Non-oxide / chalcogenide glass optics

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Special thanks to Prof. J. TROLES and Dr. L. CALVEZ


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English Channel
Strait of Dover
Dunkirk
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Lille
Arras
Valenciennes
Antwerp
Brussels
BELGIUM
Cologne
Amiens
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Cherbourg
Le Havre
Beauvais
Rouen
Caen
Sedan
LUX
Luxembourg
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Meaux
Paris
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Châlons-en-Champagne
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Nantes
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Besançon
Pontarlier
Bern
SWITZERLAND
Bressuire
Moulins
Poitiers
Geneva (CH)
Mont Blanc 4,810.45 m (15,782 ft)
La Rochelle
Roanne
Riom
Lyon
Annecy
Saintes
Limoges
Clermont-Ferrand
Chambéry
Angoulême
Bourg-Saint-Maurice
Saint-Étienne
ATLANTIC OCEAN
Bay of Biscay
Périgueux
Brive-la-Gaillarde
Le Puy
Valence
Grenoble
Turin
Aurillac
Bordeaux
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Montélimar
Agen
Alès
Avignon
MONACO
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Biarritz
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ANDORRA
Calvi
Mediterranean Sea
FRANCE
National capital

Outline

- Generality of glasses
- Why glasses and why non-oxide glasses
- Current technique for chalcogenide glass fabrication
- Challenges and future trends for chalcogenide glass and lens fabrication
- Summary

Glass and amorphous materials

What is glass?

A glass, whether in bulk, fiber or film form, is a non-crystalline solid (NCS). In principle, any substance can be vitrified by quenching it from the liquid state, while preventing crystallization, into a solid glass.

Most commercially available glasses, are prepared by melting and quenching. But deposition from a vapor or a liquid solution are alternative methods to obtain glasses, usually in thin film form, some of which may otherwise be rather difficult to prepare from the melt.

Glass formation, although in principle a property of any material, is in practice limited to a relatively small number of substances. And most commercial glasses, available in large bulk shapes, are silicates of one type or another, i.e., materials based on silica, the oxide SiO_2.

What is a glass? (another definition)

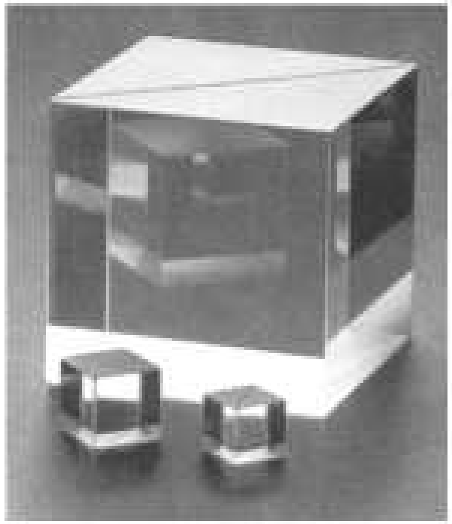
- A glass is an inorganic product of melting which has cooled and become rigid without crystallising

- So defining characteristics
  - Not crystalline, liquid like structure
  - Elastic solid
  - Transformation range behaviour

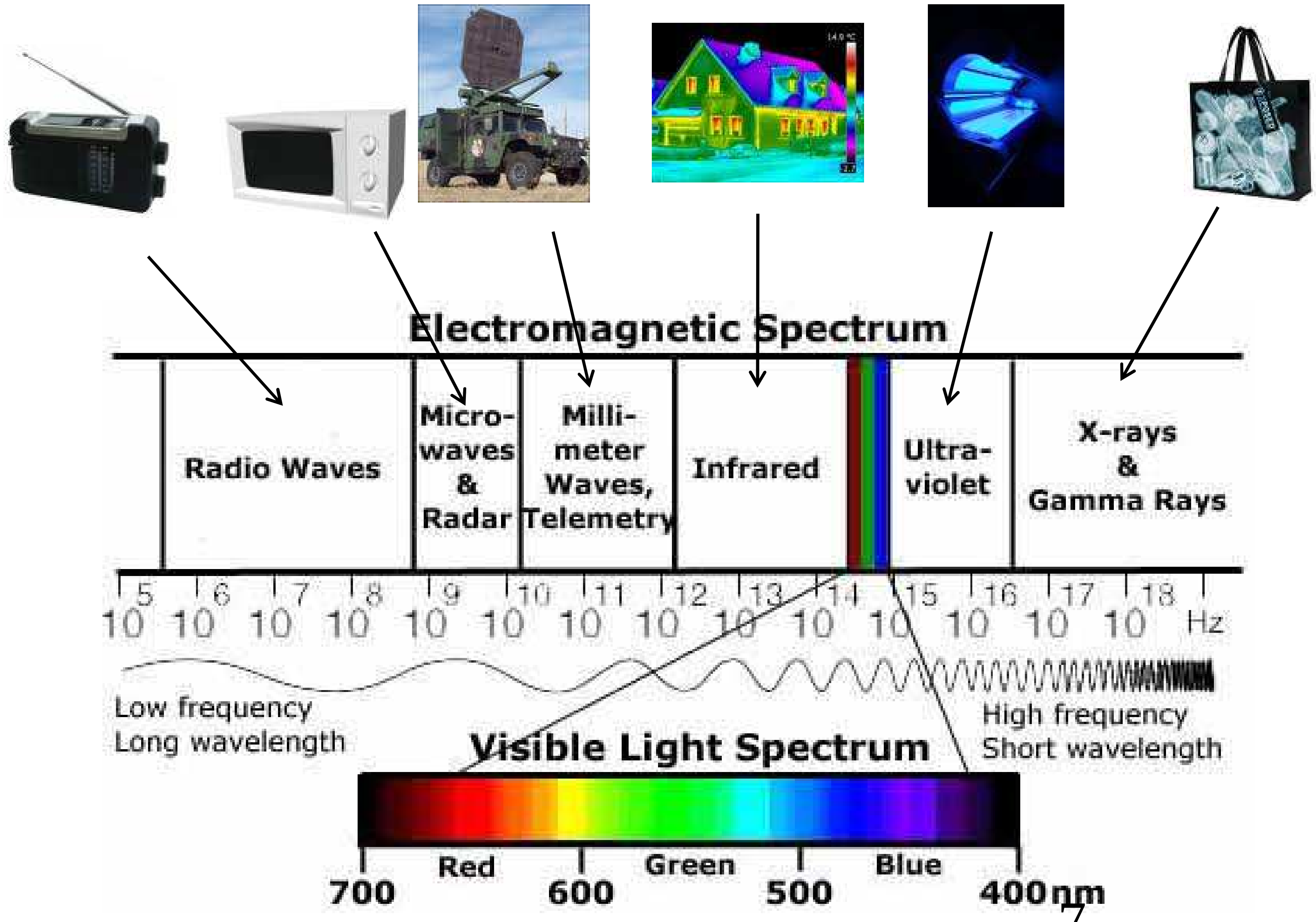
- Common features
  - Transparent – isotropic with no grain boundaries
  - Brittle, hard
- BUT
  - There are organic glasses
  - Glass can be made by methods not requiring melting

Why glass is interesting

- Transparency
- E

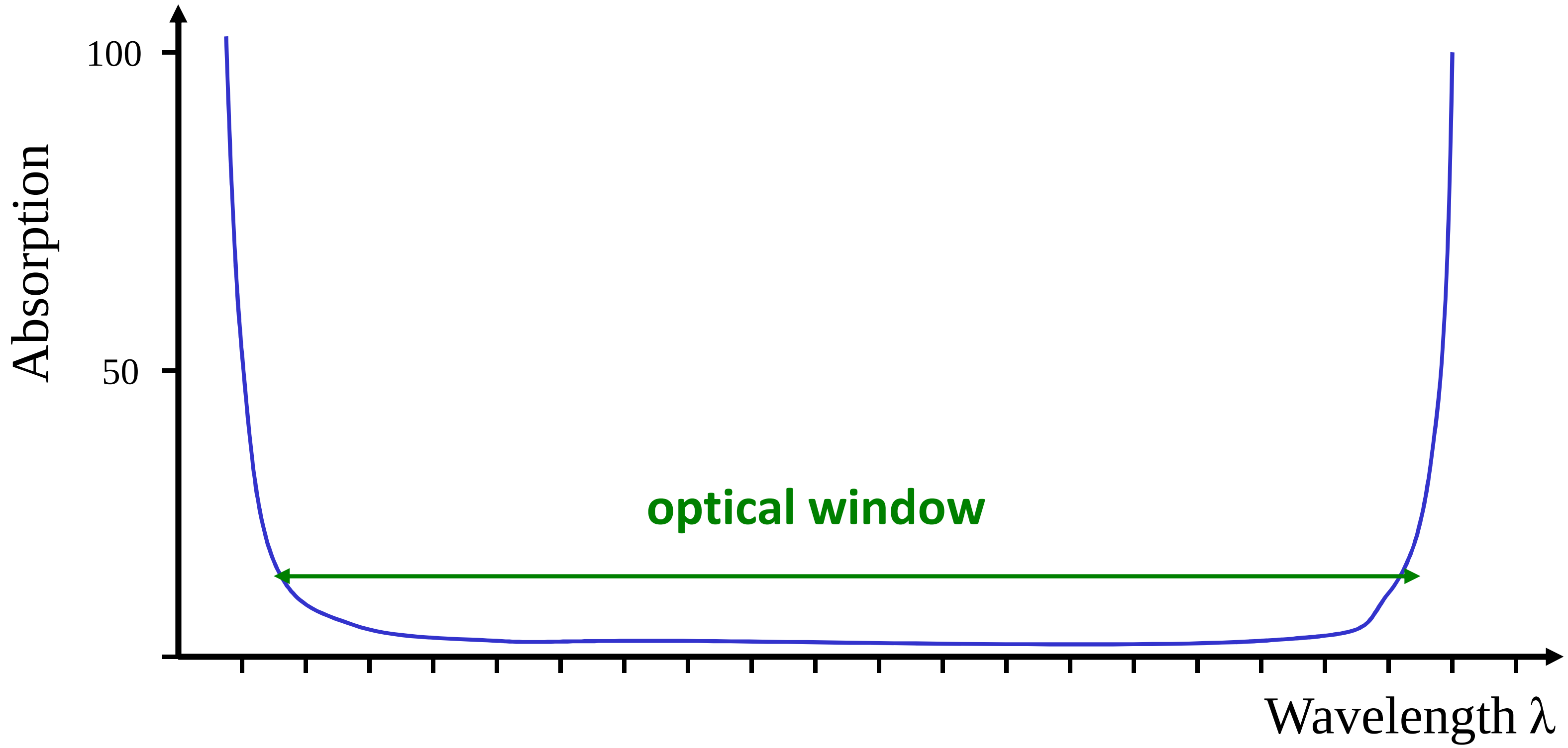


Electromagnetic Spectrum

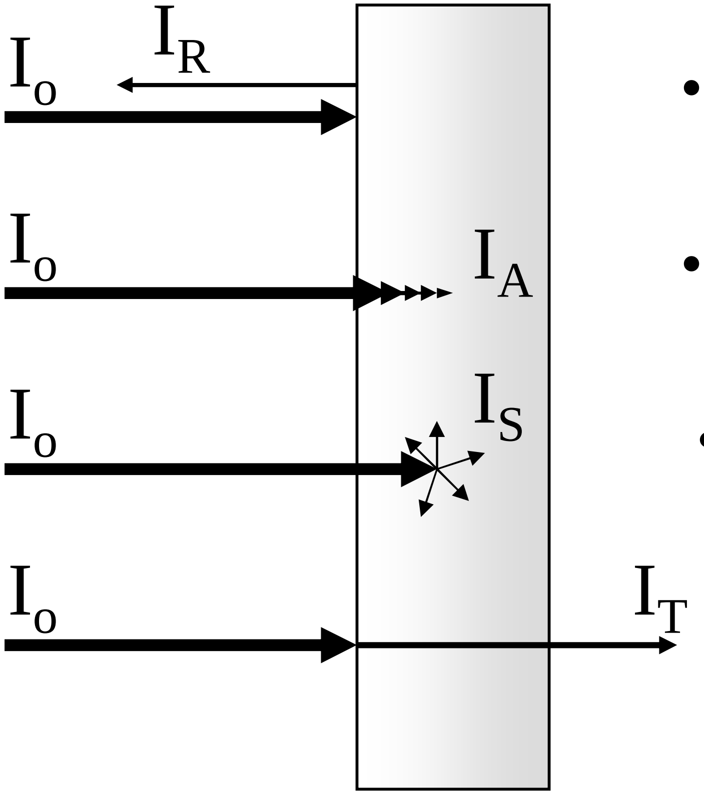


Transparency

- In a very pure solid the transparency domain is delimited on both side of the spectrum by a sharp increase in absorption.
- The material is transparent for the range of wavelength where the absorption is zero or very low.
- This is called the transparency window or **optical window**.



- Four things can happen when light proceeds into a solid.



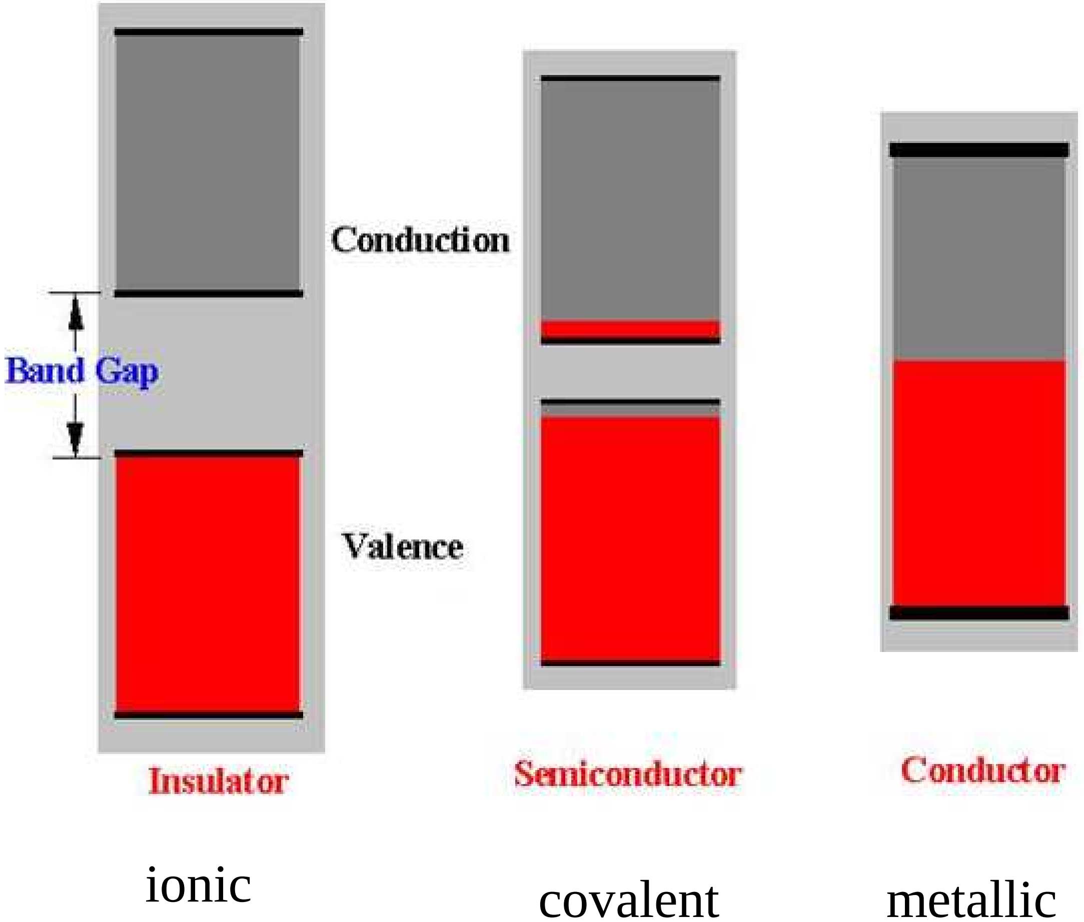
- Part of the light can be reflected by the surface of the solid. Reflection
- Part of the light can be absorbed by coupling into the solid. Absorption
- Part of the light can be scattered by the atoms and defects in the solid. Scattering
- Part of the light can be transmitted through the solid. Transmission

- Therefore, for an incident beam of intensity I_o entering the solid:

$$\mathbf{I_o = I_R + I_T + I_A + I_S}$$

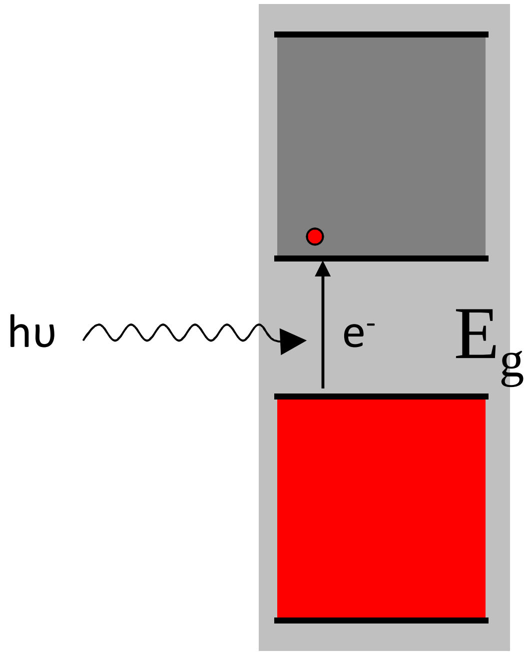
Electronic Band Structure

- On the short wavelength side, light absorption is due to electronic transitions across energy levels in the band structure.

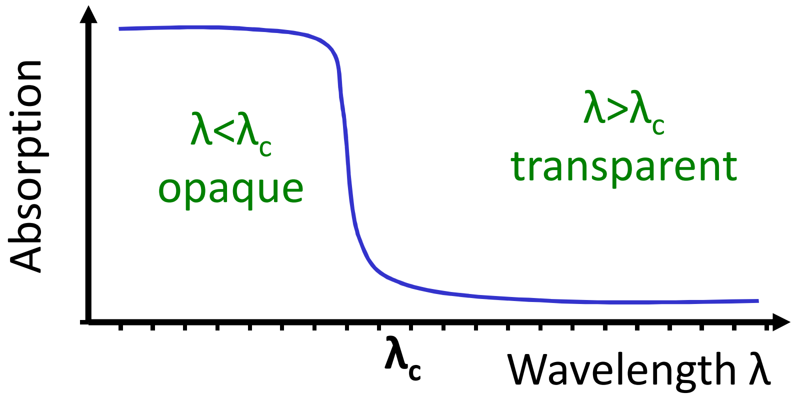


Optical window – the band gap

- On the short wavelength side the increase in absorption is due to electronic transitions in the solid.

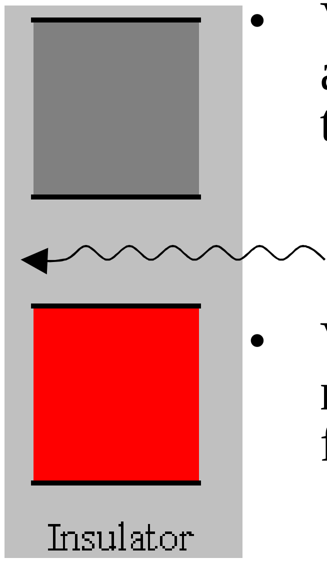


- A solid with bandgap E_g has a cut-off wavelength $\boldsymbol{\lambda_c = hc/E_g}$.
- The solid is transparent to wavelength $\lambda > \lambda_c$ which are not sufficiently energetic to induce an electronic transition.
- The solid is opaque to wavelength $\lambda < \lambda_c$ which are absorbed to promote an electronic transition.



Transparent solids

NaCl E_g=8.5 eV

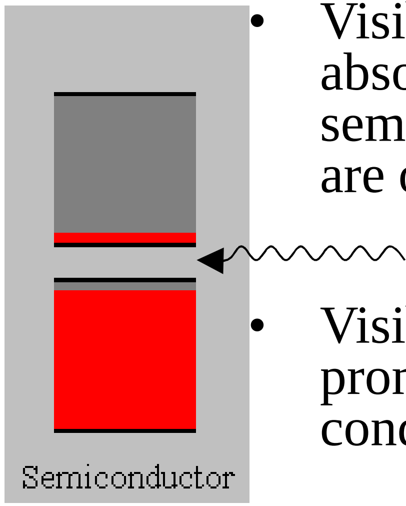


- Visible light is not absorbed by insulator: they are transparent

hυ not absorbed

- Visible photons are not energetic enough for the band gap

Si E_g=1.1 eV



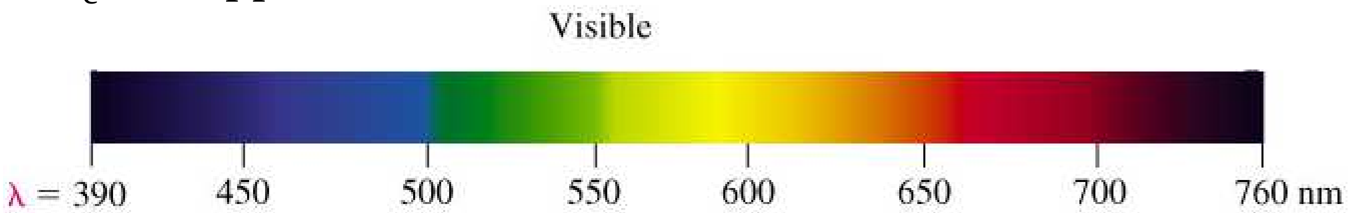
- Visible light is absorbed by semiconductors they are opaque

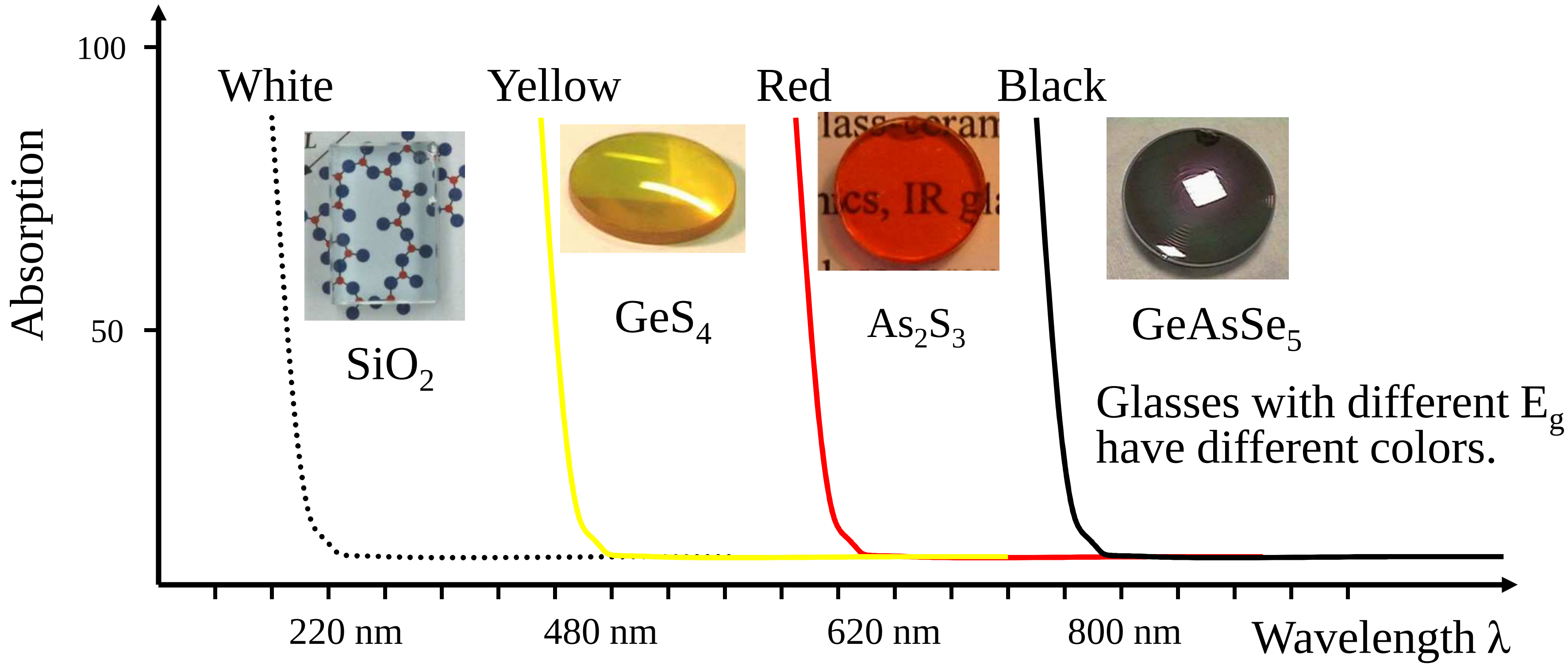
hυ absorbed

- Visible photon can promote an e^- in the conduction band.

Optical window of Transparent solids

- Due to bandgap absorption, solids filter out all the visible light with wavelength shorter than λ_c and appear colored.



