Preparation, Properties and Applications of Chalcogenide Glasses

Guorong Chen
School of Materials Science and Engineering
East China University of Science and Technology

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..

Tel：+86 21 64250189, +86 13701726294
E-mail：grchen@ecust.edu.cn
msn: grchen54@hotmail.com

References

1. A. Feltz, Amorphous Inorganic Materials and Glasses, VCH, 1993
2. W.Vogel, Glass Chemistry, Springer-Verlag, 1992
3. Journals: J. Non-Cryst. Solids, J. Am. Ceram. Soc., Chem. Phys. Lett., Chin. Phys. Lett., Appl. Phys. Lett., Opt. Lett., Opt. Express, Adv. Mater., etc.

Outline

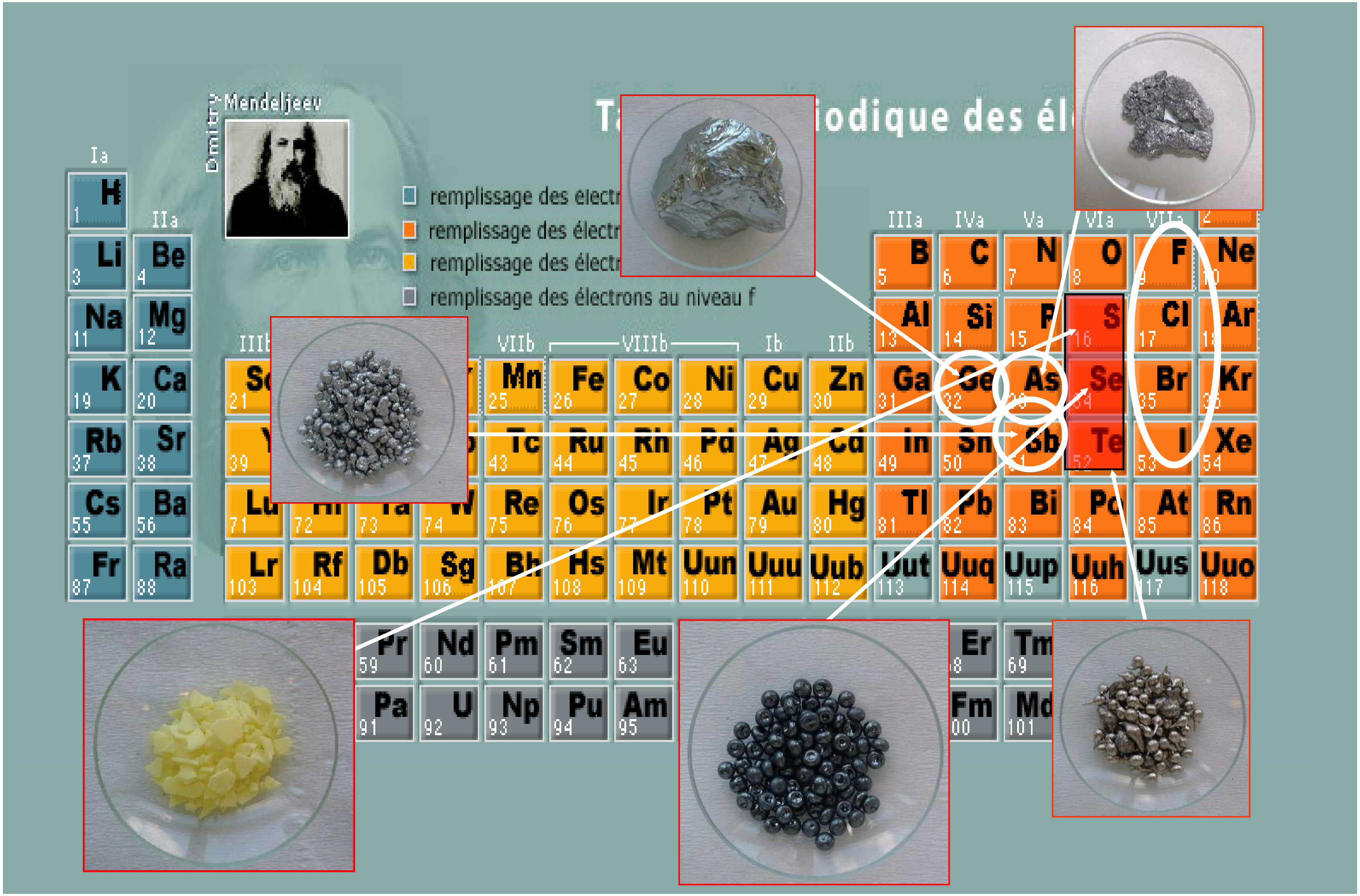
- **Generality**
- **Preparation**
- **Structure and properties**
- **Thermal treatment**
- **Main applications in passive and active infrared optics**

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_2S_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.

