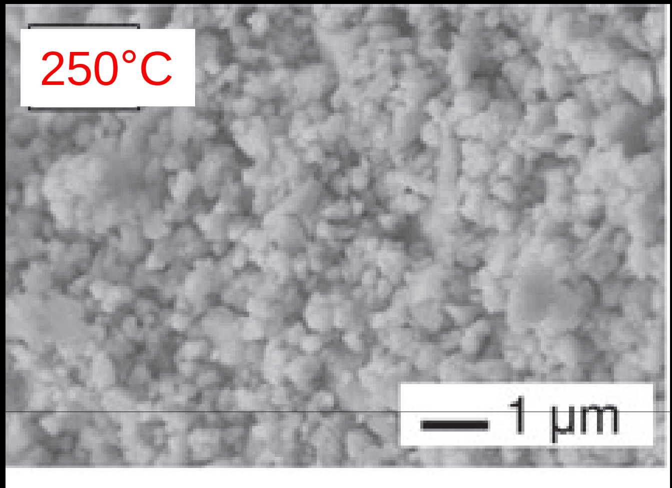
Experimental conditions

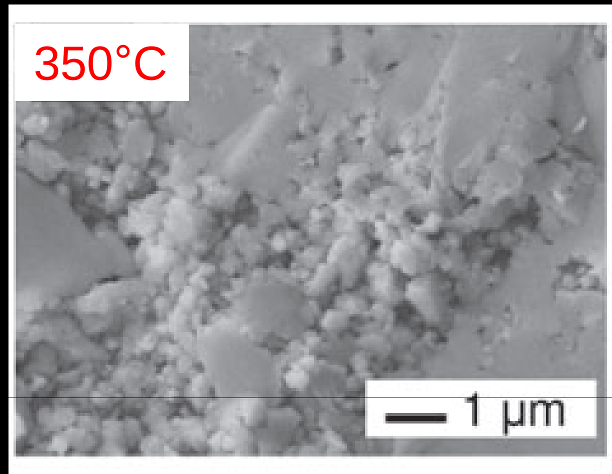
- Under vacuum
- Thermal treatment

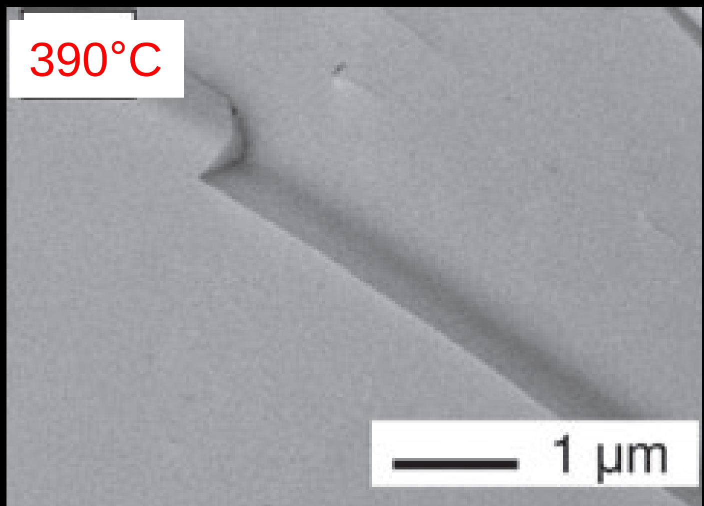


Total duration: 10 min (more than 2h for HUP)

glass bulks sintered at different dwell temperatures (50 MPa, 2-min)







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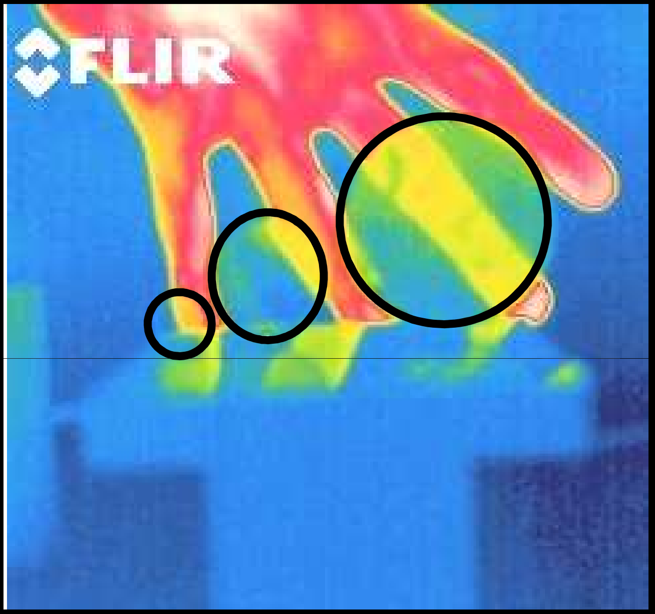
J. Am. Ceram. Soc., 95 [7] 2211–2217 (2012)