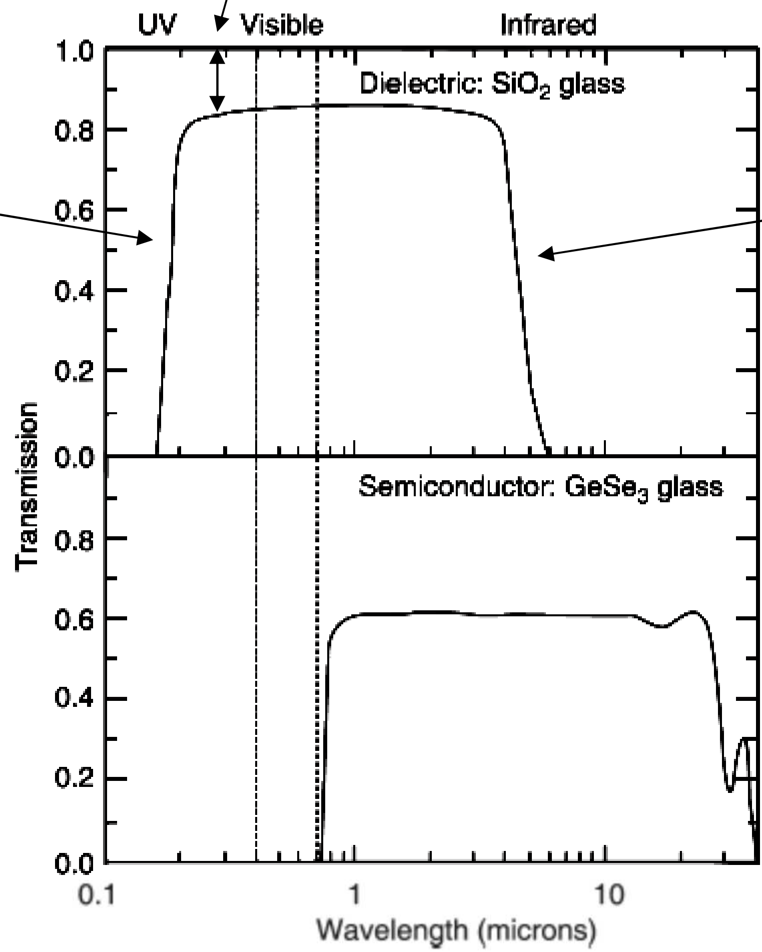


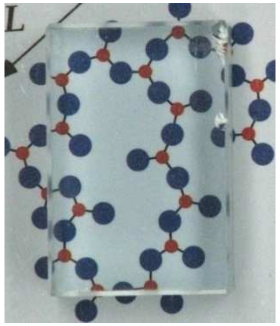
Multi-phonon absorption

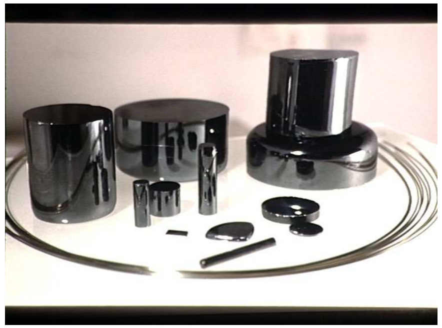
Reflection

Electronic transitions

Multiphonon vibrations



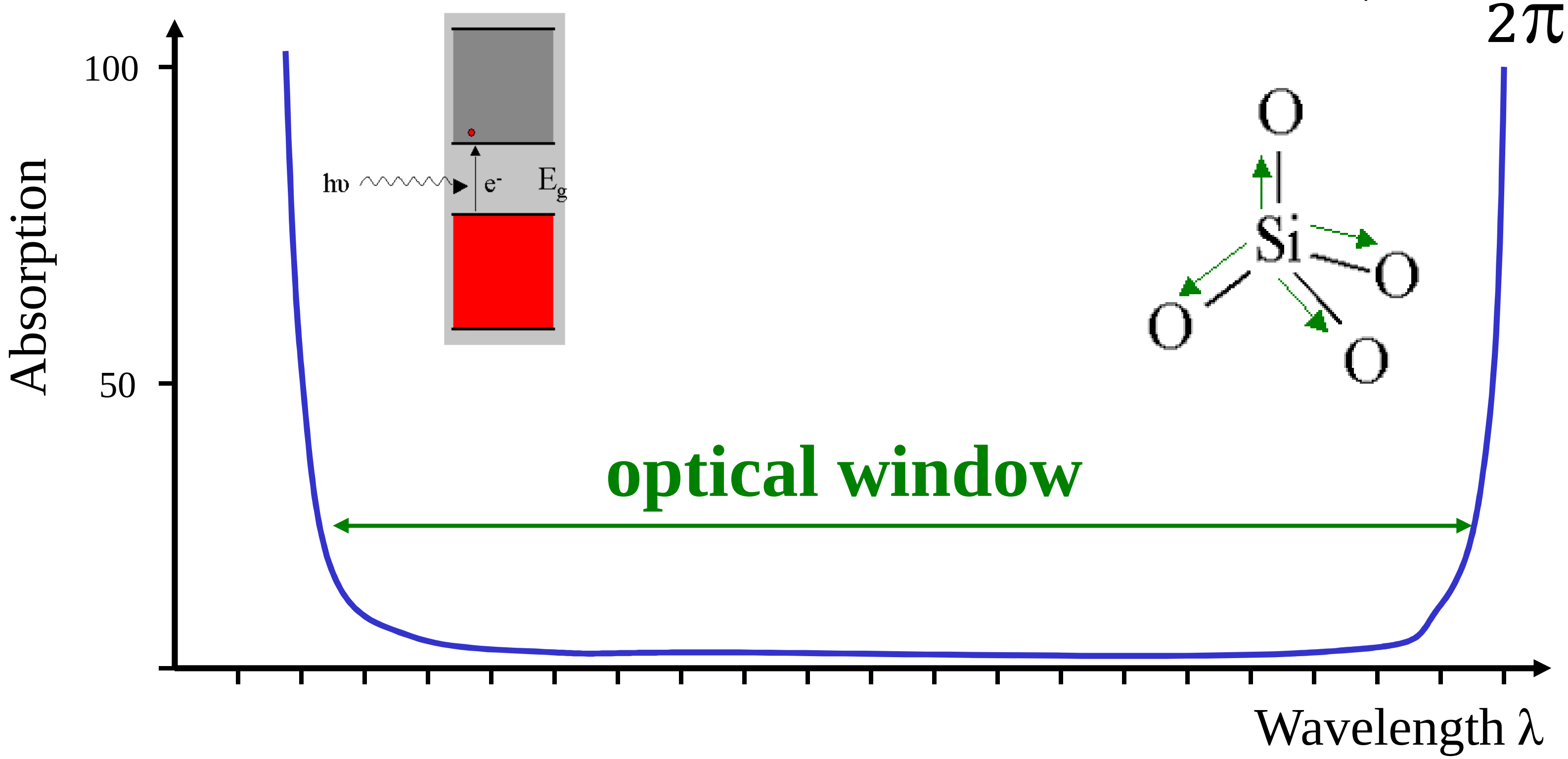




Optical window

- The optical window of a transparent solid is therefore limited at short wavelength by the electronic transitions (absorption of a photon to promote an electron into the conduction band).
- And at long wavelength by the vibrational modes in the solid (the atoms vibrate with the oscillating electric field).

$$V = \frac{1}{2\pi}\sqrt{\frac{K}{M}}$$



Infrared cut-off

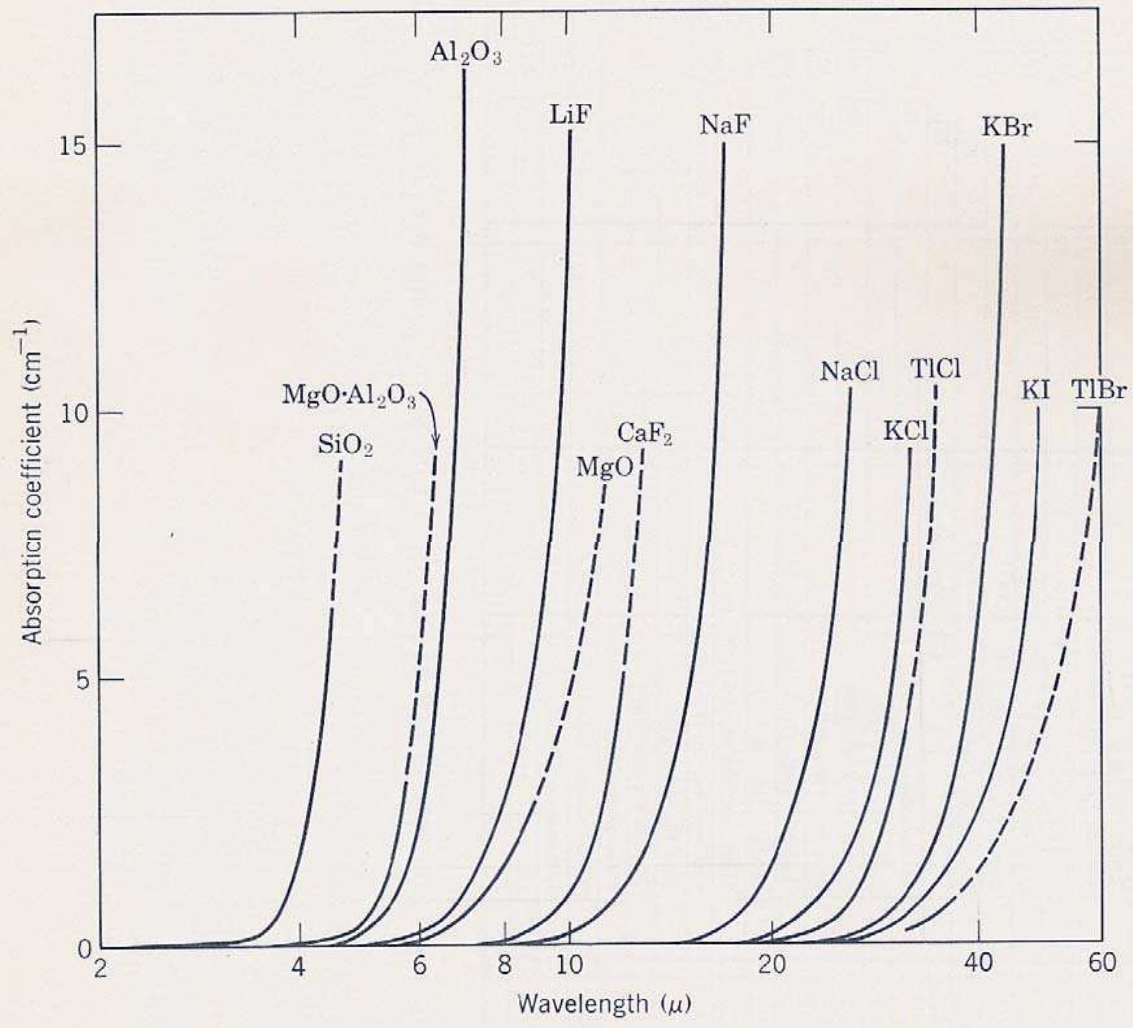


Fig. 13.2. Infrared absorption edges of ionic crystals.

Non-Oxide glasses

- Fluoride glasses
  - ZrF_4-BaF_2-LaF_3-AlF_3-NaF
- Chalcogenide glasses
  - As-S
  - As-Se
  - Te-As-Se
  - Ge-As-Se
  - Ge-Sb-Se

Heavy metal fluoride glasses

- Zr-Ba-La-Al-Na-F (the ZBLAN glass)

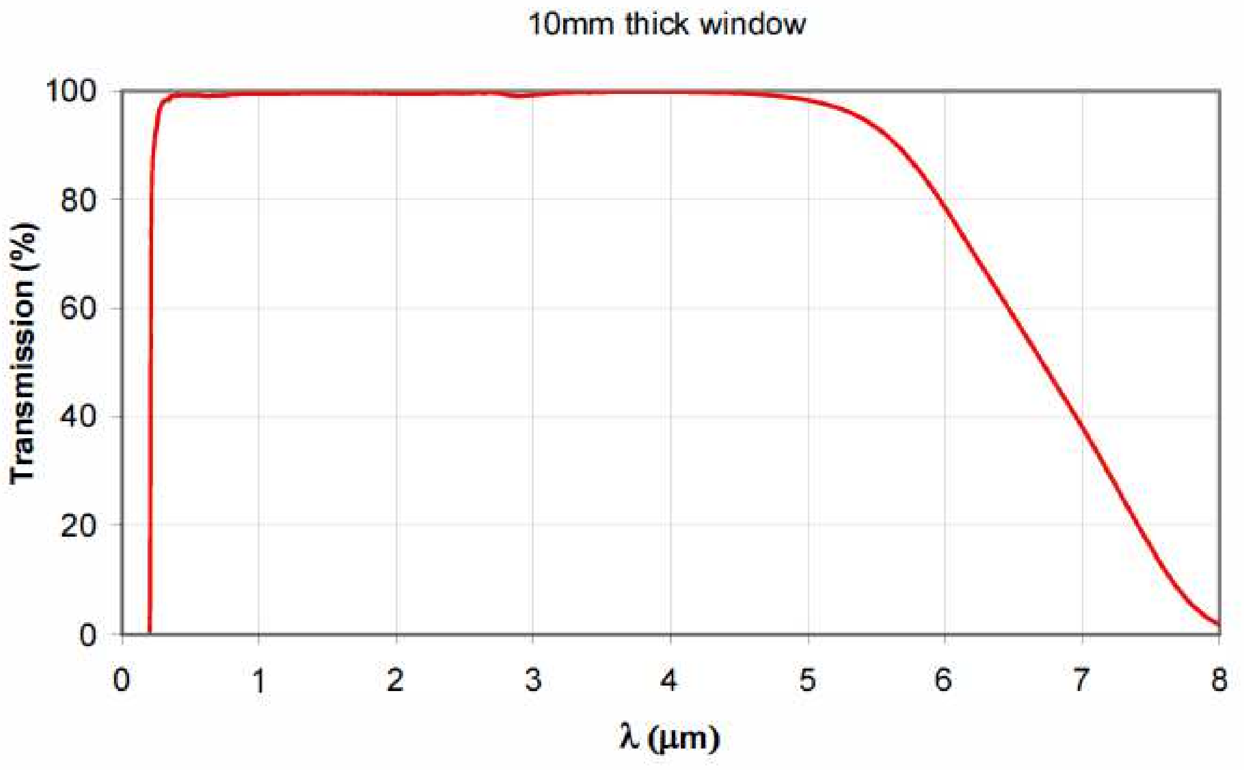
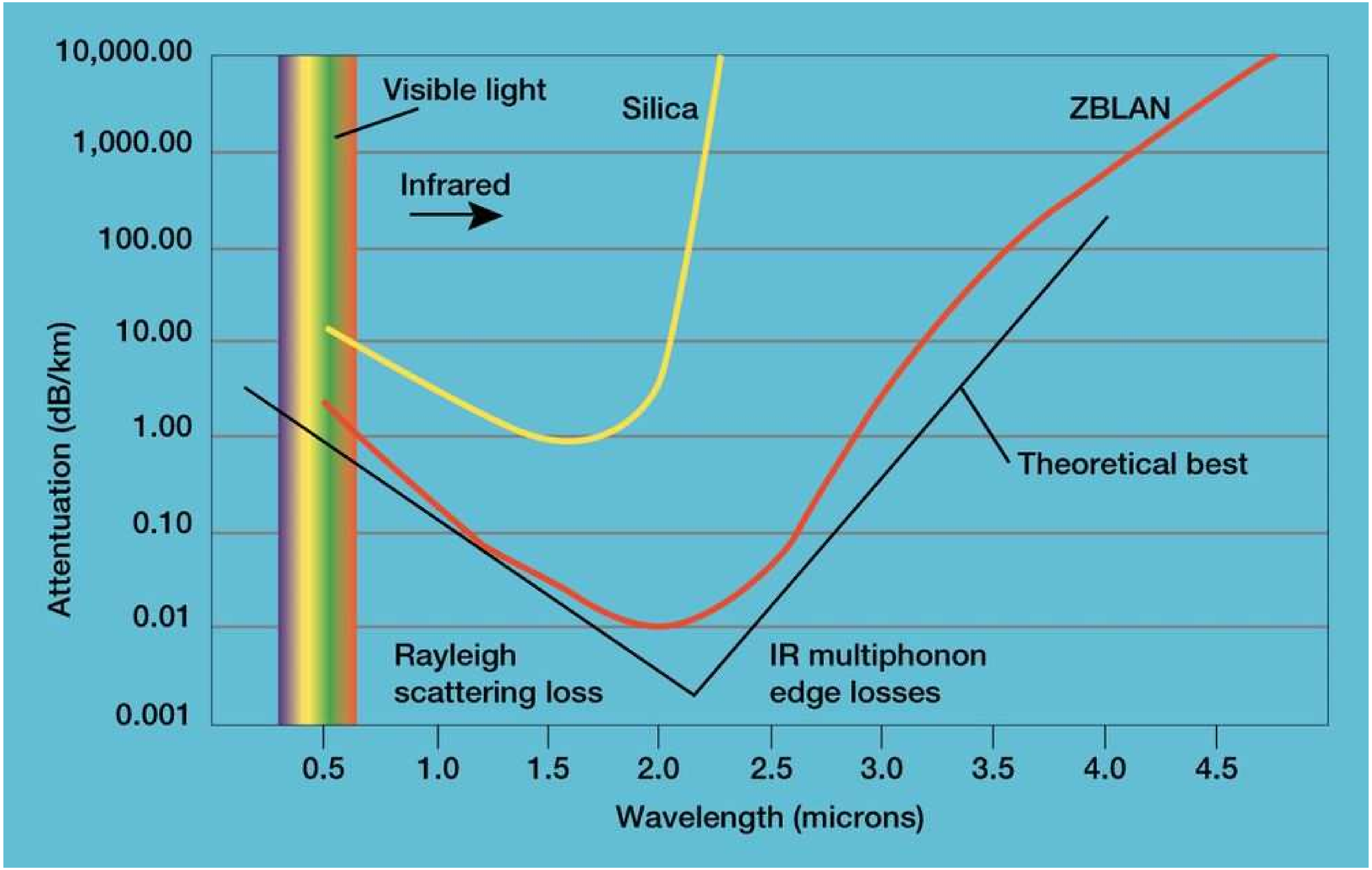


Figure 1: transmission window of Fluorozirconate glass sample (10 mm tick)

M. SAAD, SPIE-OSA-IEEE/Vol.8307

Motivation for studying fluoride glasses



http://science.nasa.gov/science-news/science-at-nasa/1998/msad05feb98_1/

Some simulations

- Silica fibre
  - Minimum losses : 0.2 dB/km
  - With an Er doped fiber amplifier : 30 dB
  - Distance between the amplifiers : 150 km

- Fluoride glass fibre
  - Minimum theoretic losses : 0.002
  - Distance between the amplifiers : 15 000 km!!

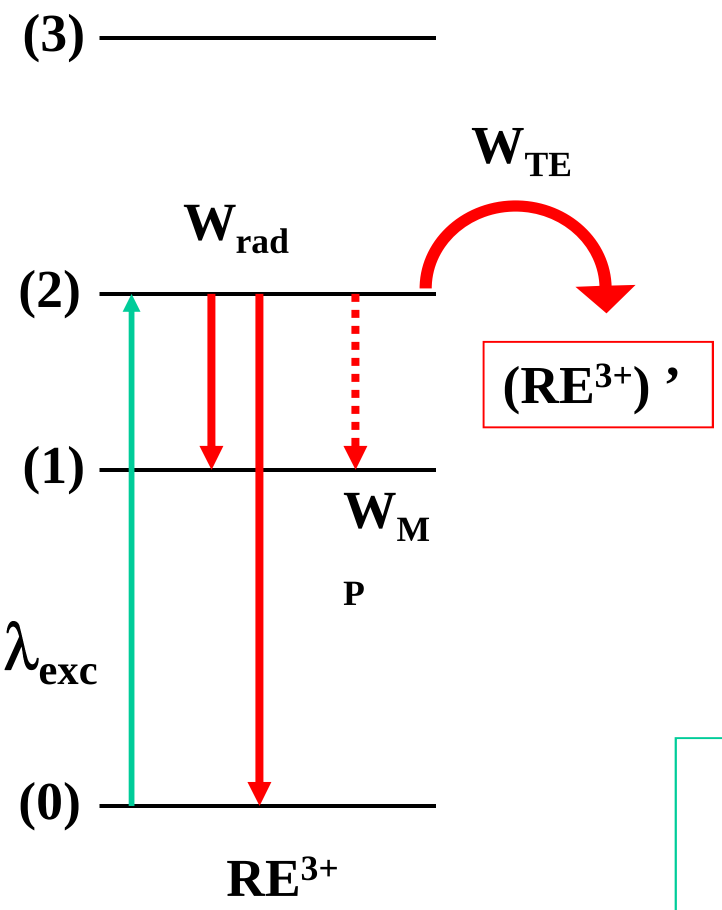
Strong worldwide motivation in the mid-1980s and 1990s

Theoretic losses never approached

- Complexity of composition
- Risk of crystallisation

Many applications possible with losses in the range of dB/km

Spectroscopy of rare earth ion RE^{3+}



Total probability of desexcitation:

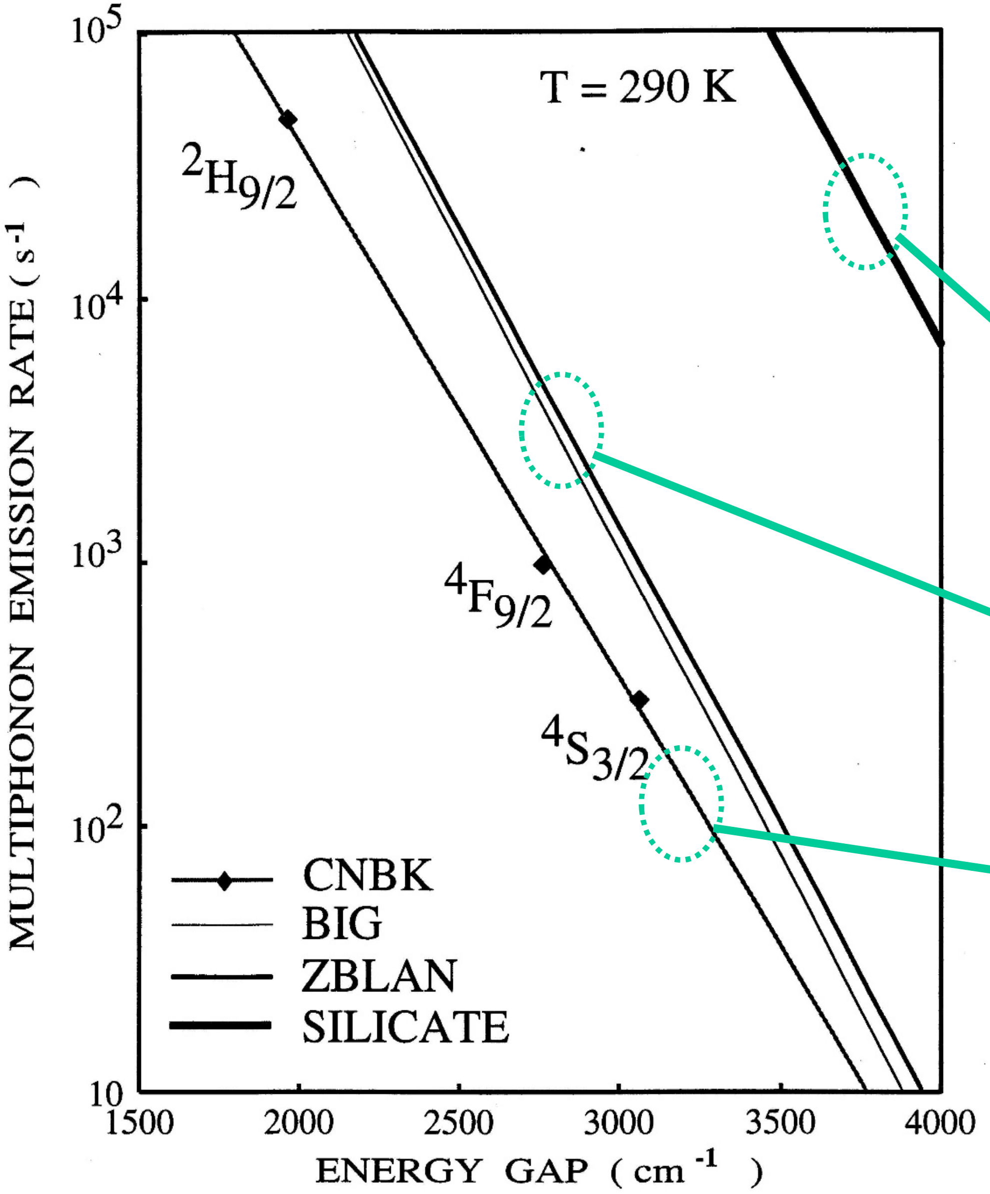
$$W_{tot} = W_{rad} + W_{MP} + W_{TE} + \ldots$$

Quantum efficiency :

$$\eta = \frac{W_{rad}}{W_{rad} + W_{MP} + W_{TE}}$$

Depends on matrix

W_{MP} ↑ with high phonon energy



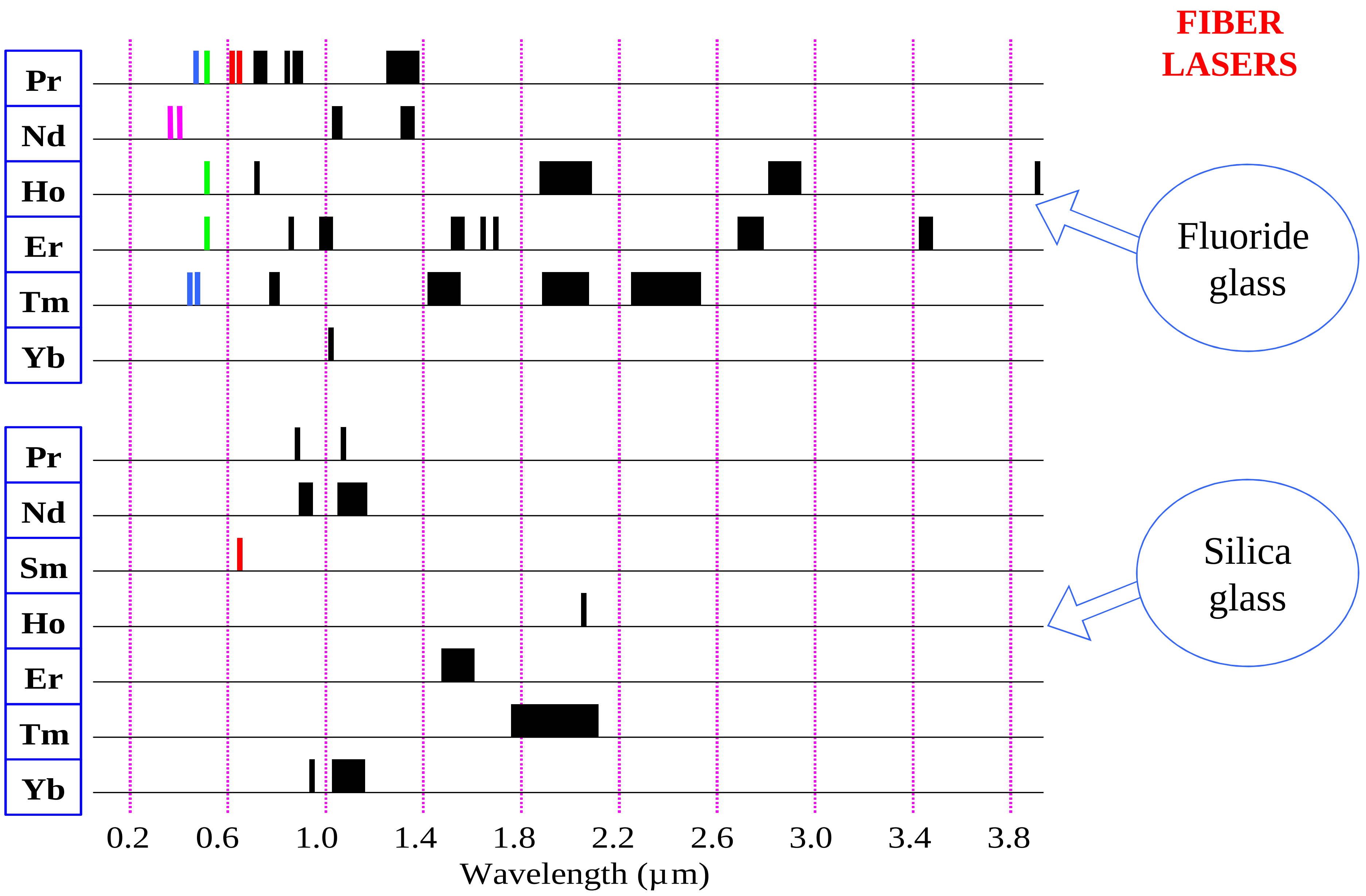
Probability of Multiphonon Relaxations in RE-Doped Glasses