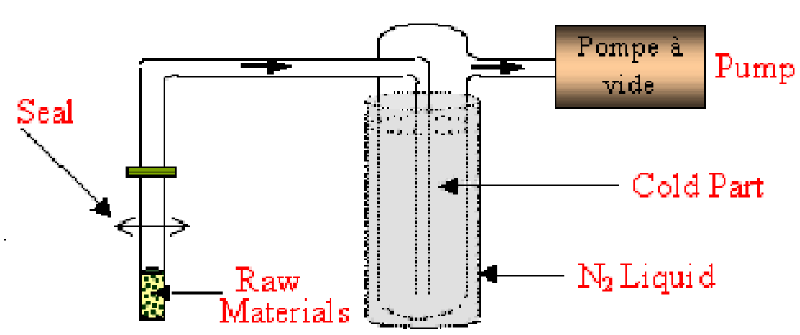
J. S. Sanghera, et al., *J. Non-Cryst. Solids*, 1999, 256-257:1-16

Active Optics

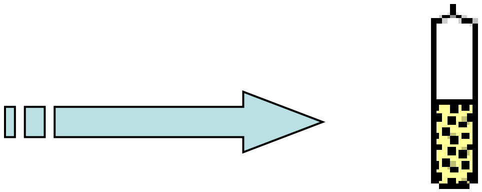
Active applications of chalcogenide glass fibers are where the initial light propagating through the fiber <u>is modified by a process</u>.

J. S. Sanghera, et al., *J. Non-Cryst. Solids*, 1999, 256-257:1-16

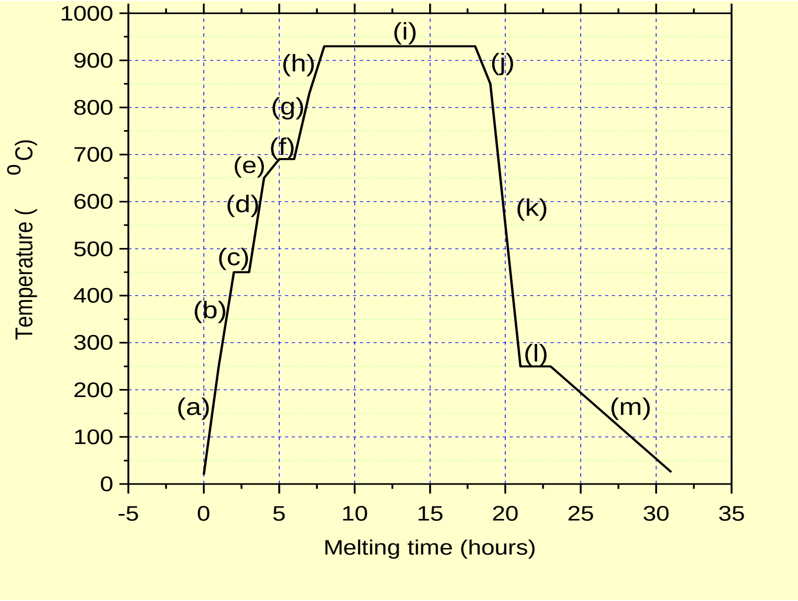
2. Preparation



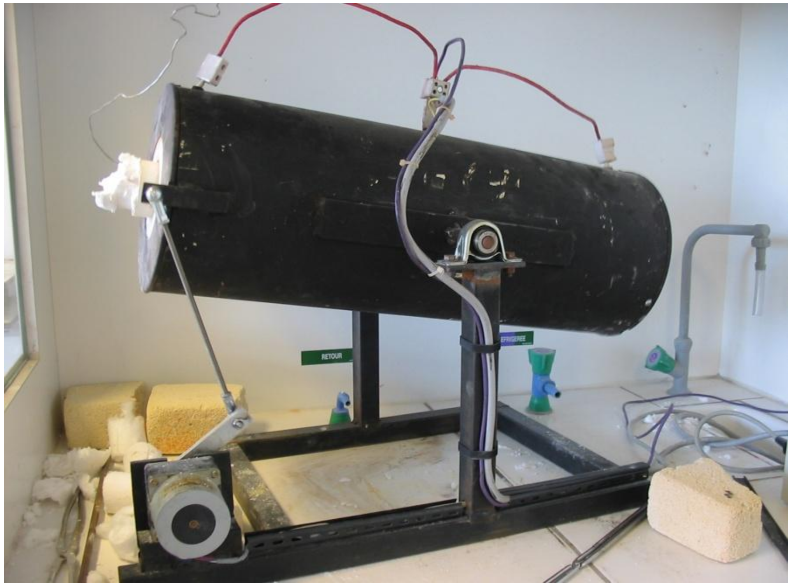
Vacuum sealing (10^{-3} Pa)