Fast sintered $80GeSe_2$-$20Ga_2Se_3$ glass discs

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

visible

Densification > 99%



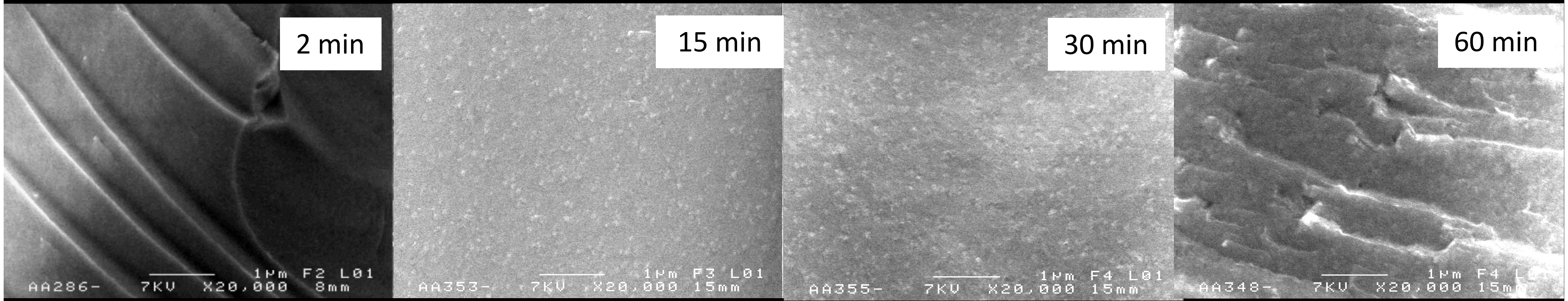
Thermal camera
8-12µm

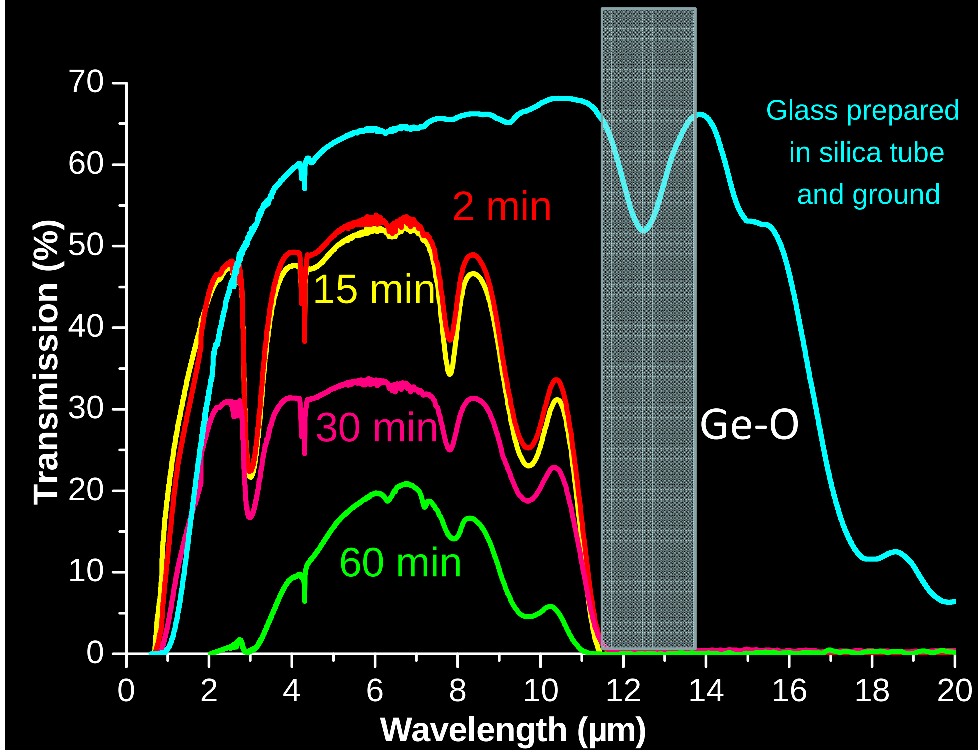
Transparent bulk samples Ø = 8 mm, 20 mm et 36 mm

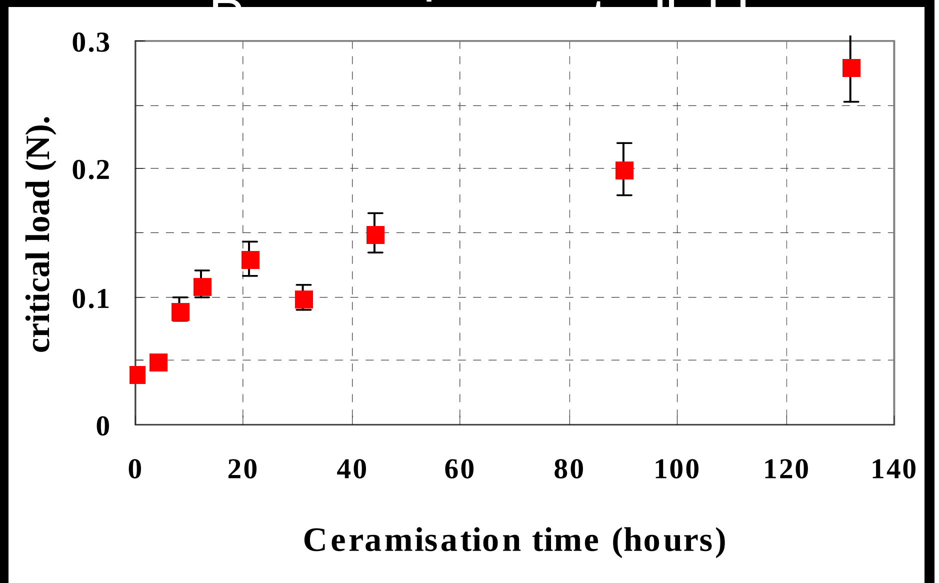
Maximum diameter obtained using silica tubes = 9 mm

Fast sintered $80GeSe_2$-$20Ga_2Se_3$ Glass-Ceramics

Sintering at 390°C for longer durations







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