Glass Phonon Energies

Si – O : 1100 cm^{-1}

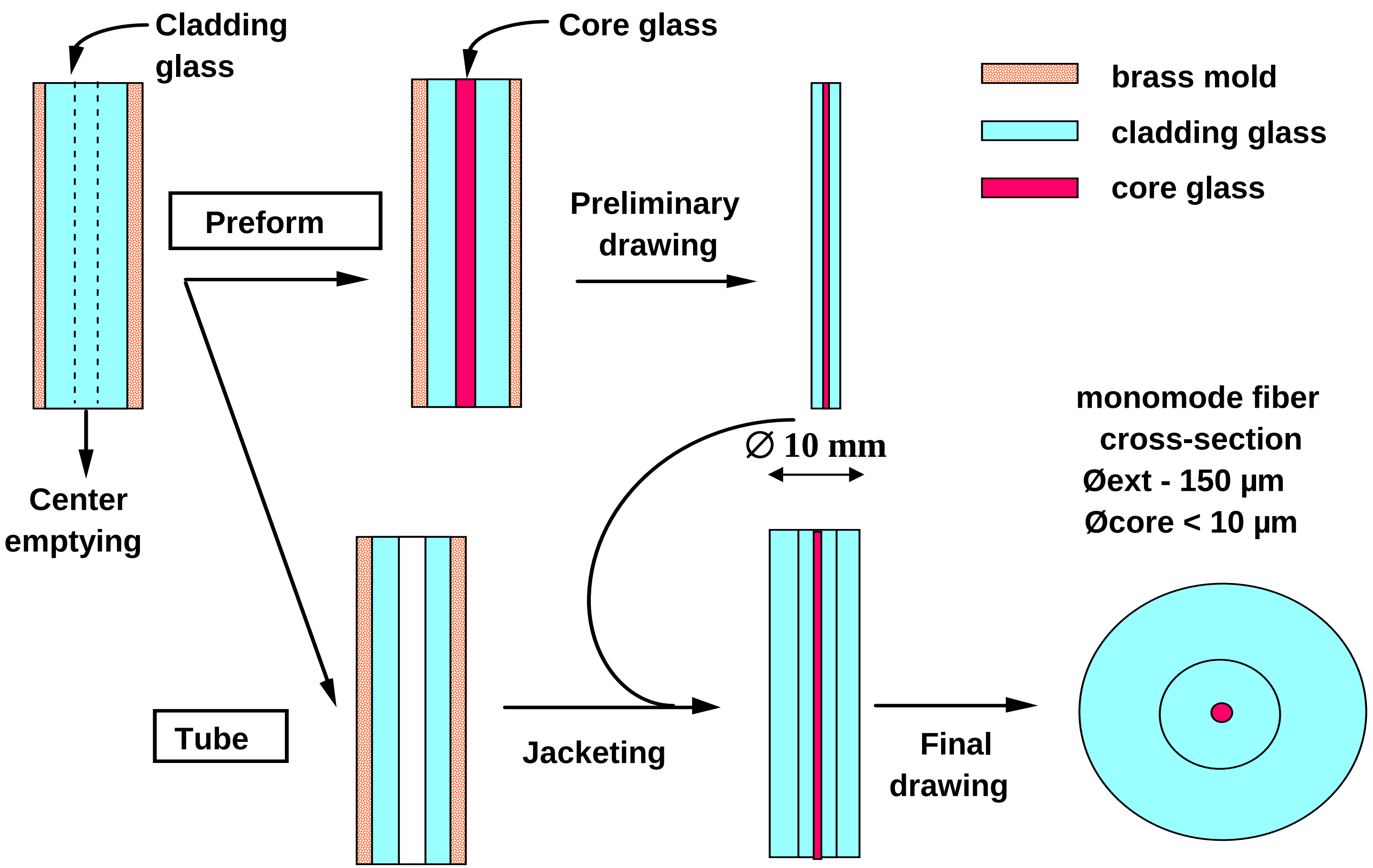
Zr – F : 580 cm^{-1}
In – F : 510 cm^{-1}

Cd – F : 370 cm^{-1}
Cd – Cl : 250 cm^{-1}

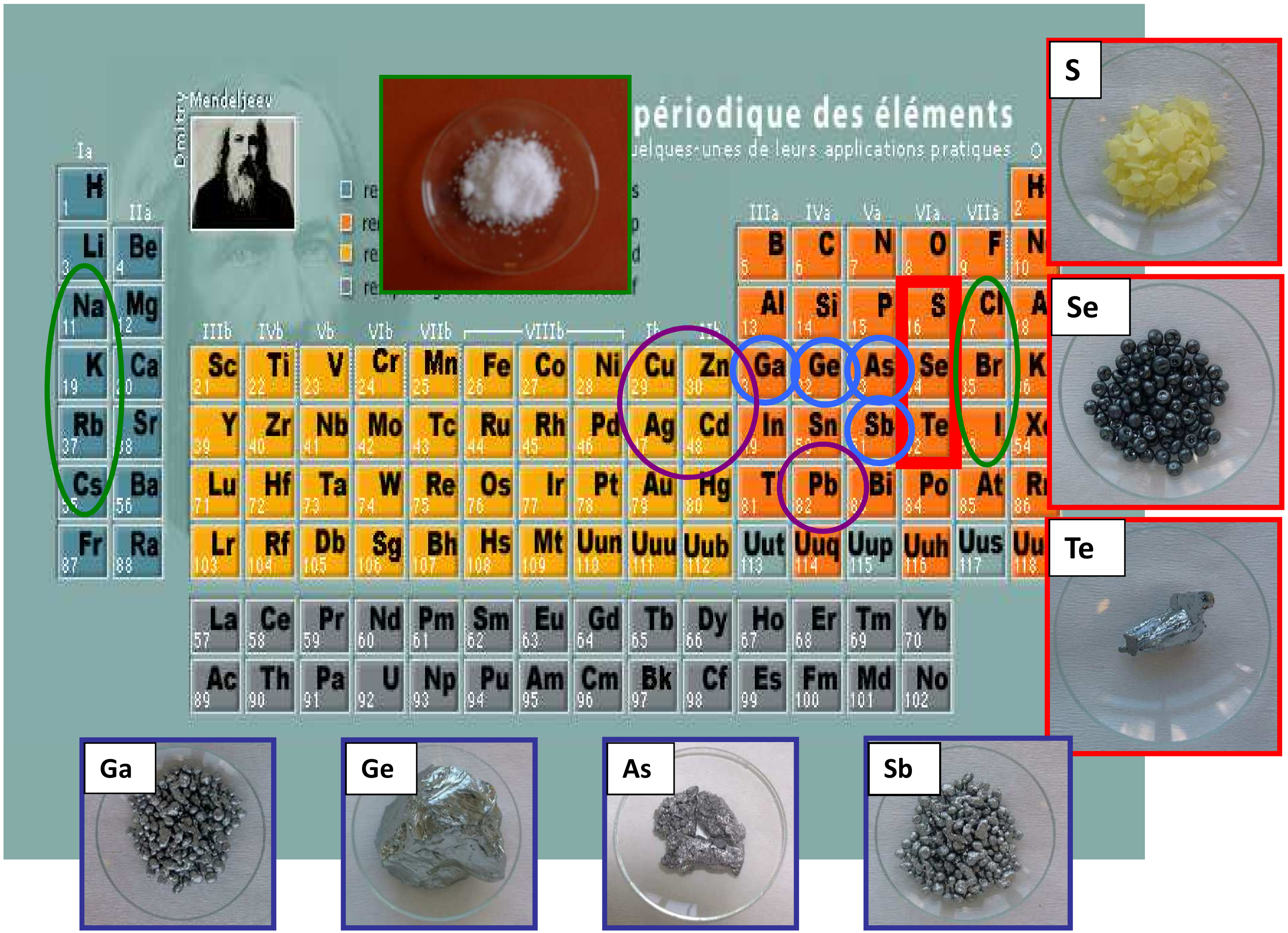


FIBER
LASERS
Pr
Nd
Ho
Er
Tm
Yb
Pr
Nd
Sm
Ho
Er
Tm
Yb
Fluoride glass
Silica glass
0.2
0.6
1.0
1.4
1.8
2.2
2.6
3.0
3.4
3.8
Wavelength (µm)

Single mode fiber fabrication in fluoride glasses

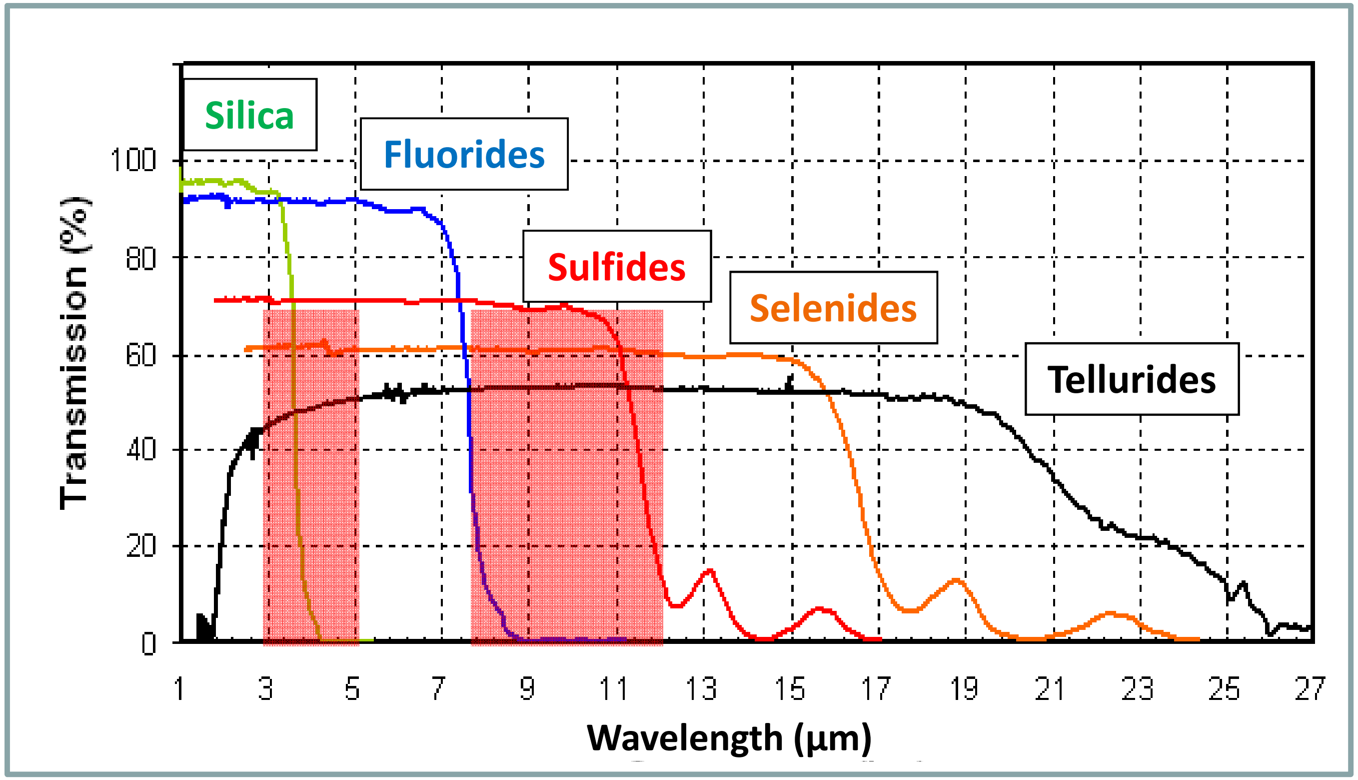


Chalcogenide glasses - Definition

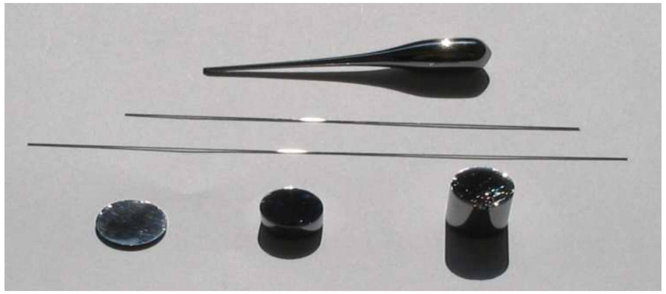


Chalcogenide glasses - Properties

Large transparency in the Infrared



moldable

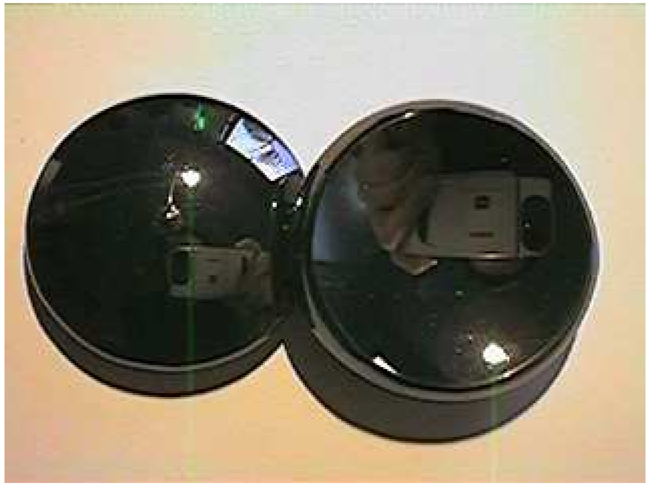


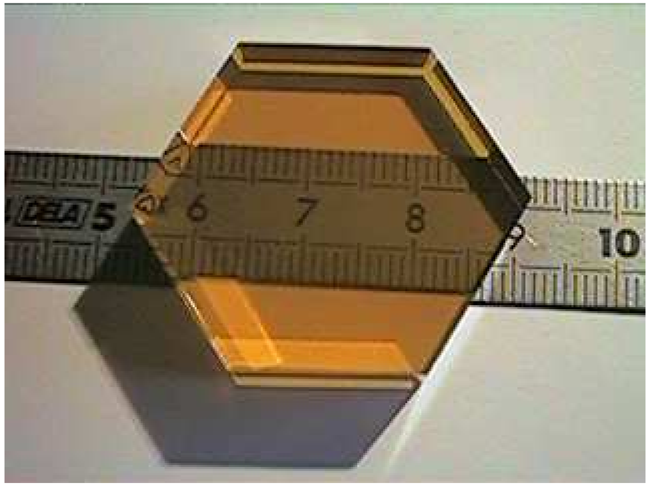
Low dn/dT

Most studied chalcogenide glasses

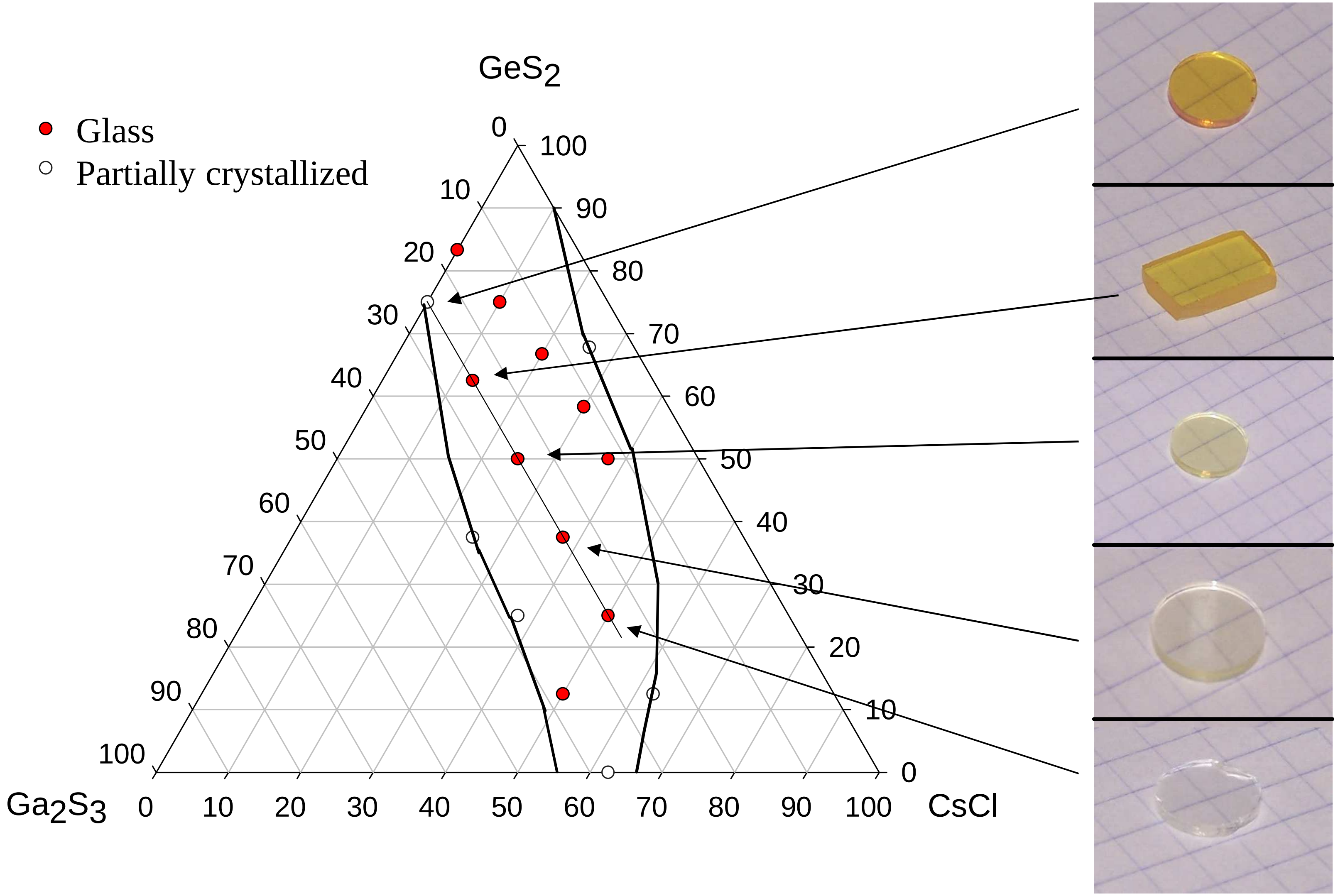
- Sulphide glass: active applications
- Te-As-Se: for fibre optic application
- As_2S_3 and As_2Se_3: for fibre optic application
- Ge-As-Se: lens, window, prism
- Ge-Sb-Se: lens, window, prism

Chalcogenide glass samples



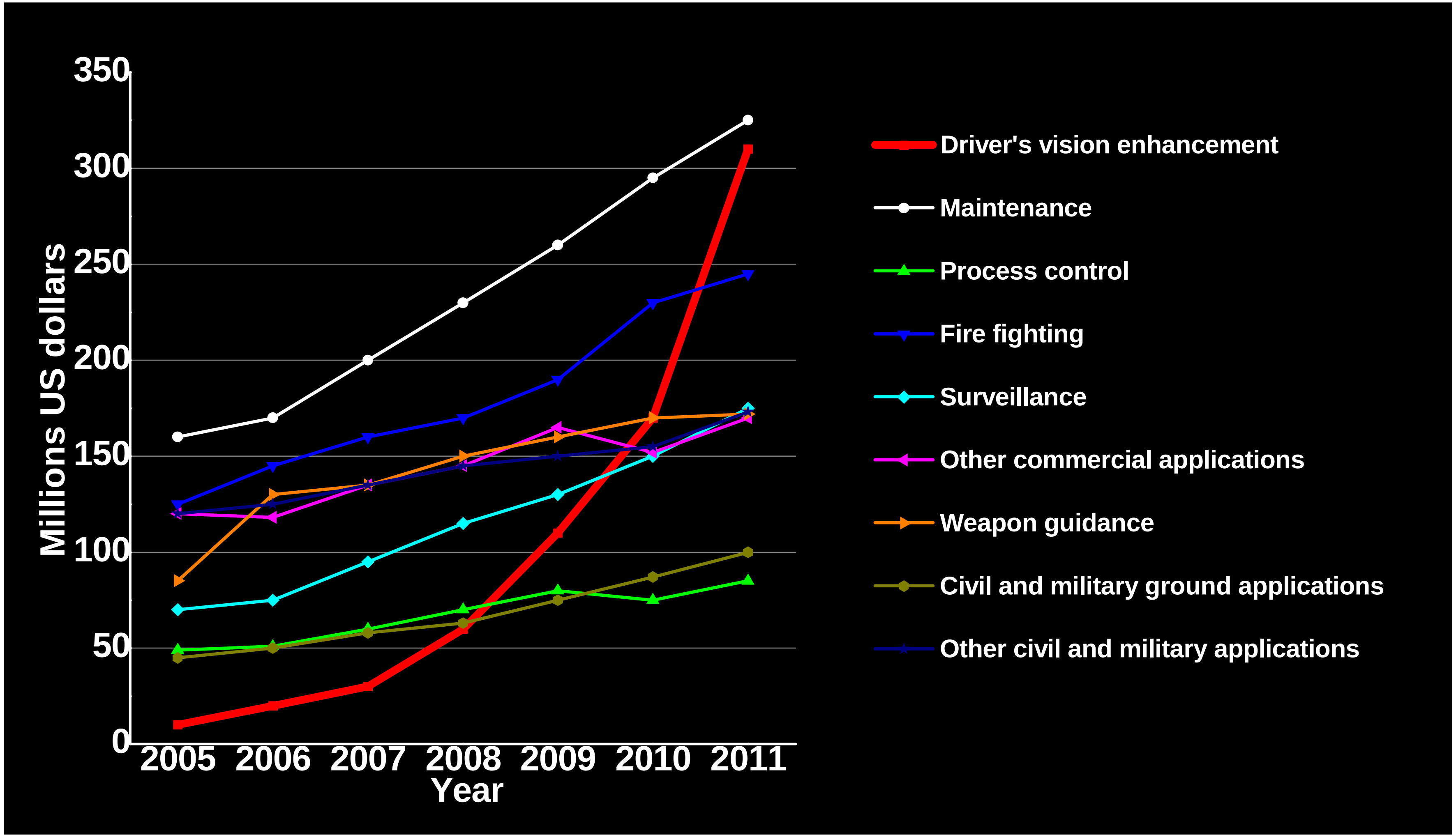


Change of color with the composition



Yannick Ledemi

Thermal Imaging – A growing market



Great progress achieved in uncooled infrared detectors

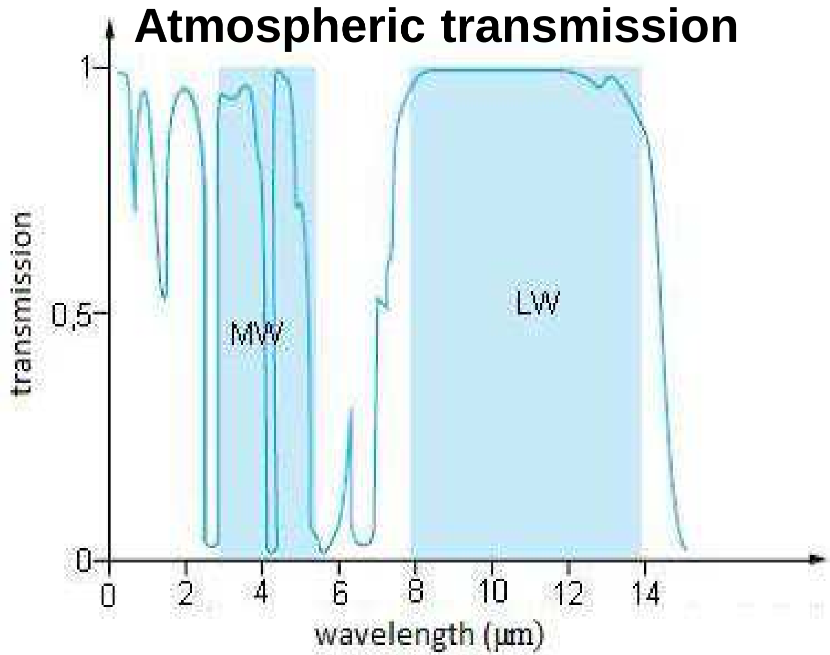
Uncooled system growth : 40% in 2014 : 3.1 b$

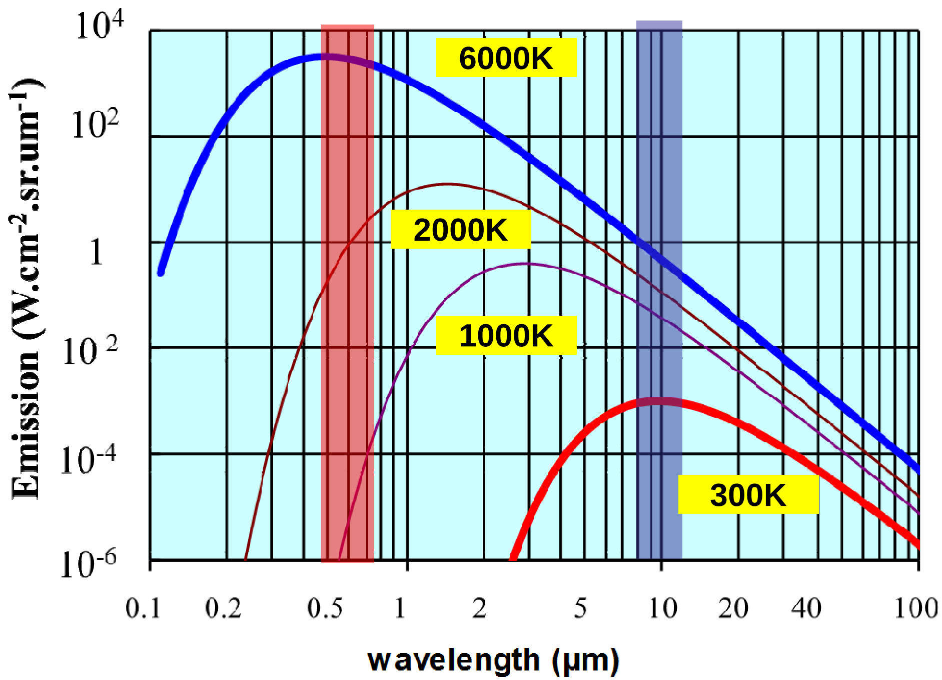
Constant need for cheaper, more efficient materials

Why infrared is interesting for driving assistance

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**

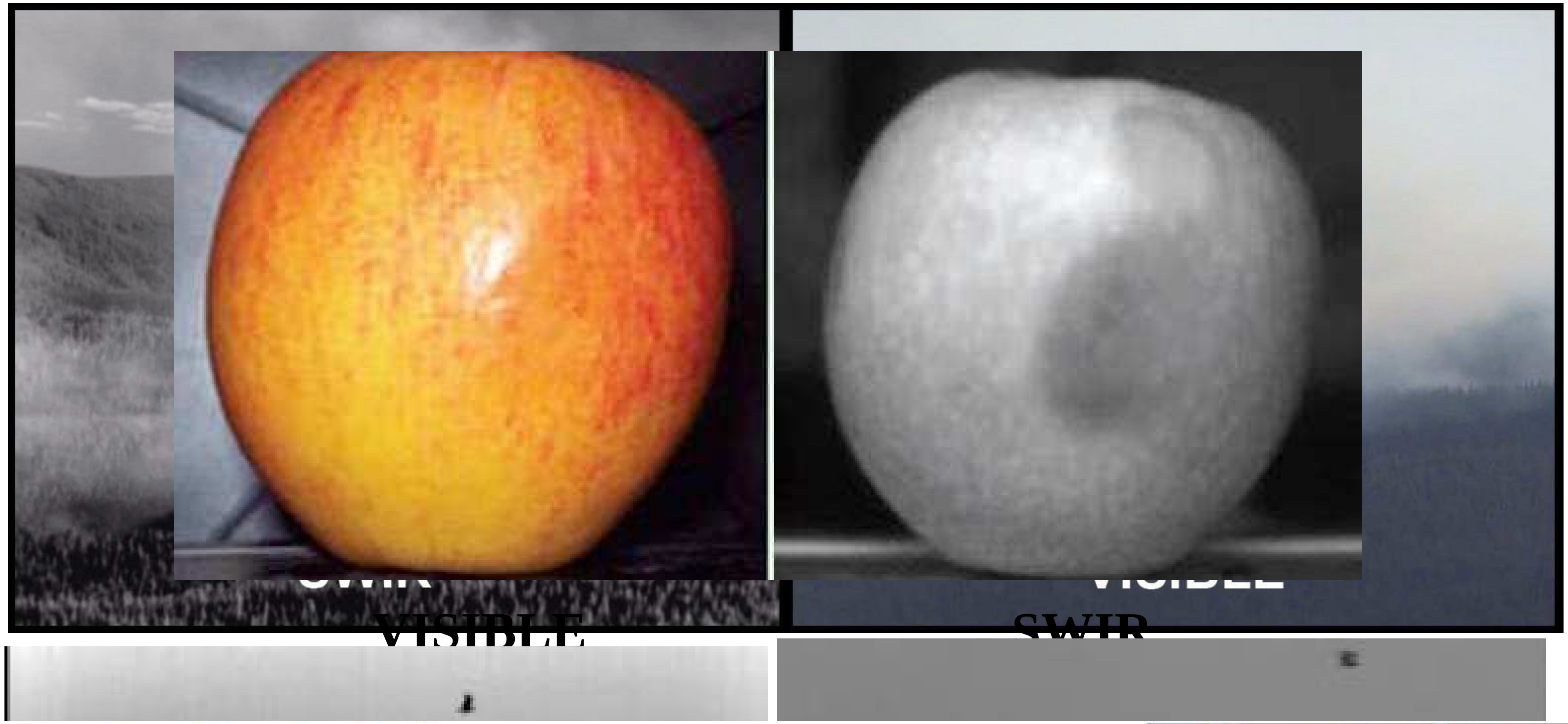
Need for materials transparent in these windows

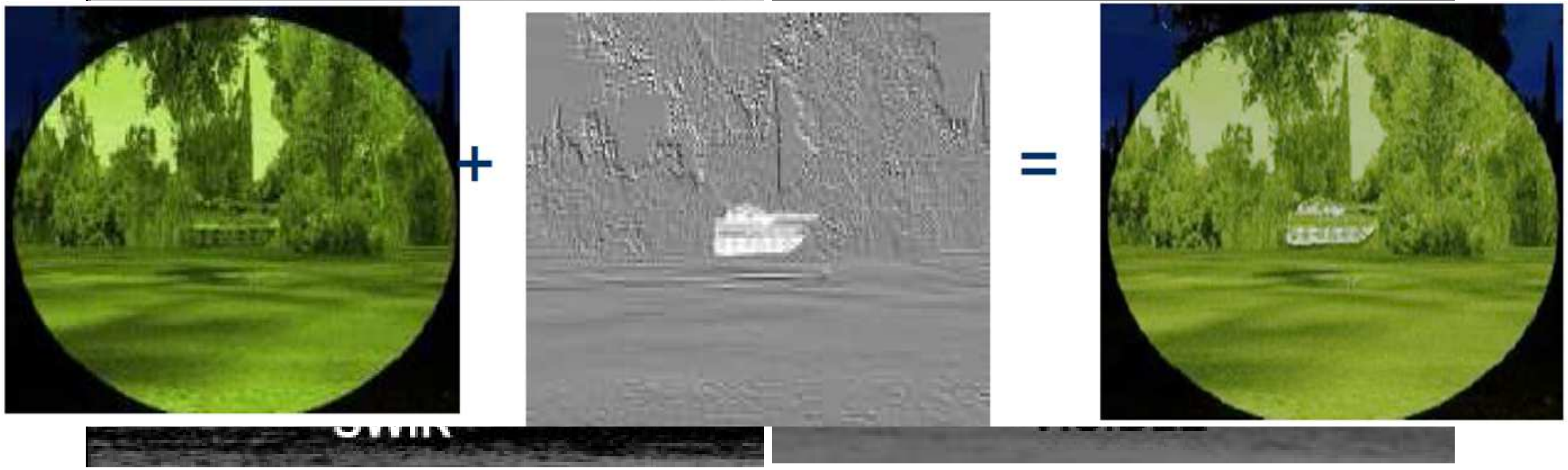
Visible 0.4-0.75 μm

Infrared 8-12 μm

Importance of multispectral imaging

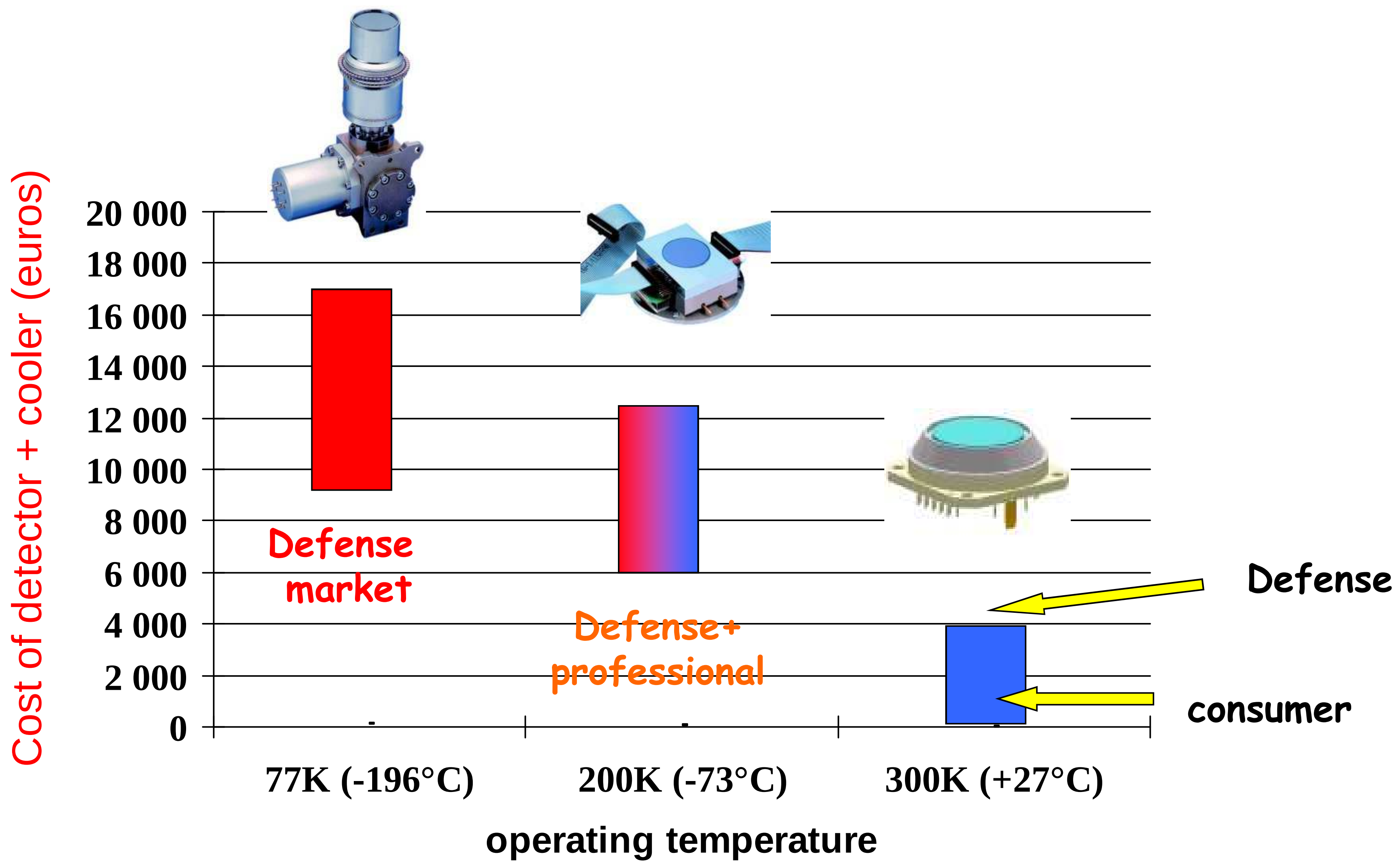
Sensors Unlimited, Inc.
seeing beyond



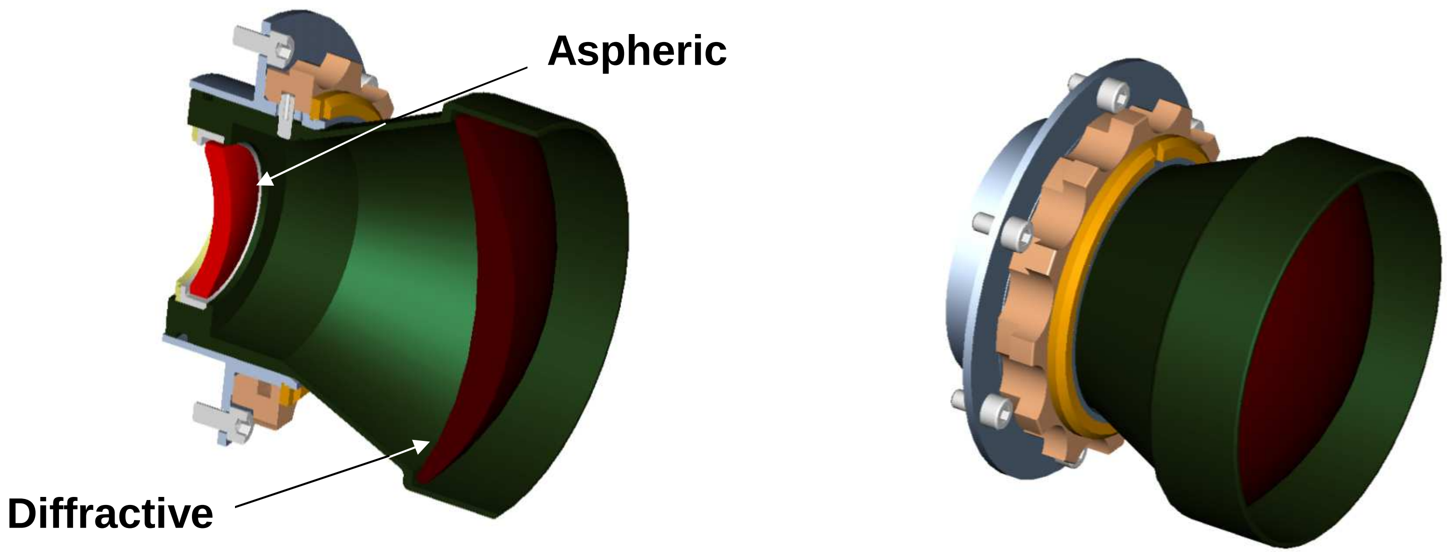


FLIR

Cost of Infrared detectors



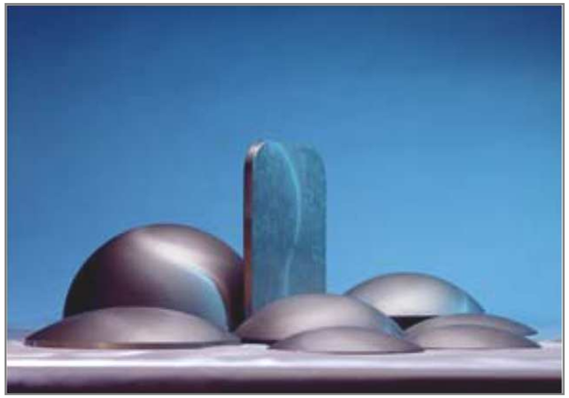
Typical IR Optics



Materials for thermal imaging optics

Single Crystalline Germanium

- Expensive
- Single point diamond turning



Polycrystalline Zinc Selenide (ZnSe)

- Synthesized by CVD
- Single point diamond turning

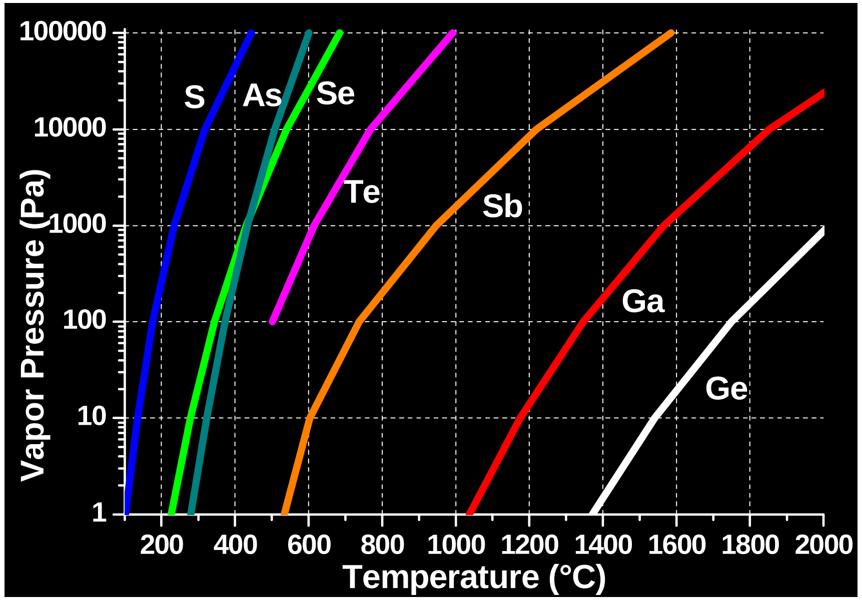
Advantages of chalcogenide glasses (compared to Ge)

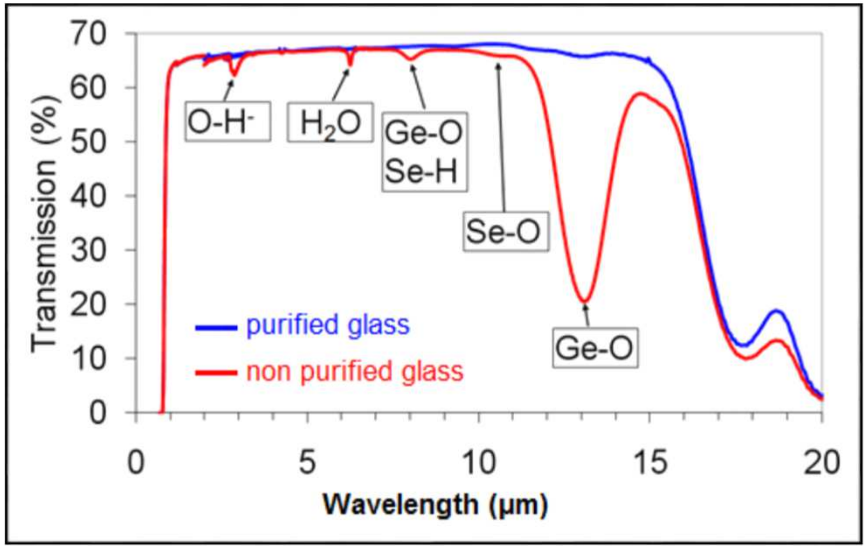
- Low cost of raw materials
- Simple production technique
- Glassy materials (mouldable)
- Transparent at high temperature
- Lower dn/dT
- Flexibility of compositions

Synthesis of chalcogenide glasses

Important difference in vapor pressures for the different elements

Closed systems

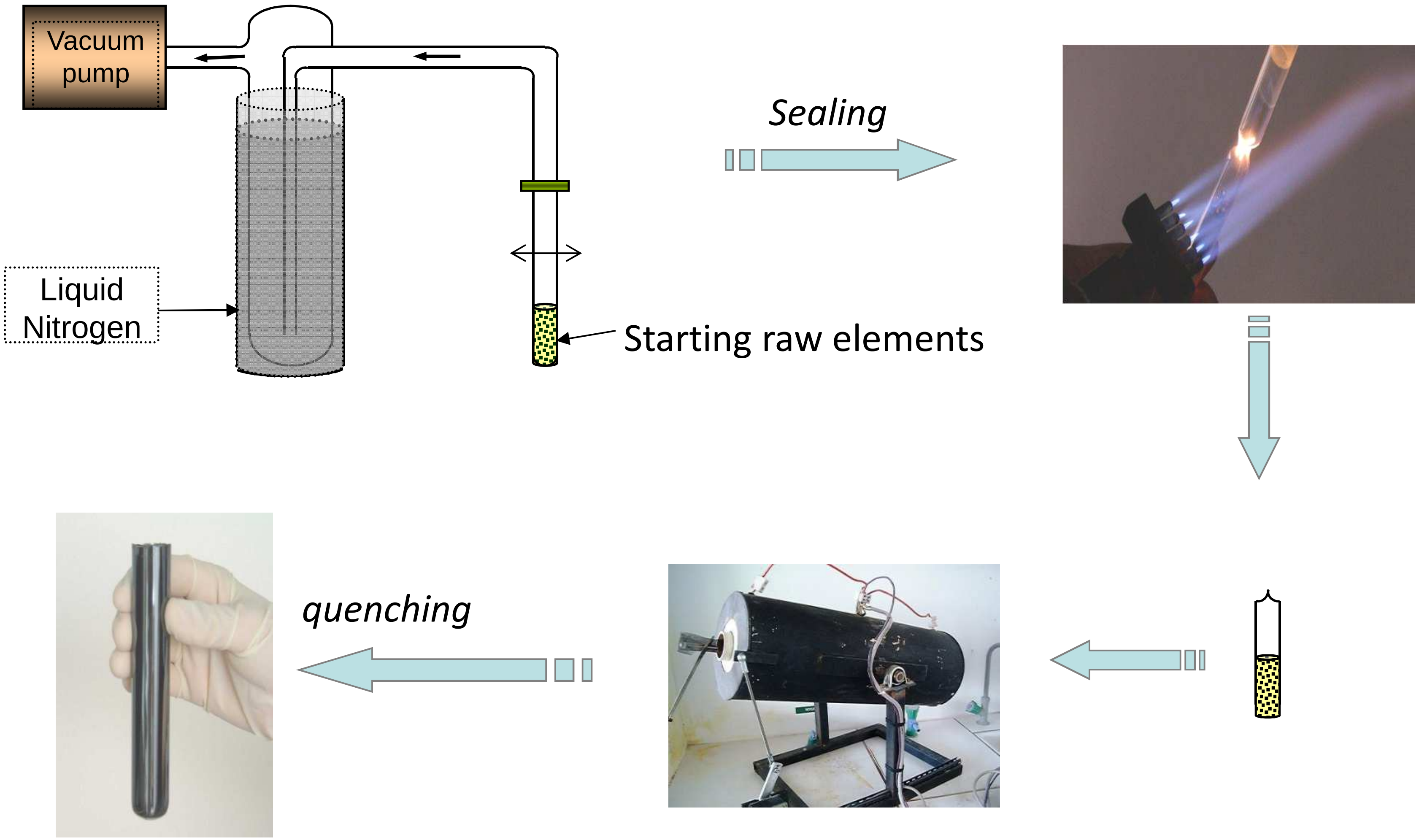




Highly sensitive to contamination by oxygen

Controlled atmosphere

Chalcogenide glass synthesis

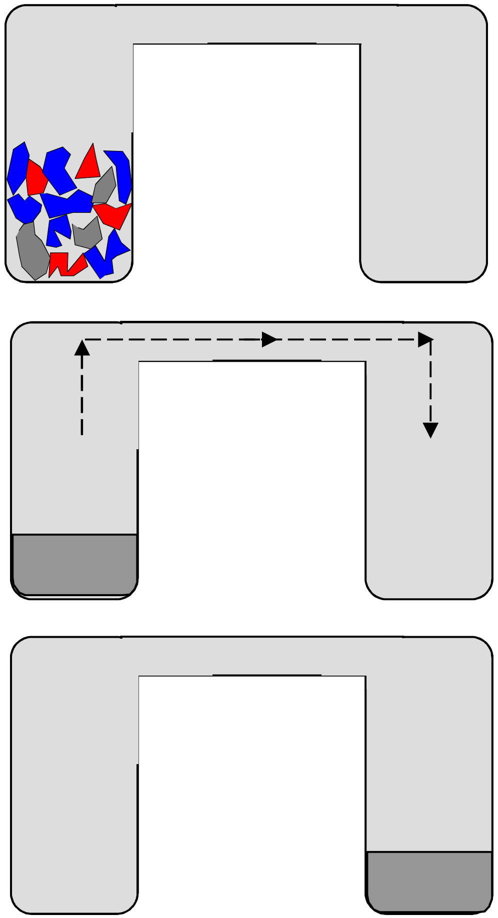


Chalcogenide glass production

Raw materials, sealed under vacuum

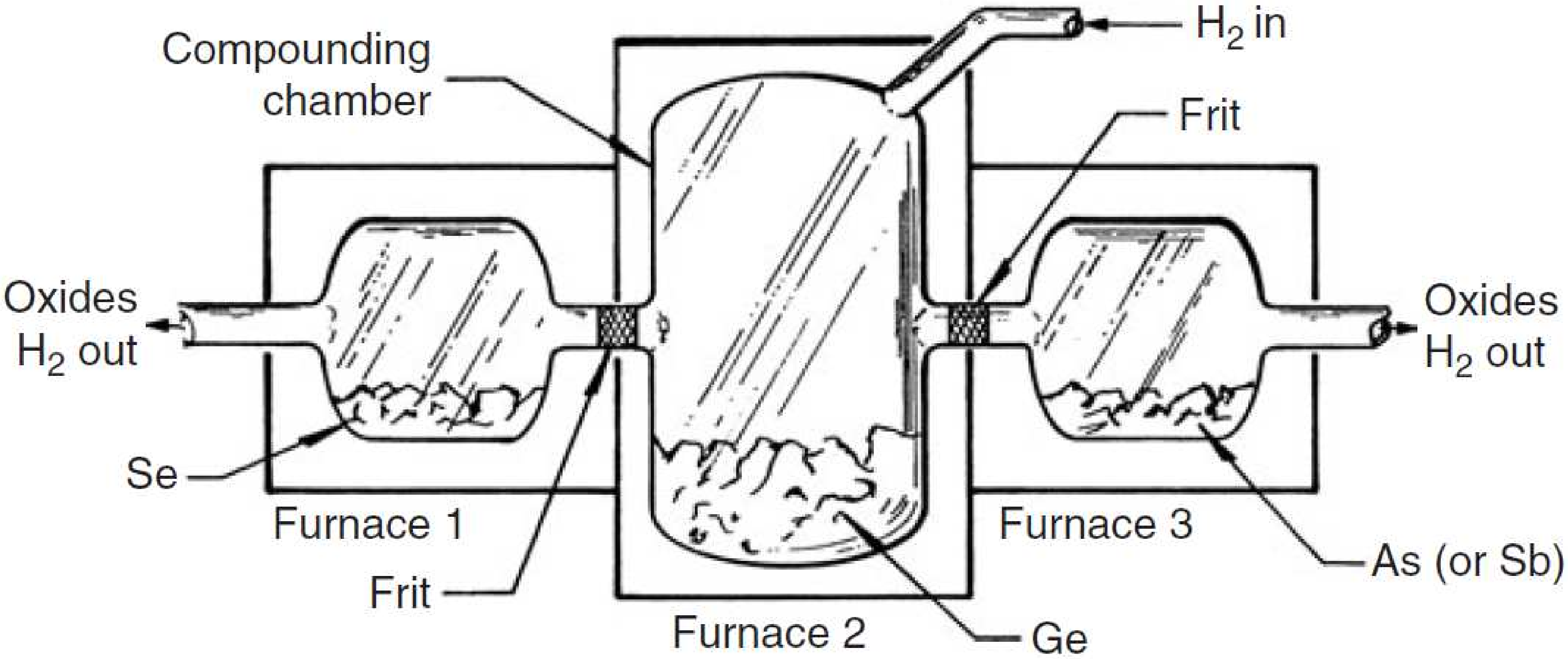
Reaction et distillation

Homogenisation, cooling and annealing



Industrial fabrication of chalcogenide glass Ge-As-Se

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



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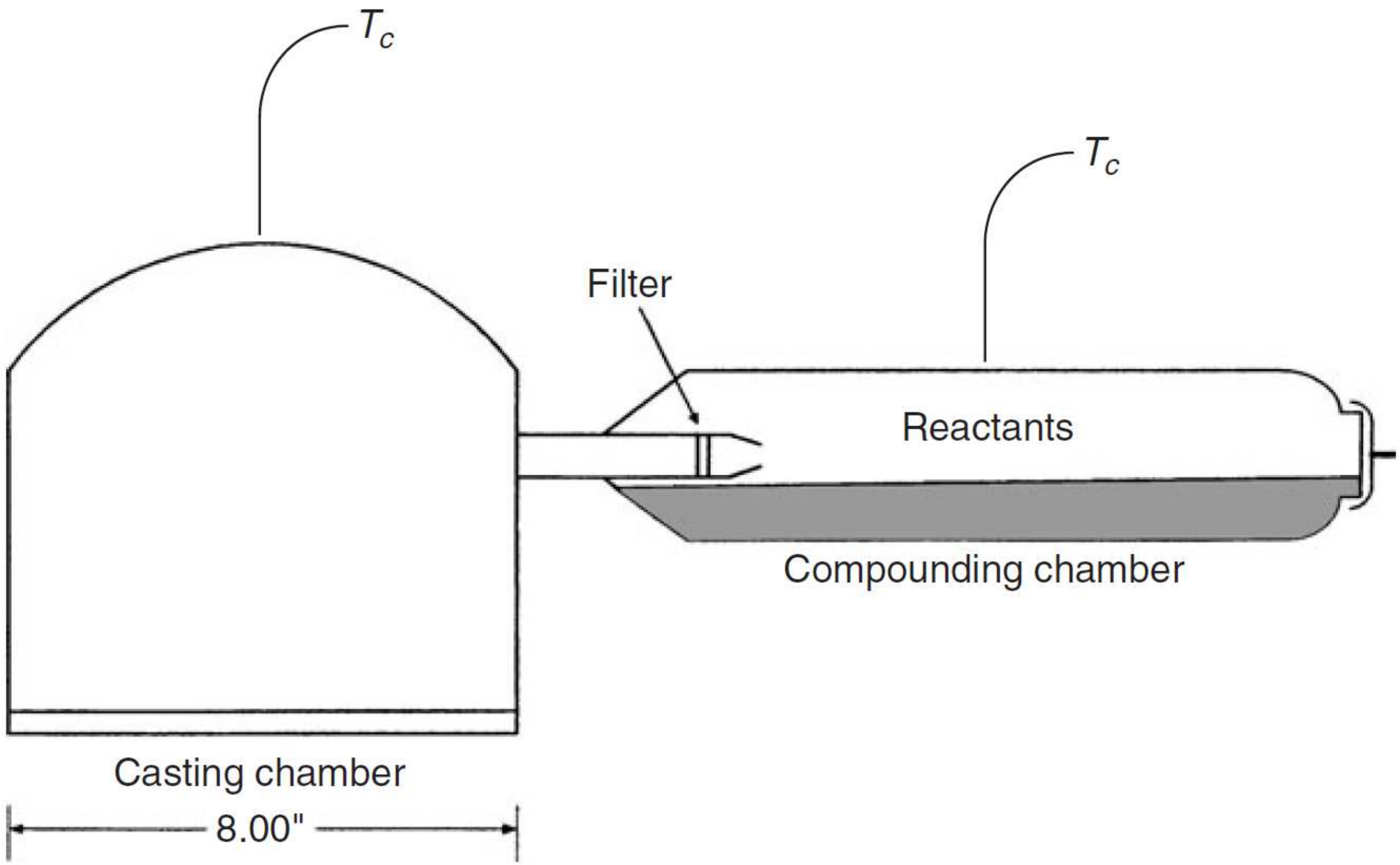
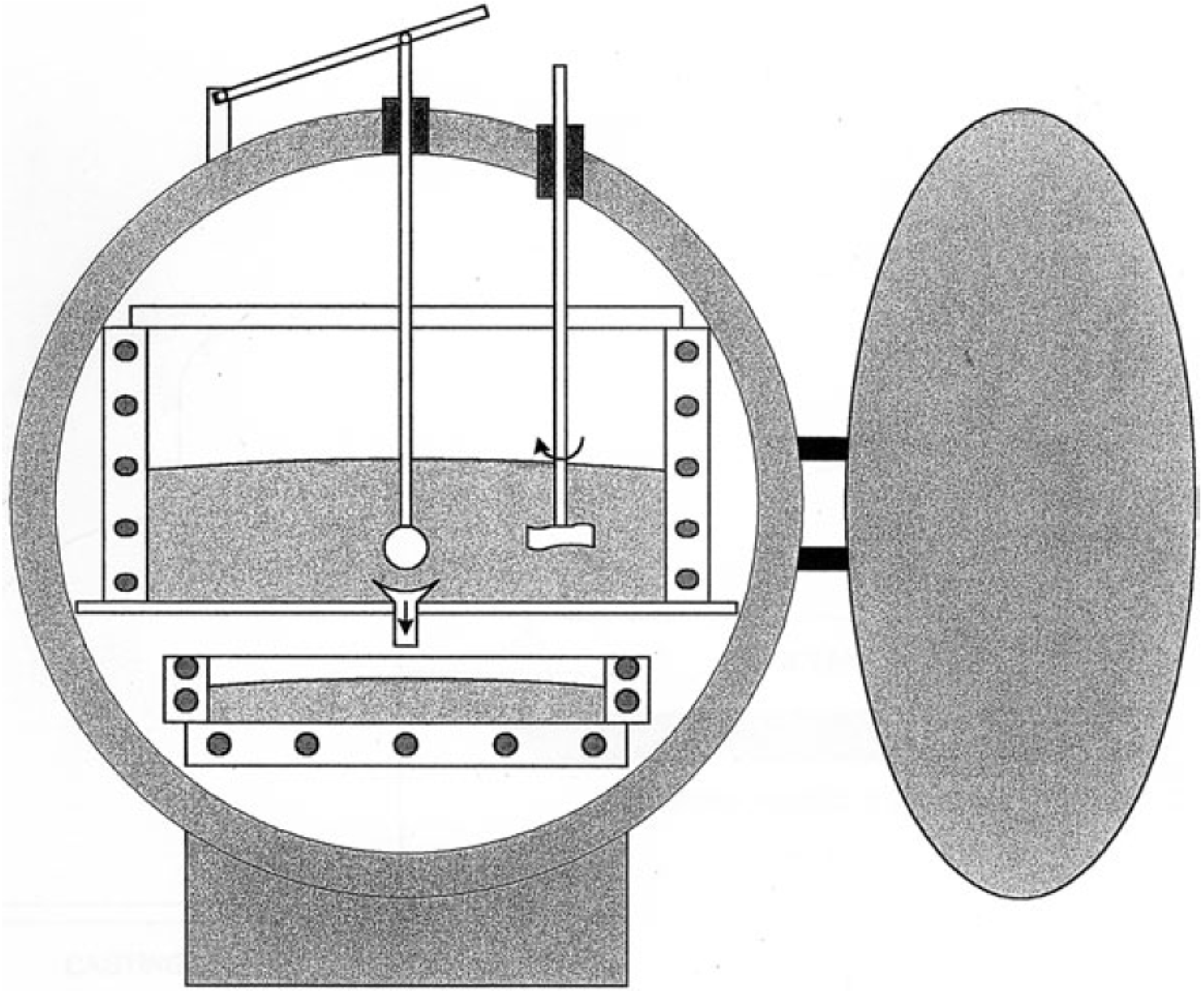


Casting of chalcogenide glass



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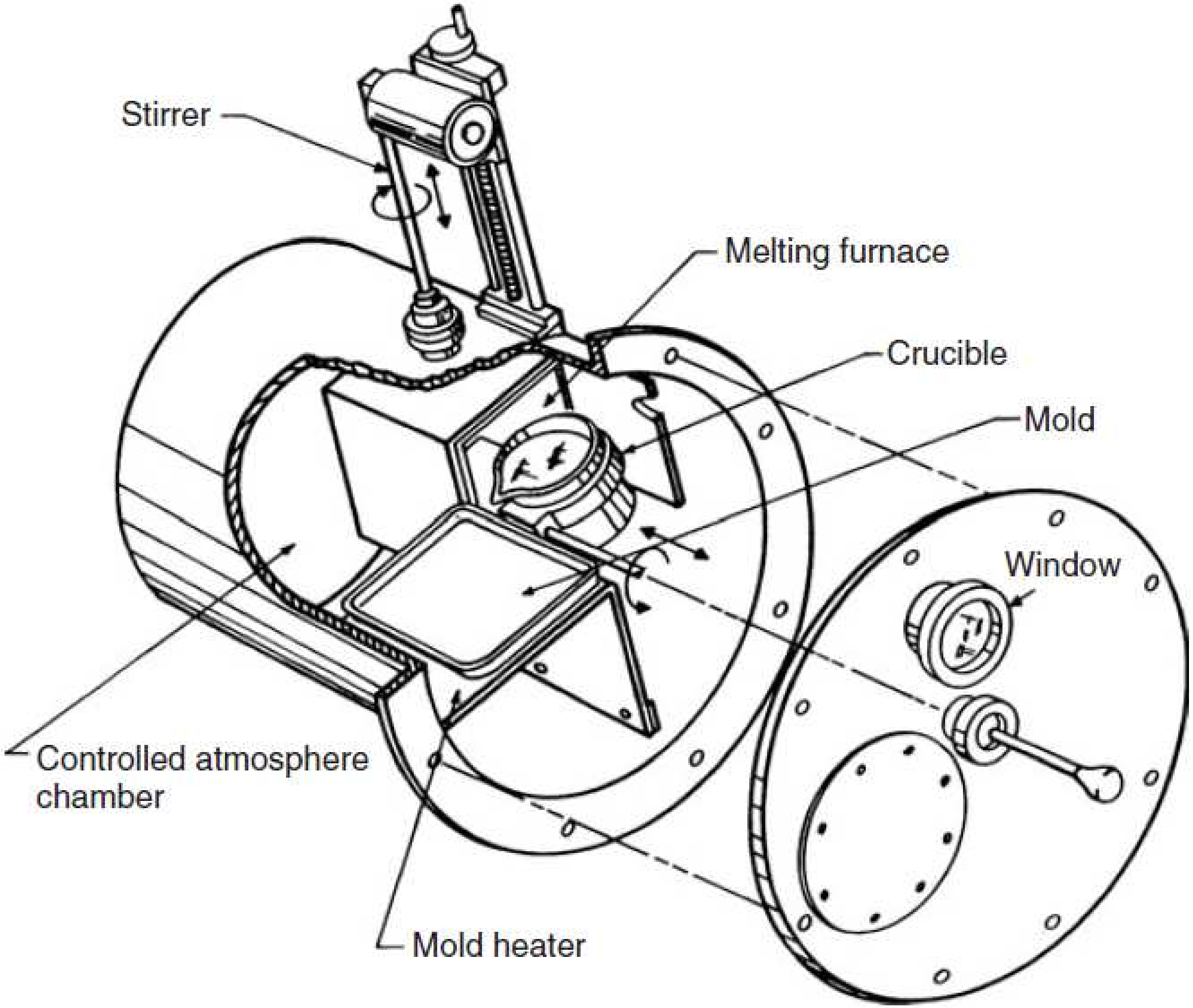
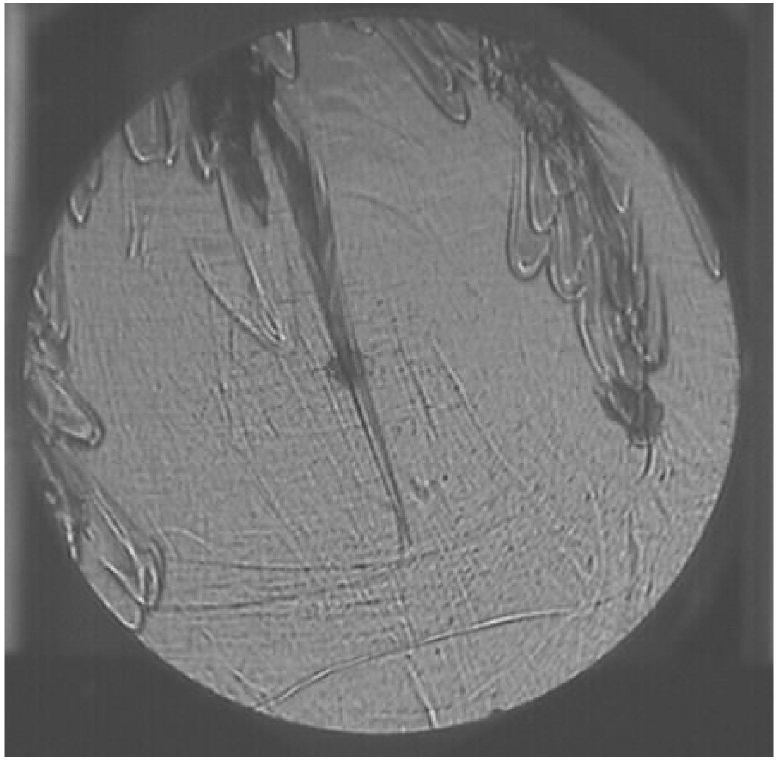
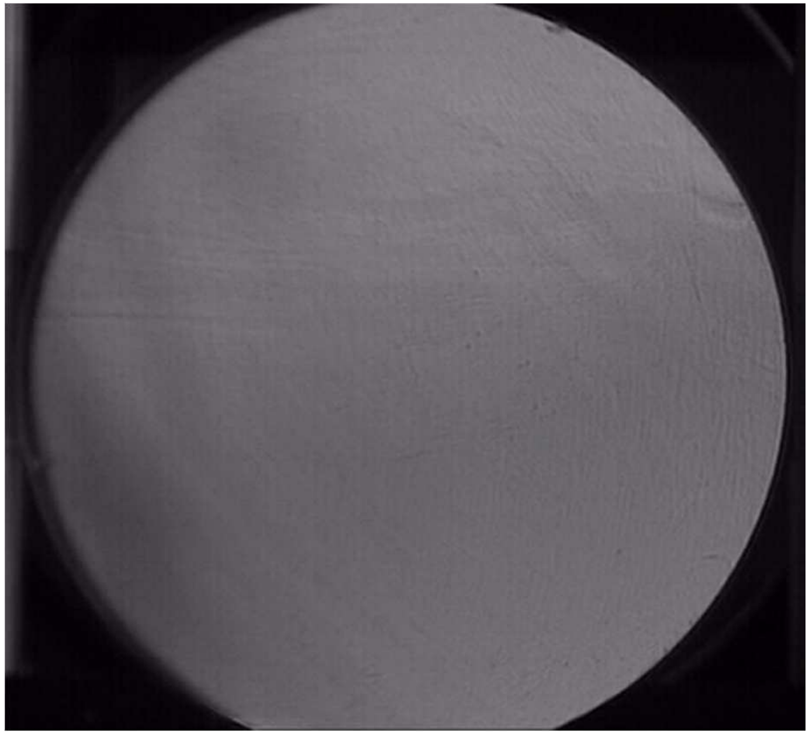


Chalcogenide glass ingots

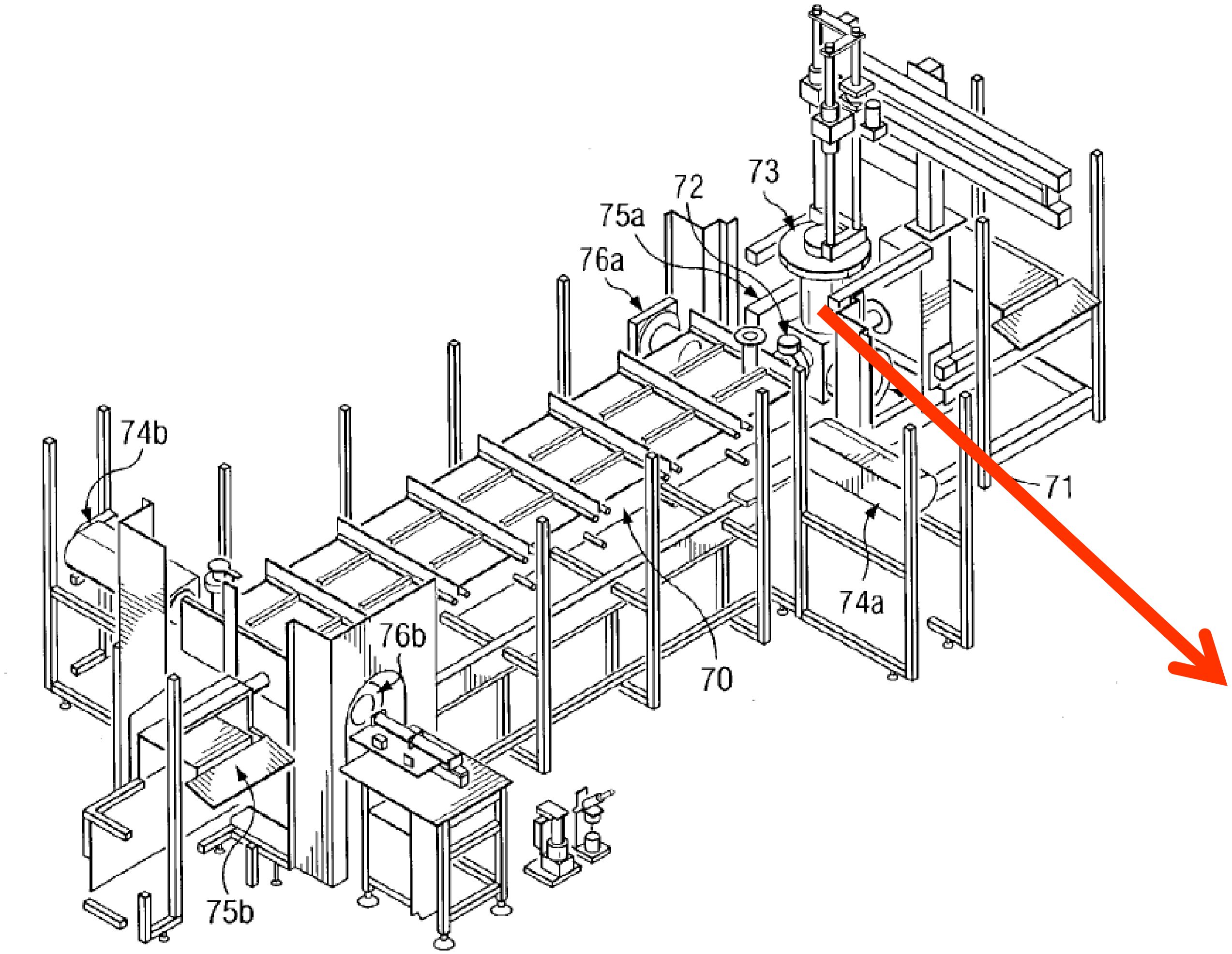
Homogeneity control

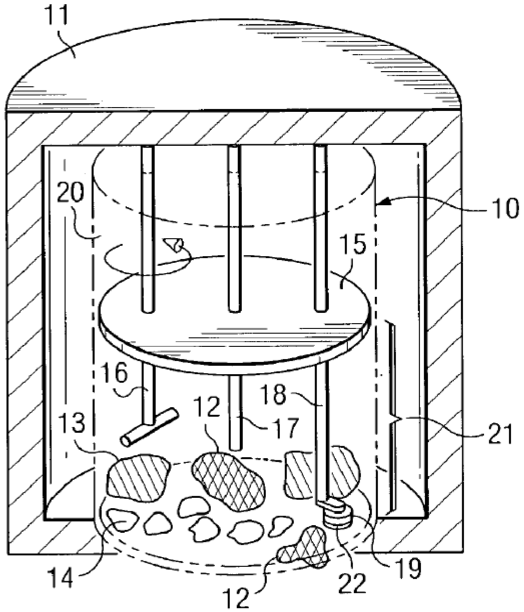




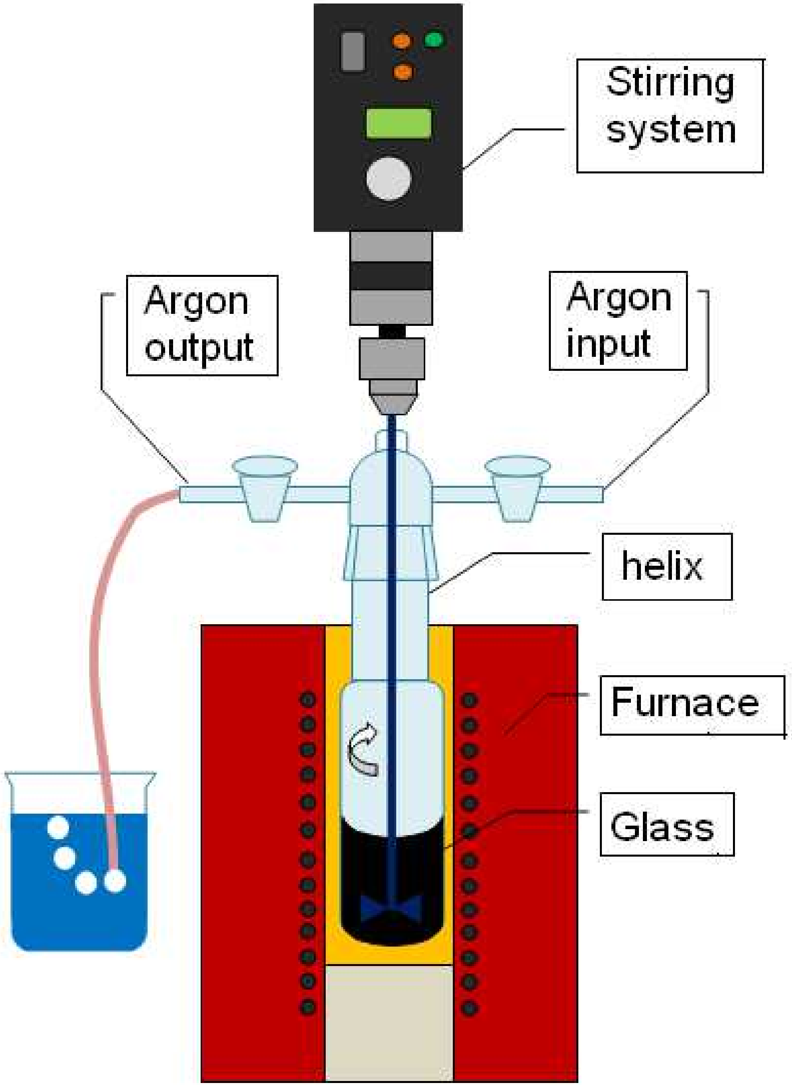
Continuous production line

Umicore patent
For IR optics

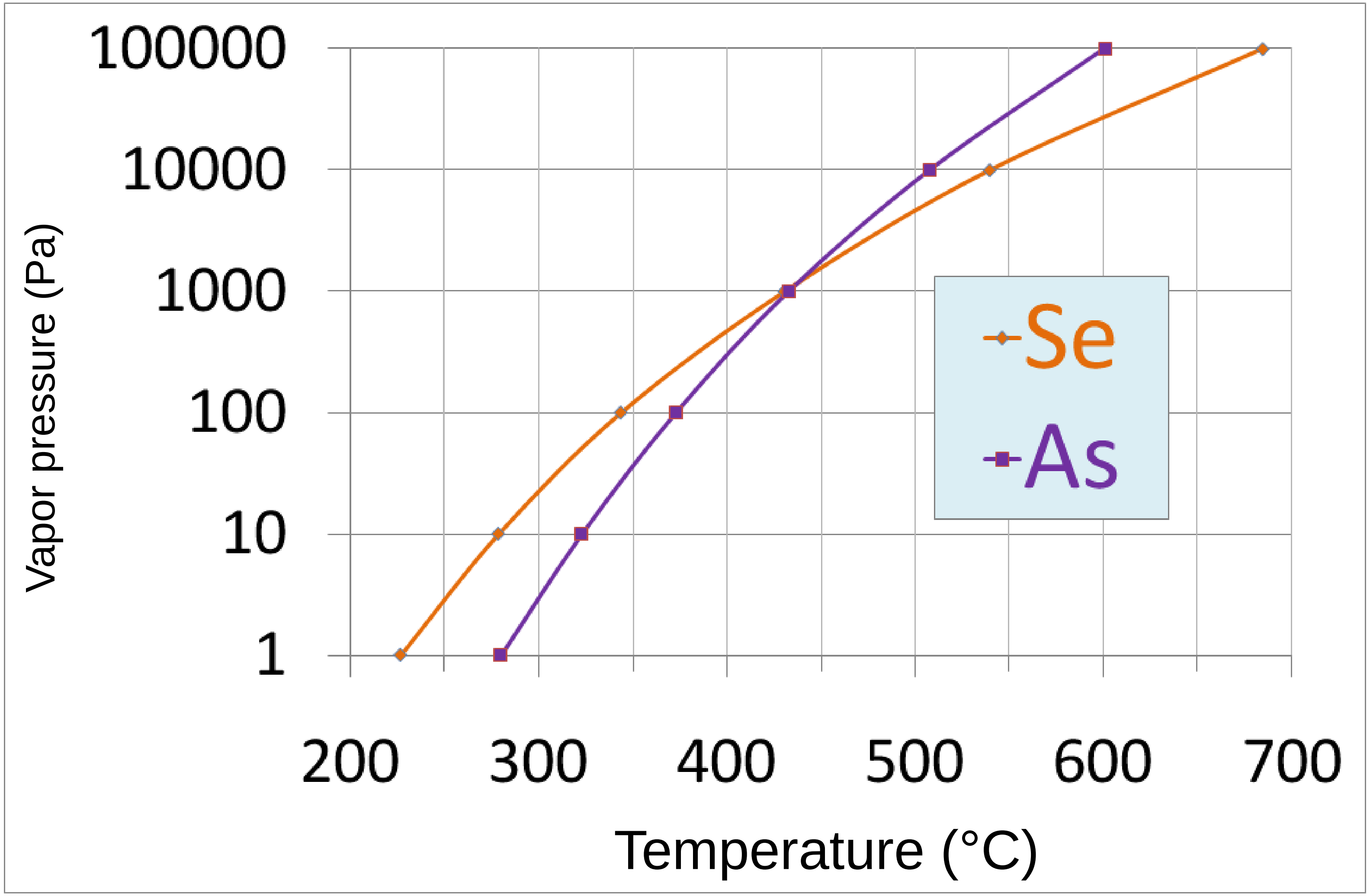




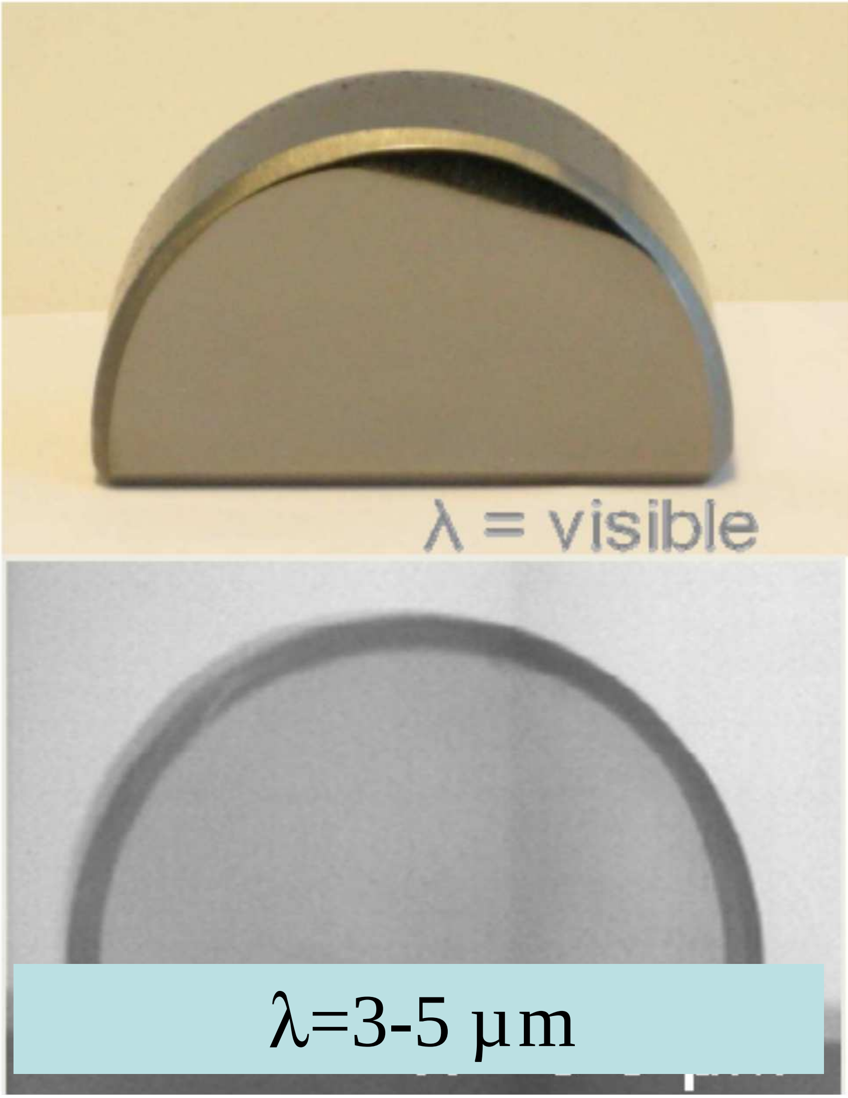
Set-up for chalcogenide glass synthesis in argon

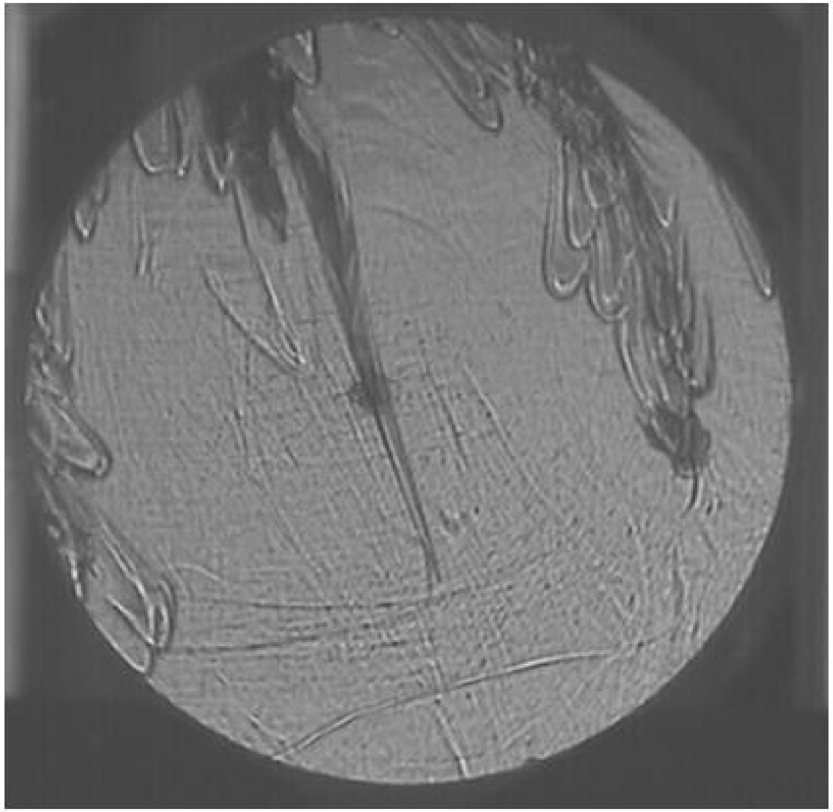


Vapor pressure of As and Se



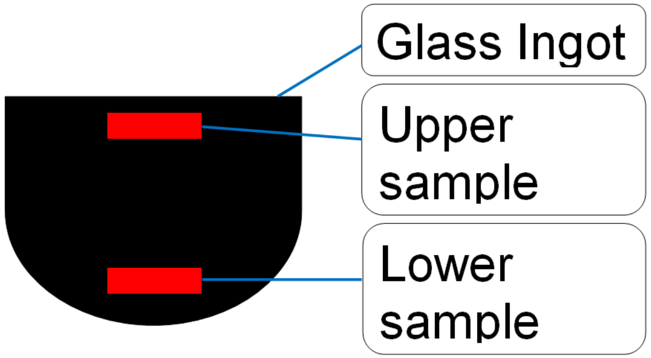
Homogeneity of infrared glasses





Example of glass obtained with sealed silica tube

Index reproducibility



3 glasses tested

Index precision :2.10^{-3}

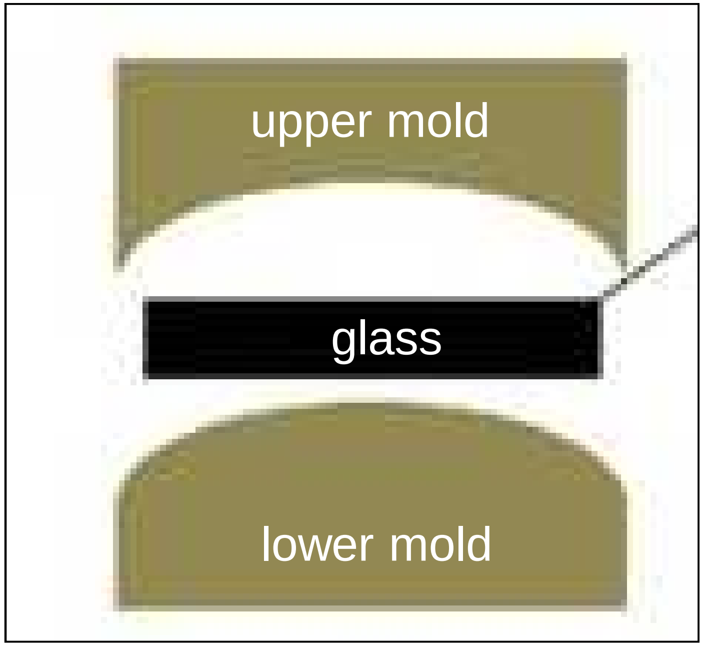
glasses	Index at 1.55 µm		difference
	Lower sample	Upper sample	
A	2.8204	2.8198	$6. 10^{-4}$
B	2.8112	2.8120	$- 8. 10^{-4}$
C	2.8099	2.8104	$- 5. 10^{-4}$

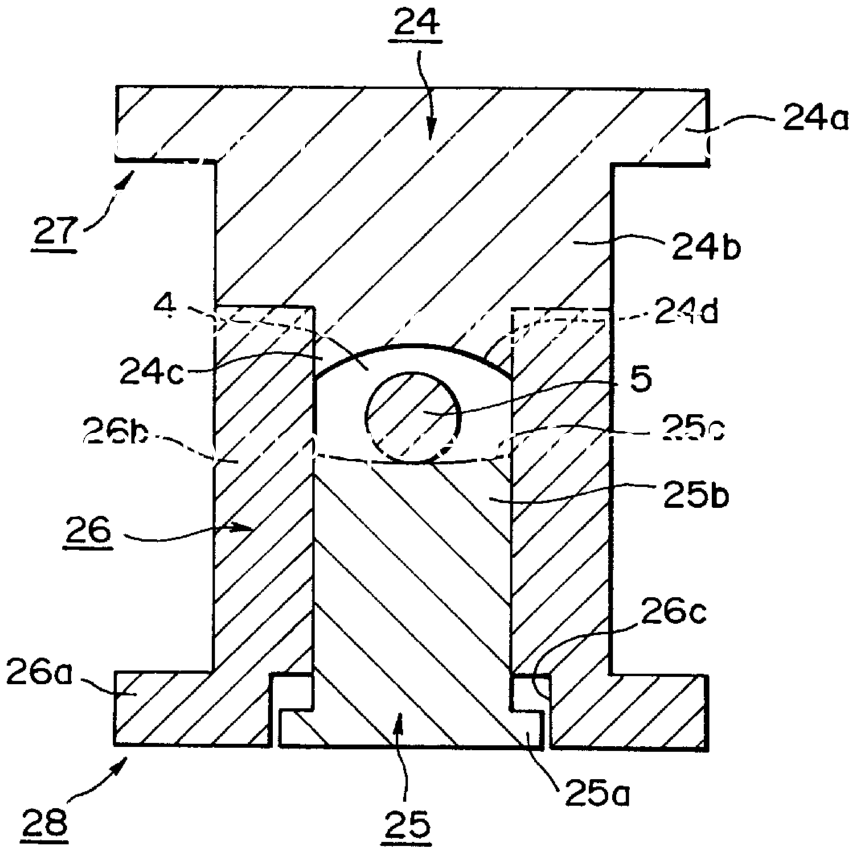
Technique can not be used for synthesizing Germanium containing glass

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

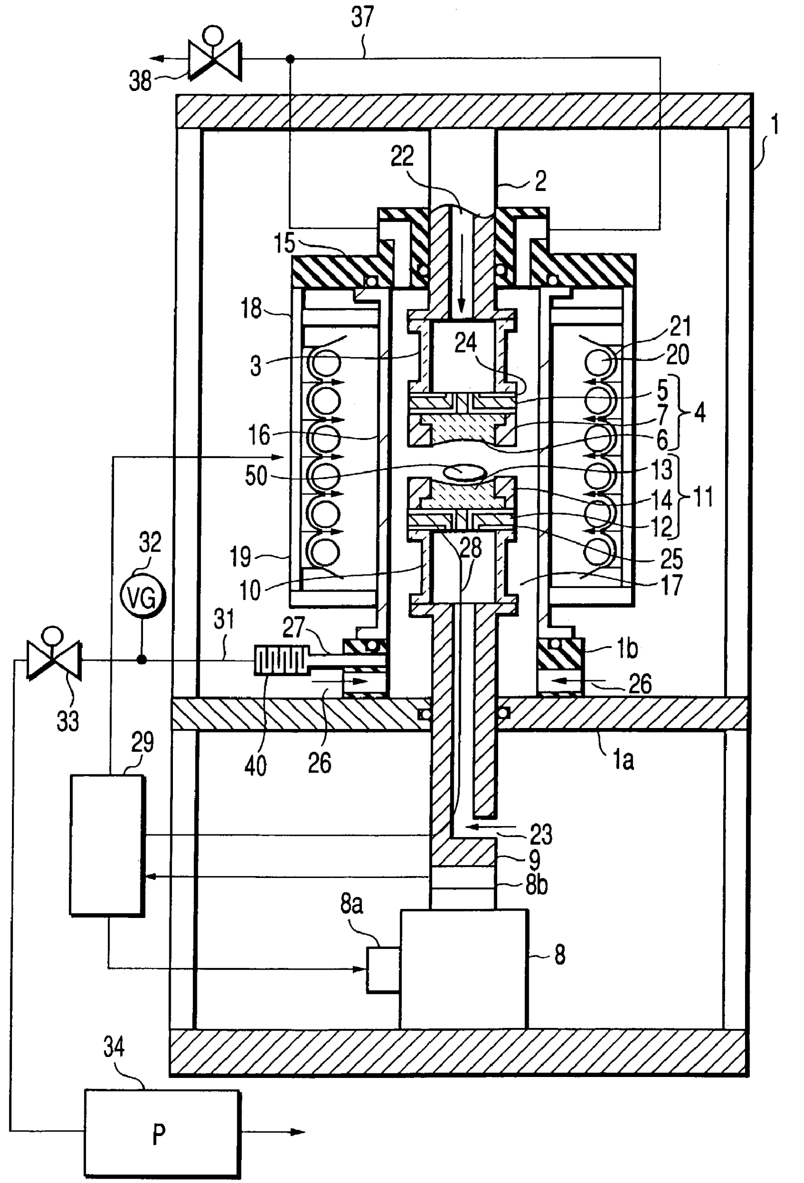
Fabrication of optical lenses

Challenges for chalcogenide glass molding





Toshiba patented molding machine



SCHOTT IRG Glass Ball Preforms

Product Information

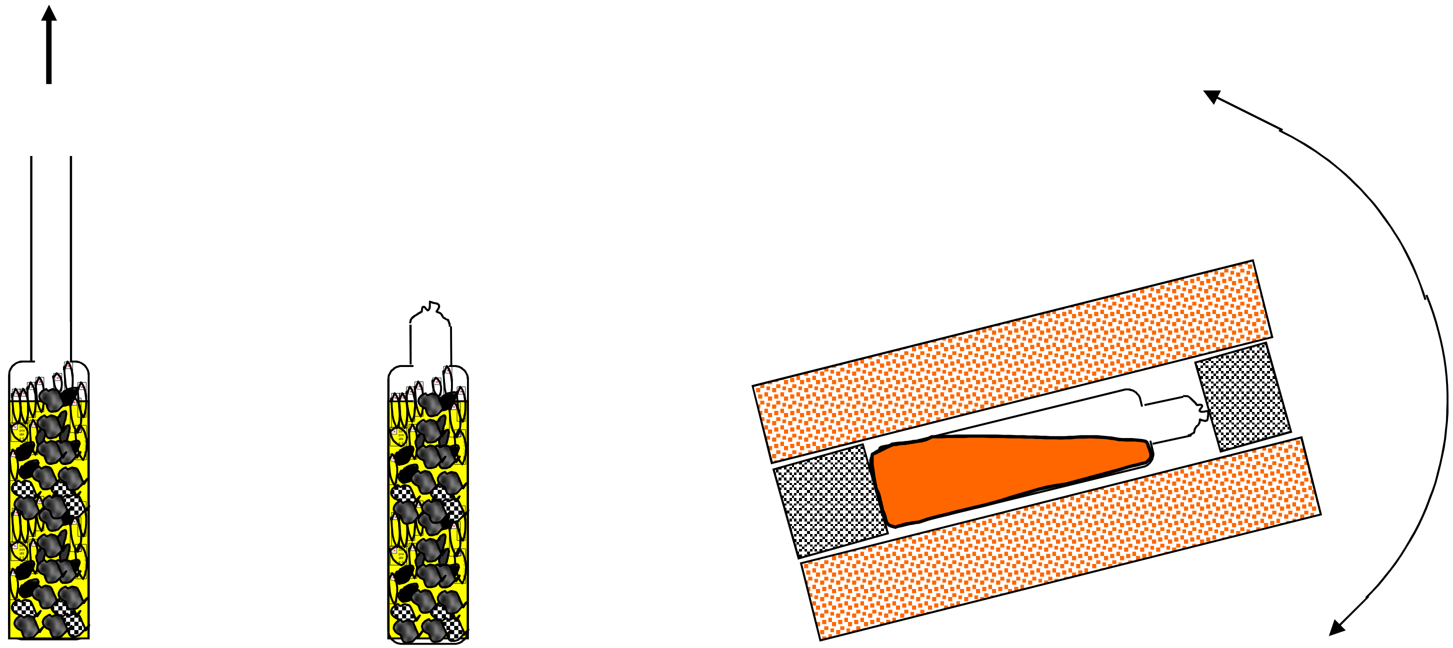
Ball preforms offered by SCHOTT from the IRG glass series are optimized for processing using precision molding to support low- to high-volume component-level aspheric lens manufacturing. The SCHOTT IRG family of chalcogenide glasses (IRG22 – IRG26) are ideal for IR imaging and sensing applications, can be combined with other IR materials to support cost-effective and high-performance optical designs in the common IR transmission bands 3 – 5 microns and 8 – 12 microns, as well as be able to transmit as low as 900 nm. SCHOTT's preform production guarantees excellent part-to-part uniformity. SCHOTT can process small quantity orders for process development/scale-up as well as very high volume quantities to support high capacity production. From hundreds of parts to millions of parts, SCHOTT is ready to meet your production demands.

Examples of molded chalcogenide glass optics

Chalcogenide glass ceramics:

To improve the mechanical properties

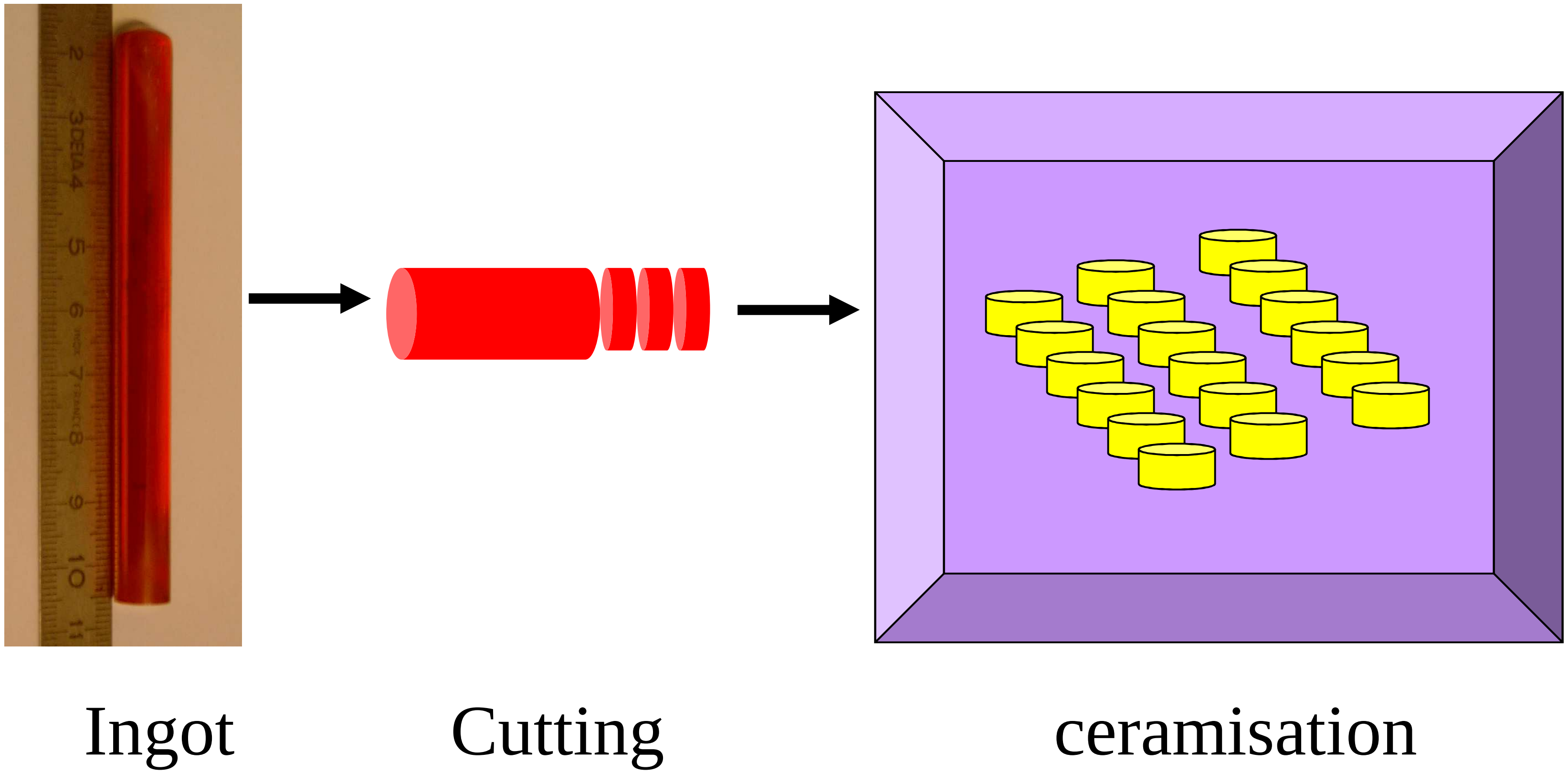
Fabrication of sulfide glasses



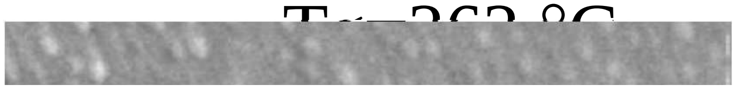
Raw materials
Ge, Sb, S…

Rocking furnace

Fabrication of transparent glass ceramics



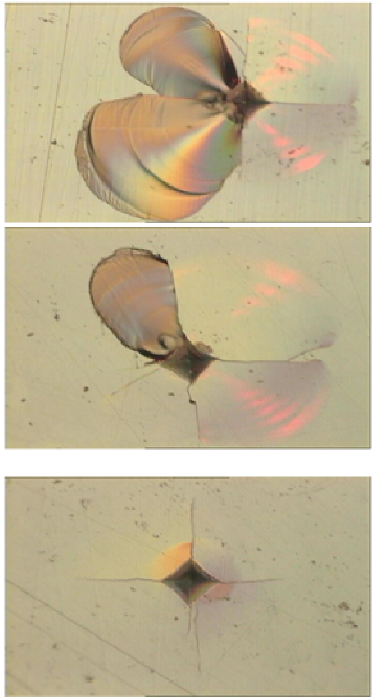
62.5GeS_2- 12.5Sb_2S_3-25CsCl glass heated at 290 ° C

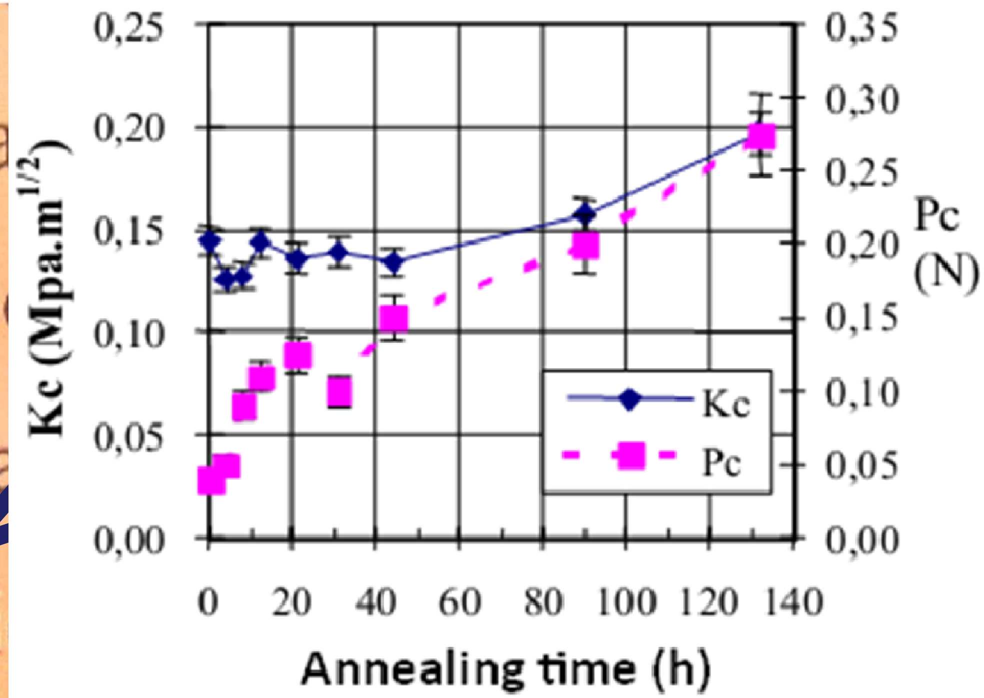


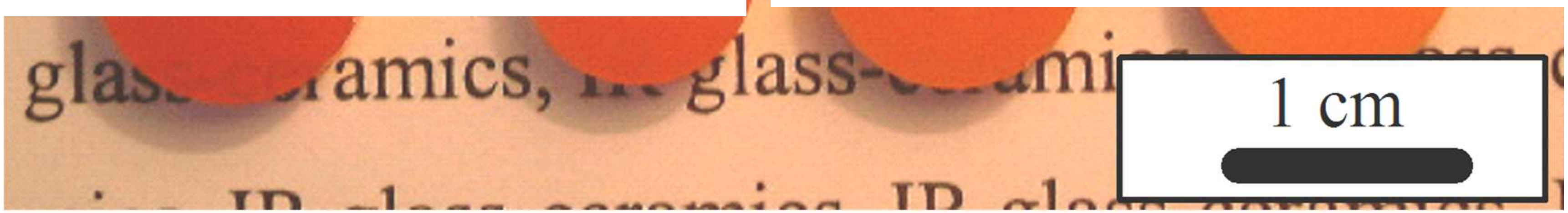
glass

Glass ceramic 1

Glass ceramic 2

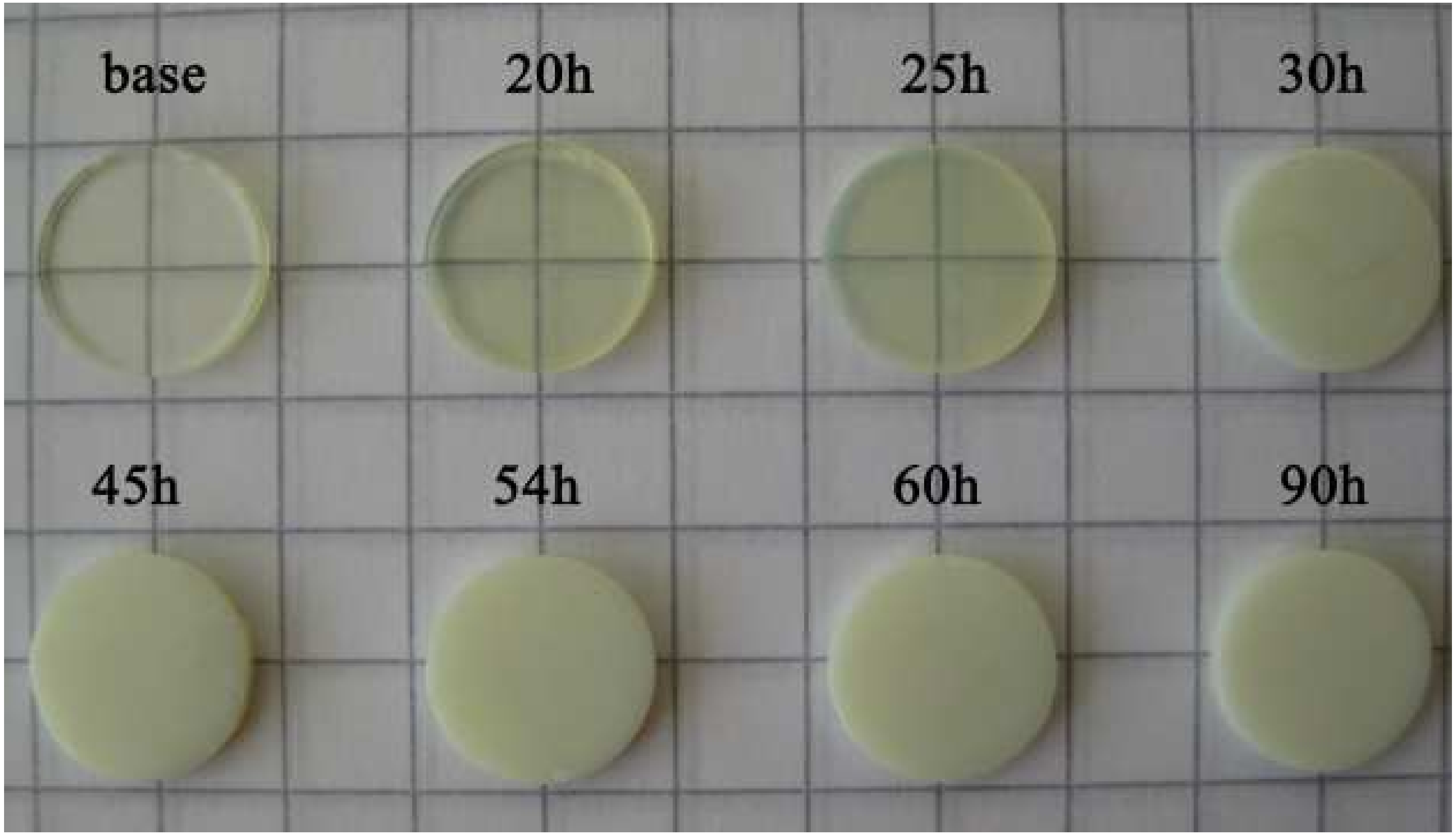






sulfide glass ceramics for down conversion

GeS_2-Ga_2S_3-CsCl glass ceramics

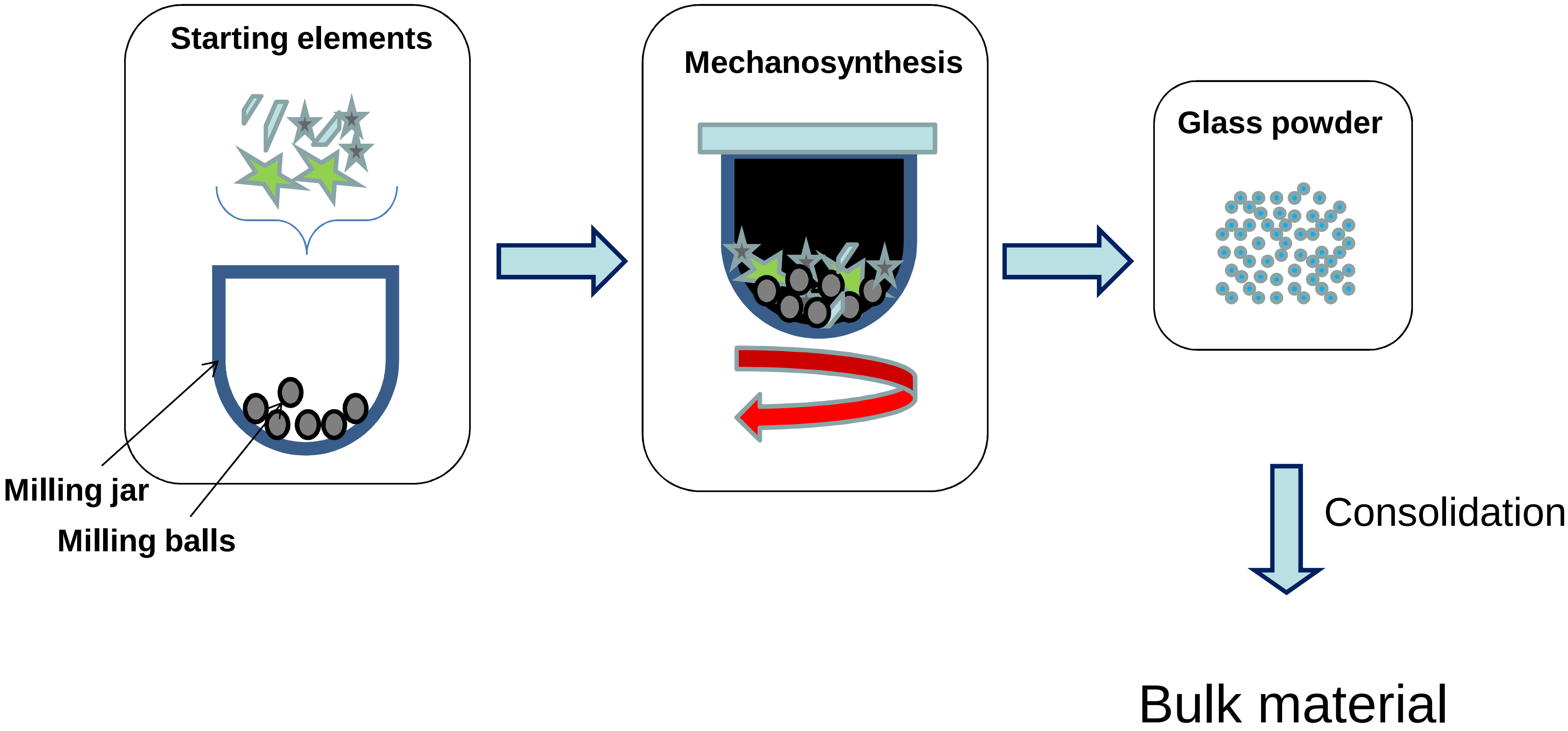


New approach for

chalcogenide glass production

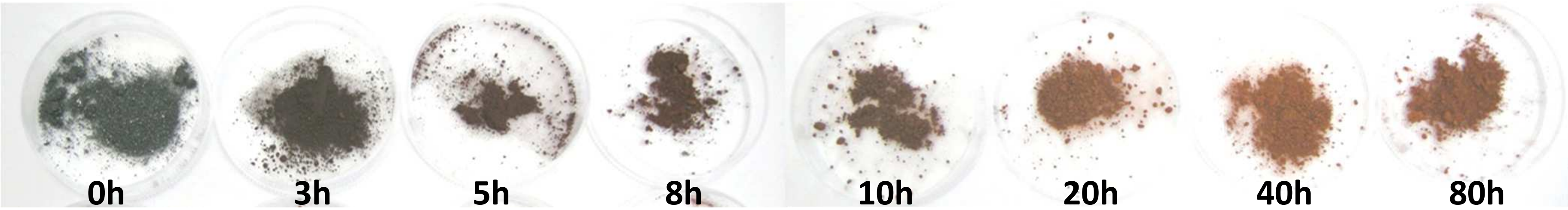
Mechanosynthesis

using mechanical energy instead of thermal energy to induce chemical reaction



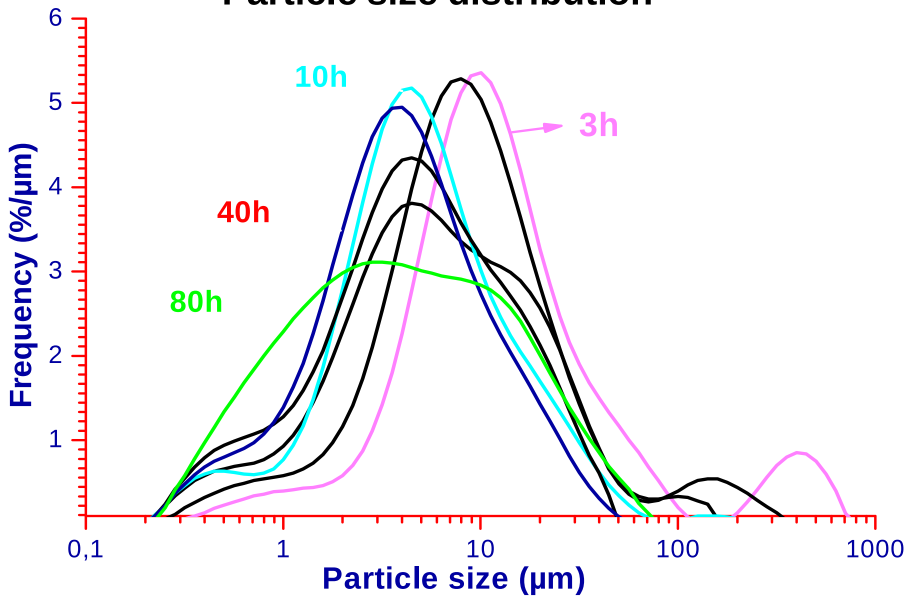
Mechanosynthesis $80GeSe_2$-$20Ga_2Se_3$

Starting materials : Ge, Ga, Se

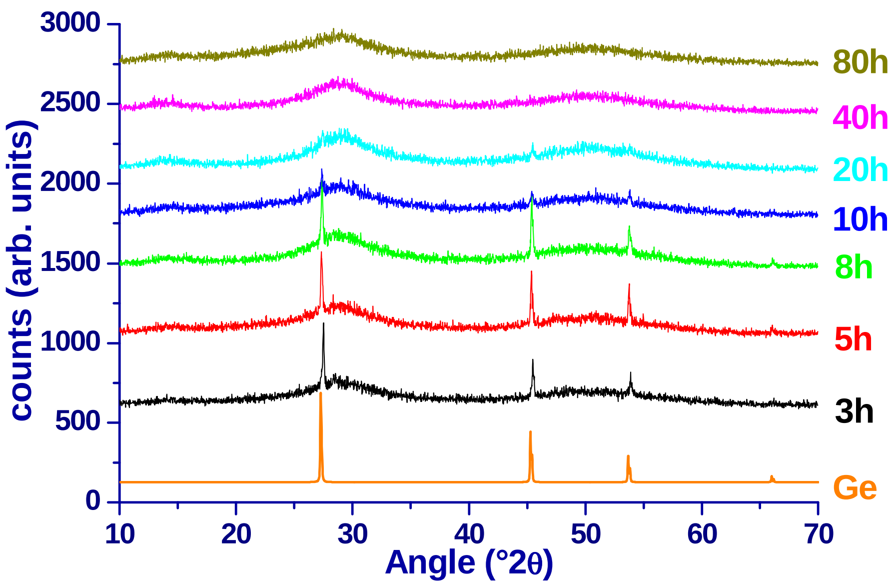


Progressive reaction between the elements and lowering of particle size

Particle size distribution



XRD Spectra



Mechanosynthesis

- **Synthesis of micrometric glass powder**

- **Thermal properties close to that of glasses prepared in sealed silica ampoule**

- **Extending the glass forming region**

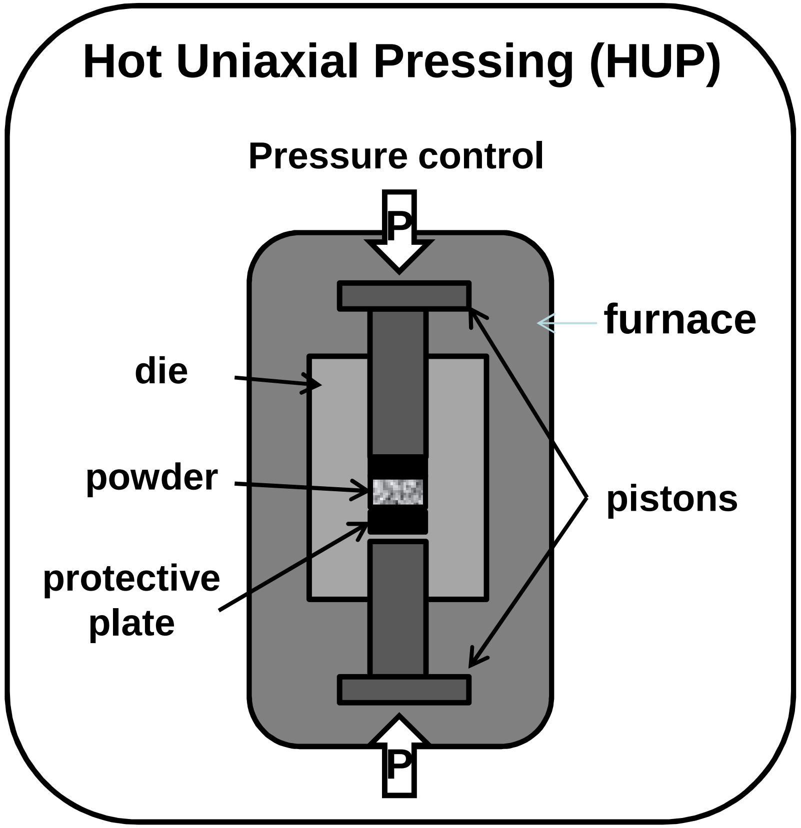
To produce bulk glasses or optics

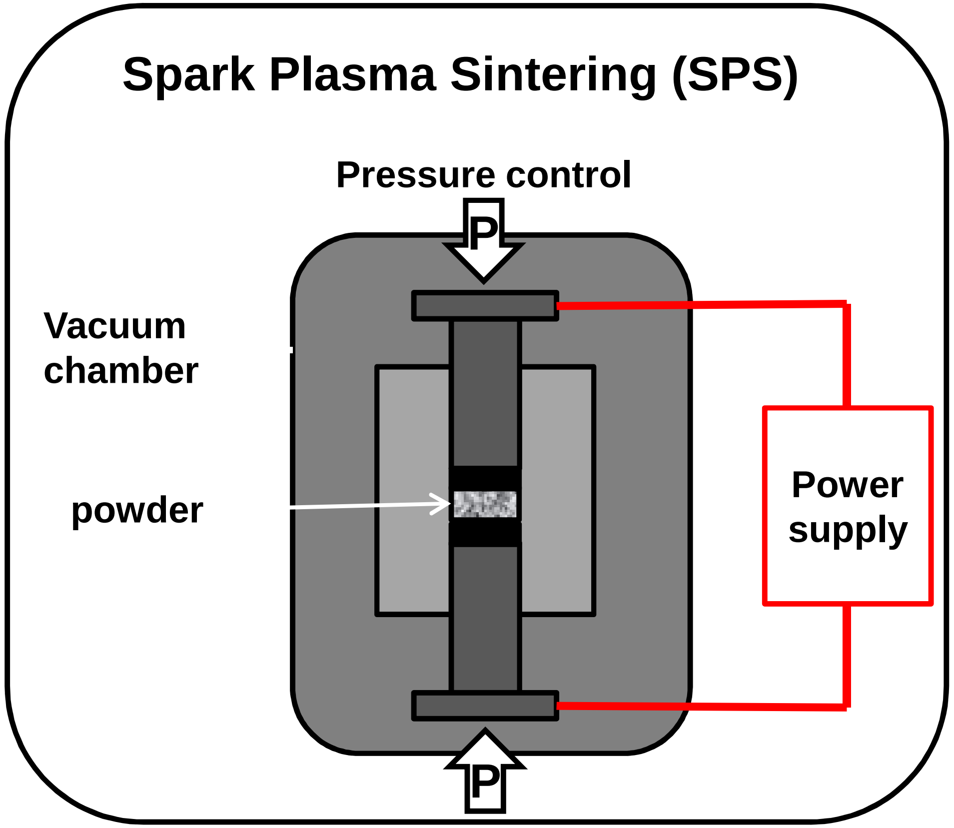
Melting and casting

Sintering

Bulk glass/lenses fabrication by hot pressing

<u>Principle:</u> 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

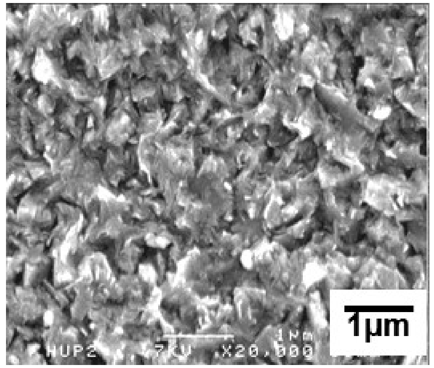
$80GeSe_2$-$20Ga_2Se_3$ composition: ΔT<100°C

Materials obtained:

- Inhomogeneous sintering (thermal profile of the press)

- Uncontrolled crystallization

- No optical transmission



Crystallization due to prolonged stages at T>Tg

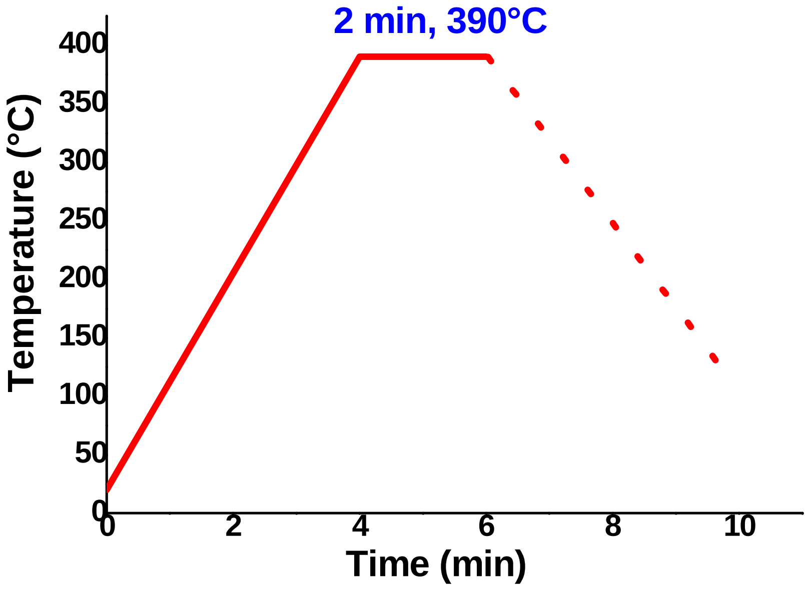
Need to reduce sintering process duration => SPS

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

Dr Synter 505 Syntex SPS machine

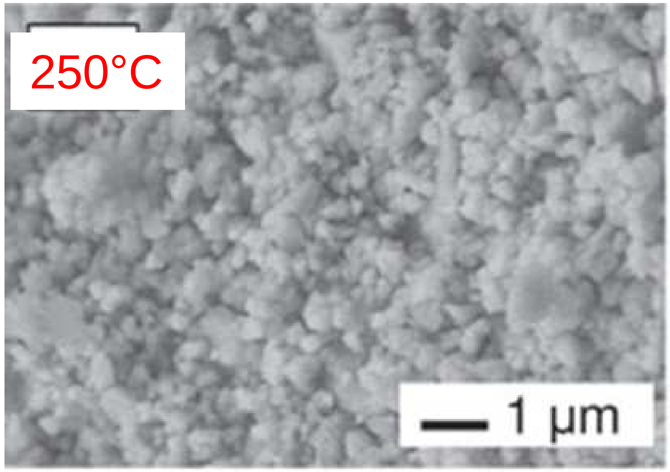
Experimental conditions

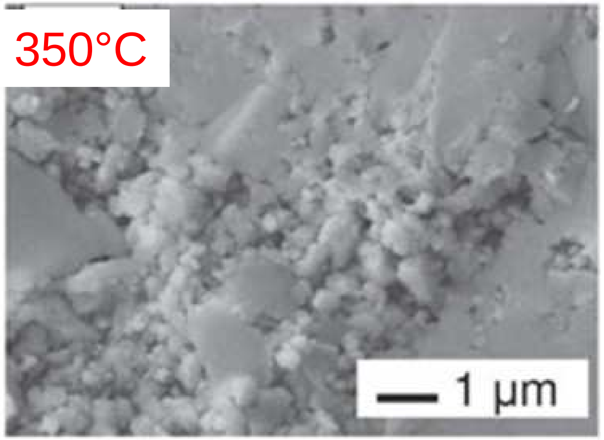
- Under vacuum
- Thermal treatment

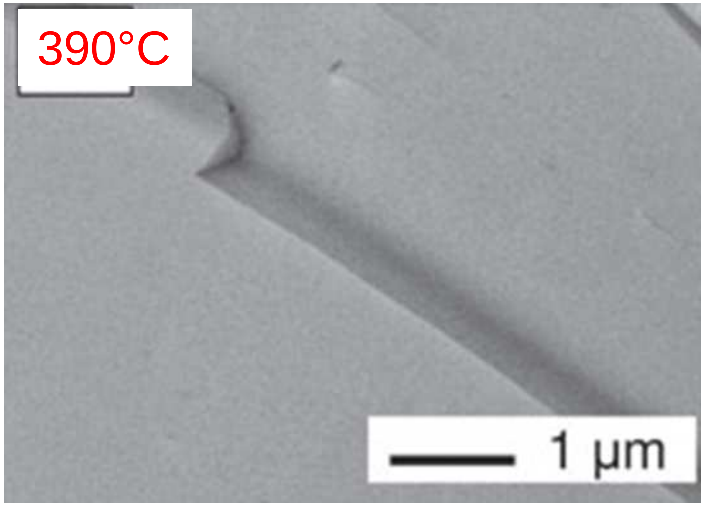


Total duration: 10 min (more than 2h for HUP)

$80GeSe_2$-$20Ga_2Se_3$ glass bulks sintered at different T (50 MPa, 2-min)







G. Delaizir et al

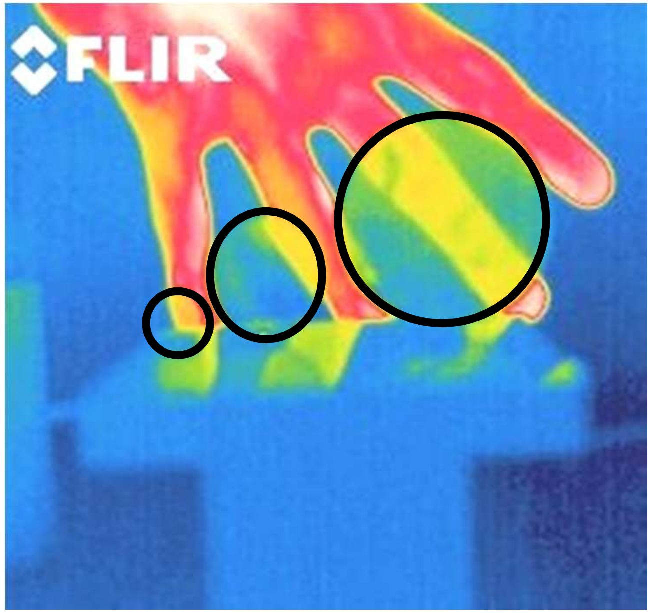
J. Am. Ceram. Soc., 95 [7] 2211–2217 (2012)

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

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

visible

Densification > 99%



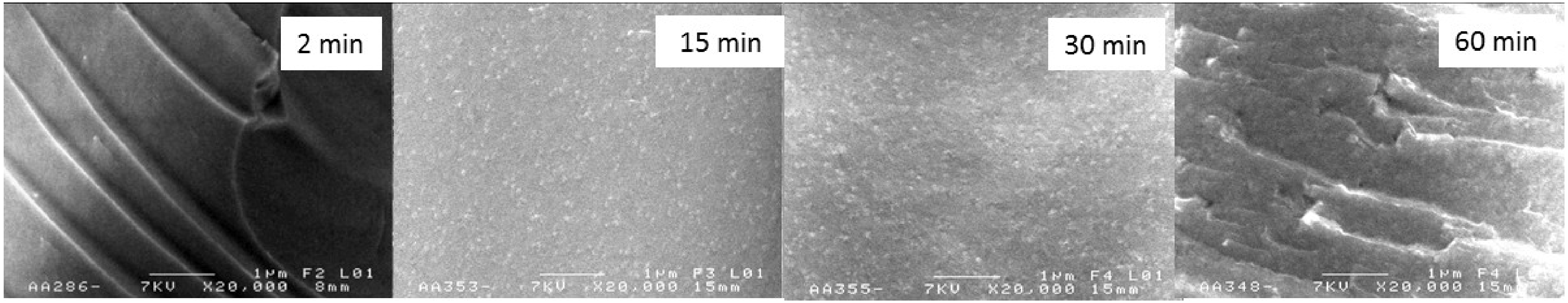
Thermal camera 8-12µm

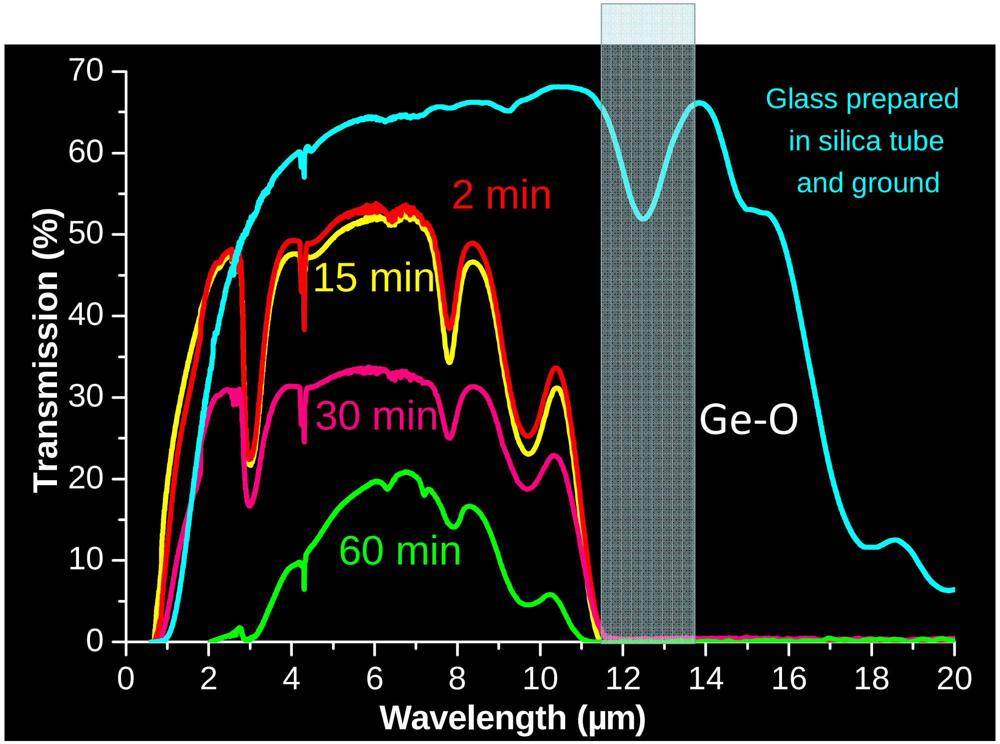
Transparent bulk samples Ø = 8 mm, 20 mm et 36 mm

Maximum diameter obtained using silica tubes = 9 mm

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

Sintering at 390°C for longer durations





- Progressive controllable crystallization (crystals < 100 nm)
- Glass-ceramics transparent in the infrared range
- Important pollution by oxygen (transmission cut-off at 12 µm)

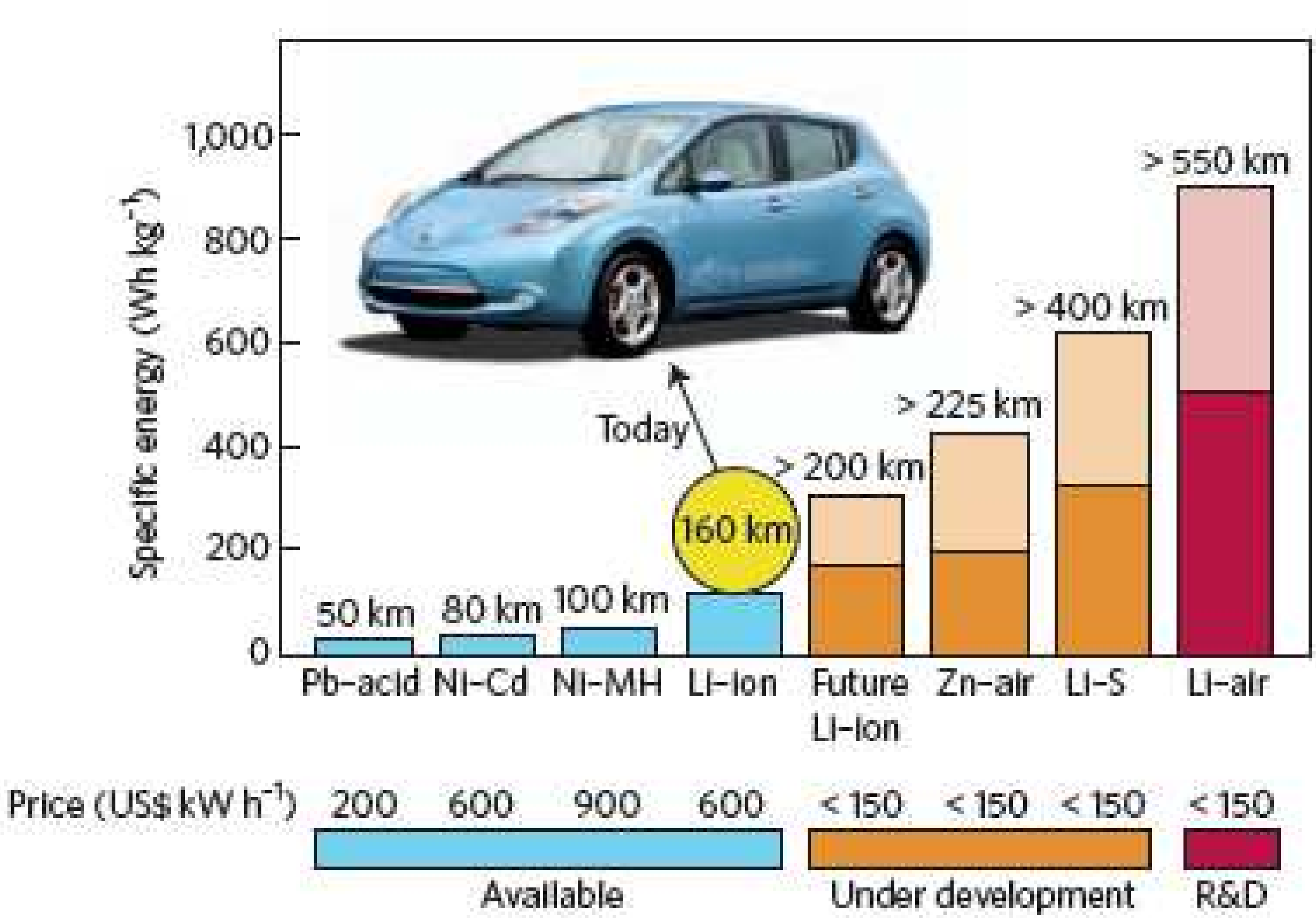
Chalcogenide glasses for energy application

Energy storage

Energy conversion

Two issues with current Li-ion battery

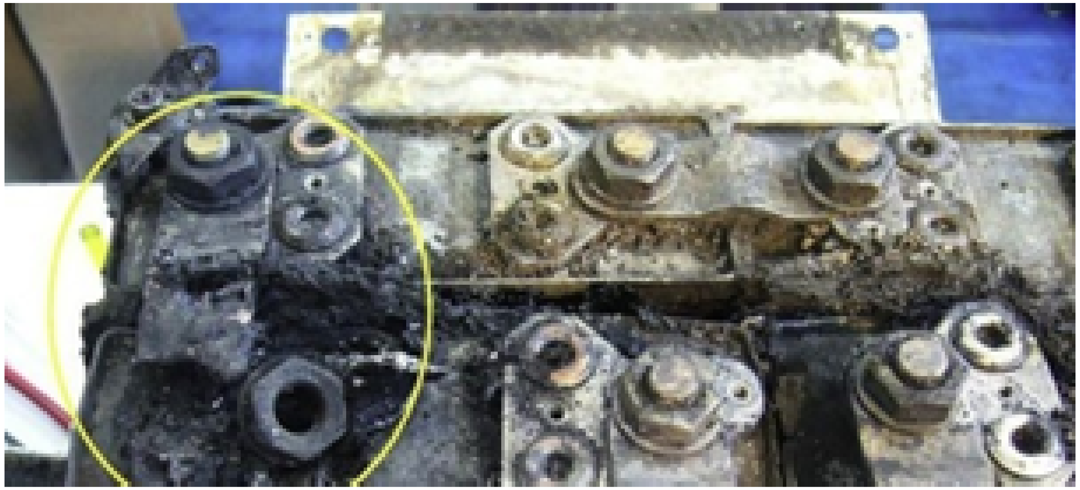
1. Energy density



P. G. Bruce. NATURE MATERIALS 11(2012),19-30

Two issues with current Li-ion battery

2. safety



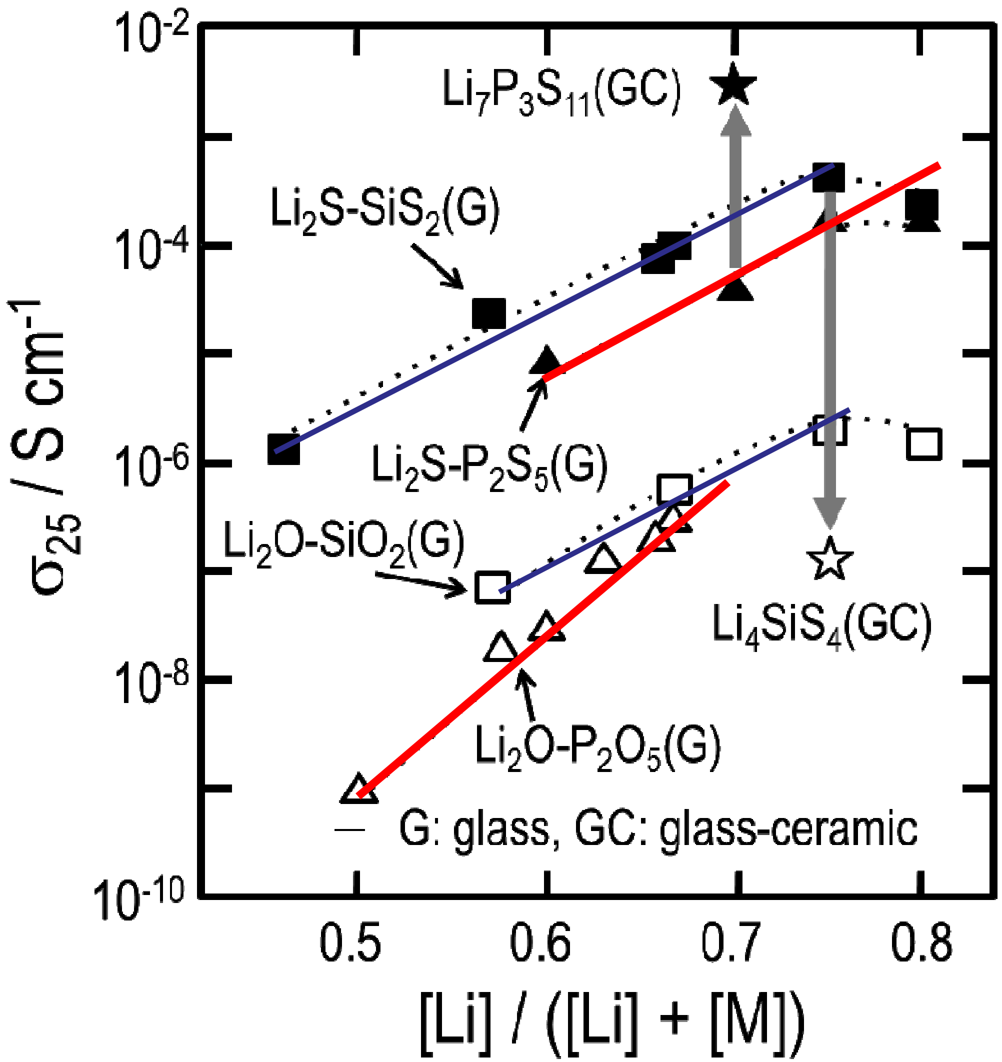
Li-ion battery in Boeing 787

A commercial electric car

Chalcogenide glasses for high capacity and safe Lithium battery

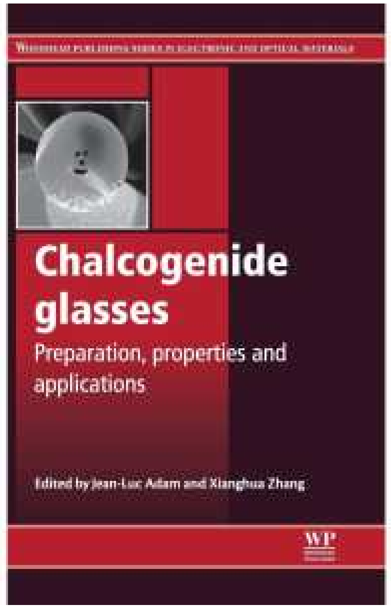
- Among the highest Li^+ conductor ($10^{-3}\ \Omega^{-1}cm^{-1}$ at 25°C)
- Increases safety : preventing the formation of Li dendrite
- Increase energy density : allowing the use of Li metal anode

Composition dependence of conductivity at 25 °C for oxide and sulfide glass-based electrolytes.



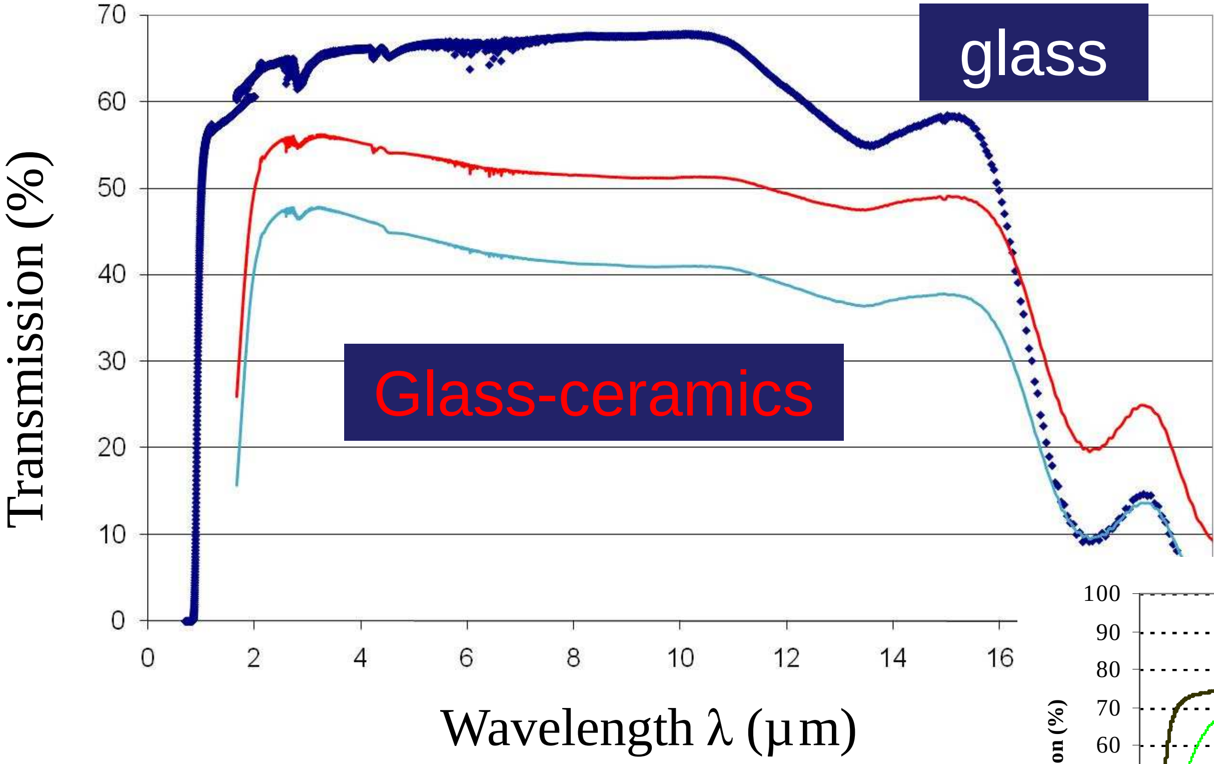
Masahiro Tatsumisago & Akitoshi Hayashi

Chalcogenide glasses as electrolytes for batteries



Chalcogenide for photoelectric applications

« unusual »behavior of $GeSe_2$-Sb_2Se_3-CuI glass-ceramics



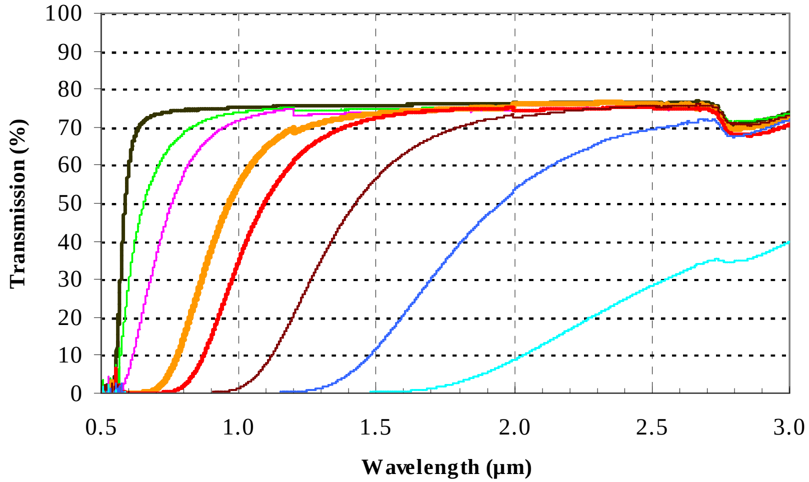
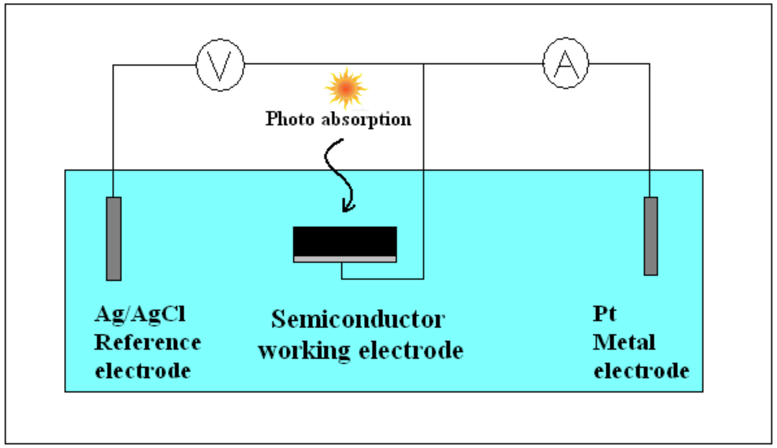
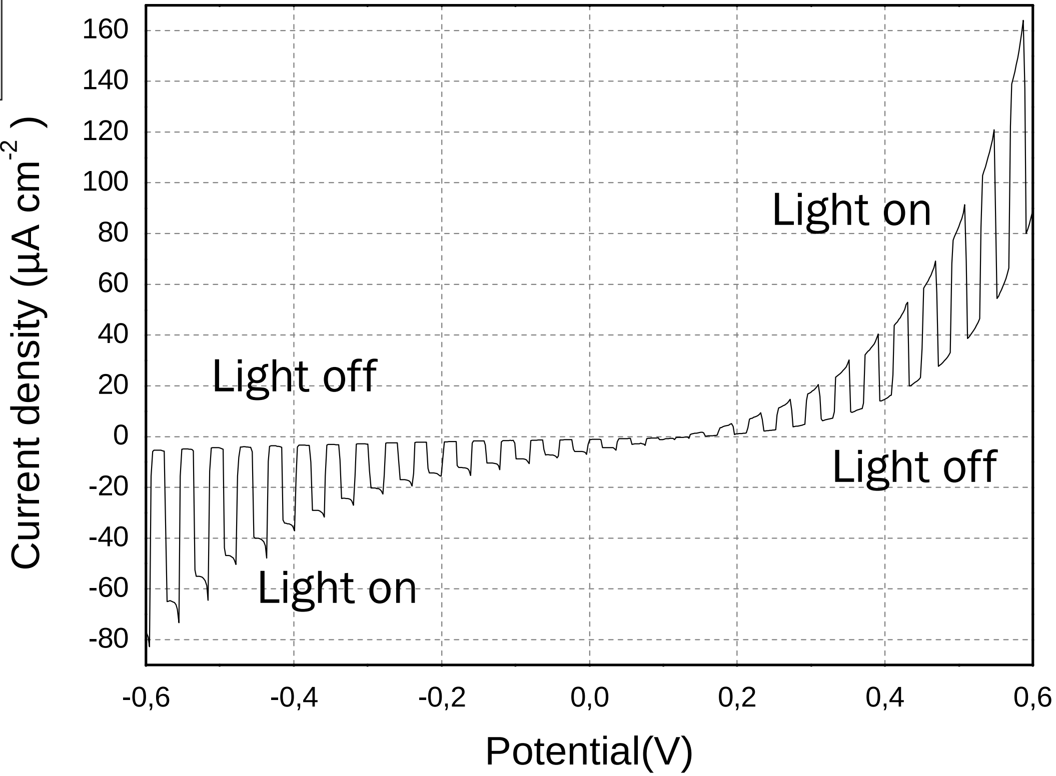


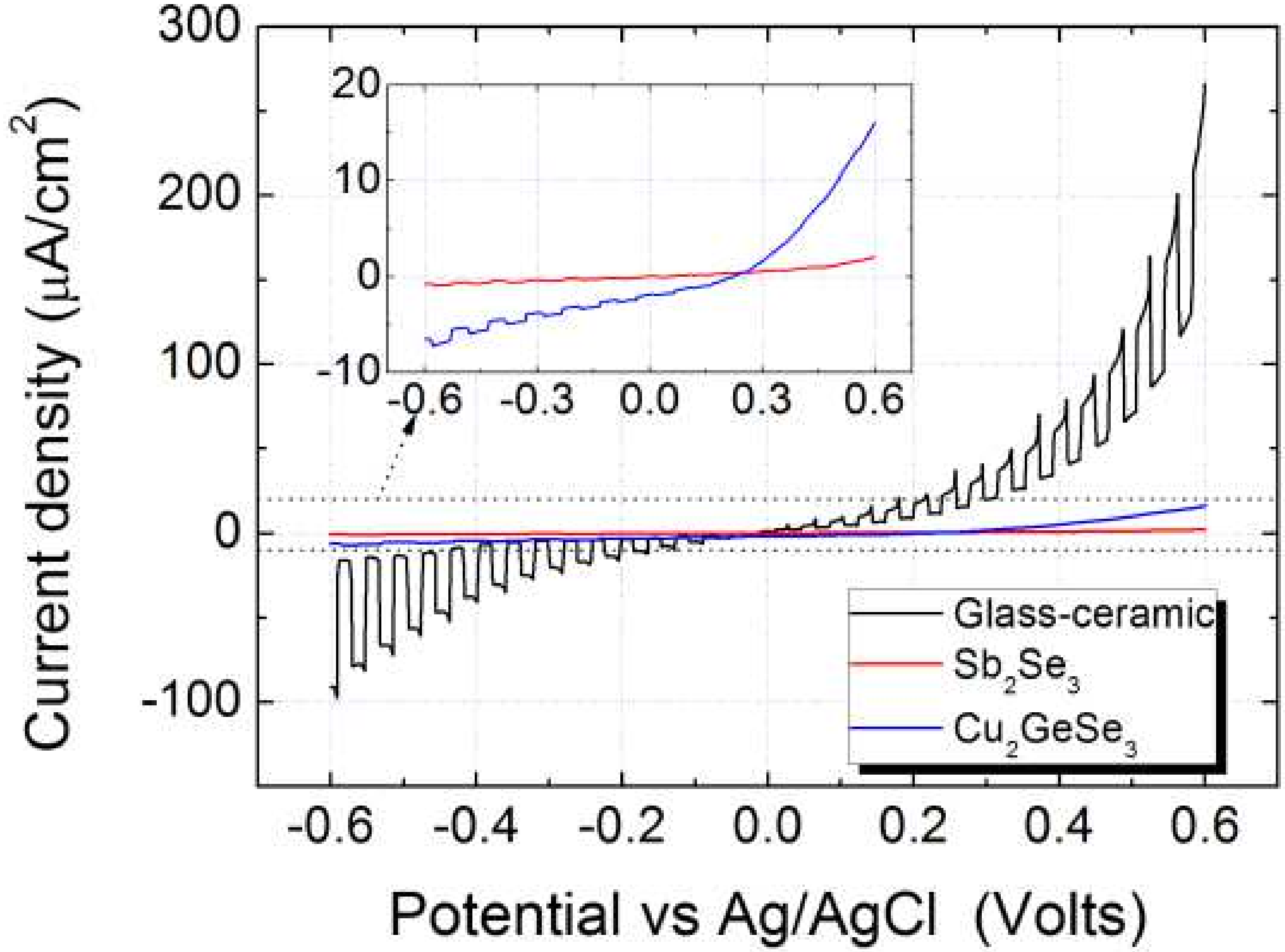
Photo-electro-chemical measurement



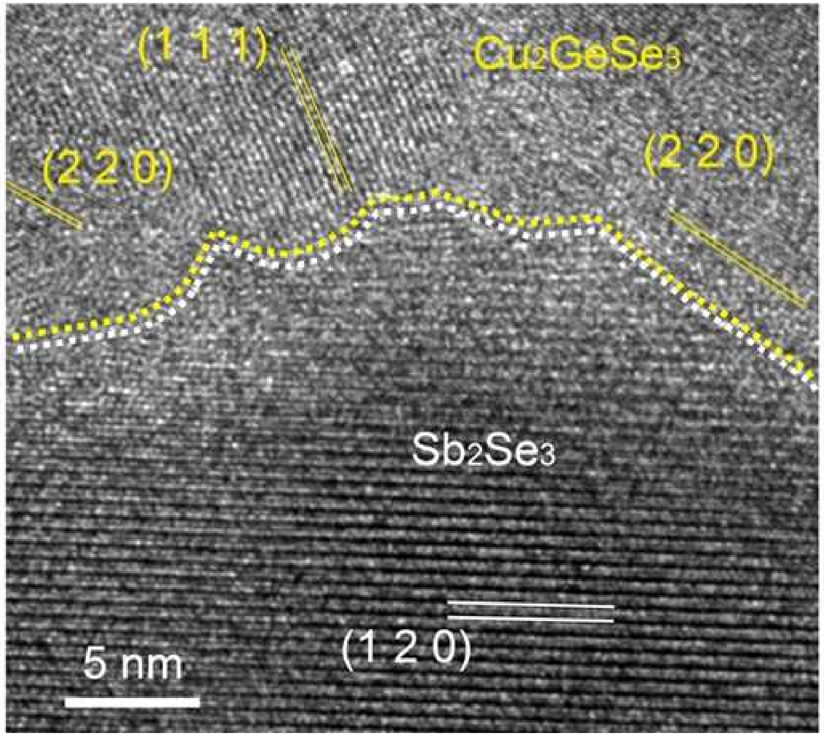
$GeSe_2$-Sb_2Se_3-CuI
glass ceramic

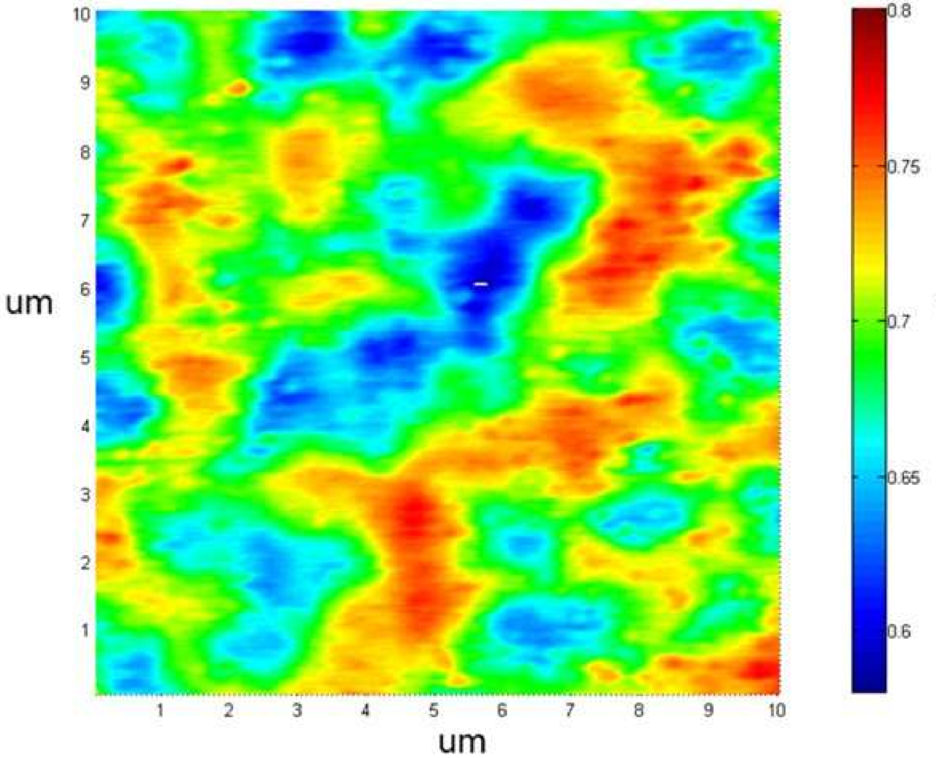


Photocurrent of different compounds



Formation of heterojunctions and conductive channels





- ❑ Enhanced charge separation
- ❑ Long lifetime of charge carriers
- ❑ Conductive channels for efficient charge collection
- ❑ Strong photocurrent density
- ❑ Promising results for photoelectric and photocatalytic application

Summary

- **Non-oxide glasses**
  - **Fluoride glasses : UV-MIR transmission, high RE solubility, low phonon energy**
  - **Chalcogenide glasses : Transparent in the thermal imaging window**

- **Chalcogenide glasses**
  - **Alternative to Ge for thermal imaging**
  - **Others applications : chemical and biologic sensing …**
  - **Other fabrication techniques needed to be developed**

- **Chalcogenide glasses**
  - **Interesting for energy applications**

- **Chalcogenide glasses are "old materials"**
- **With more and more new applications**
- **We need process revolution**