Quartz glass ampoule with batch



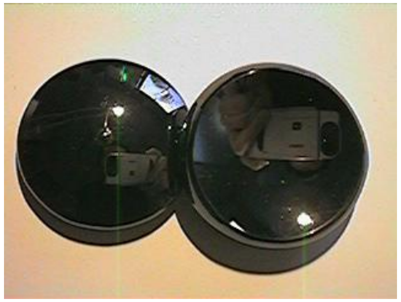
Melting process



Rocking furnace

Purification

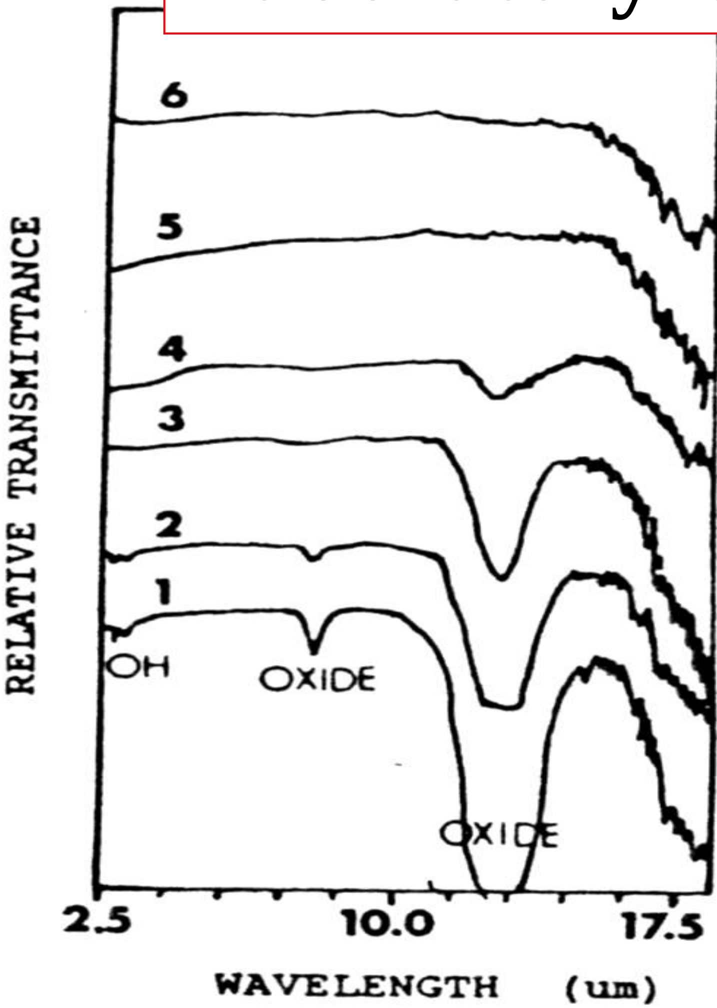
Purification in order to remove impurities containing O, H and C



- **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)**

An exa

Naval Research Laboratory USA



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

J.S. Sanghera, et al., J. Non-Cryst. Solids, 1993, 161: 320-322

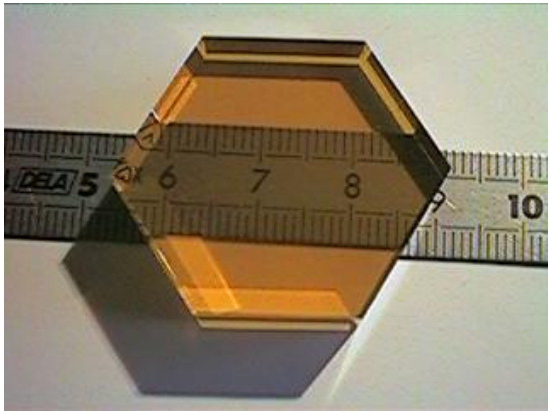
Purification virus O_2 content

Purification conditions	Abs. coefficient α (cm^{-1} at 10.6 μm)	Estimated O_2 content (ppm wt)
Ge-As-Se system		
1 Unpurified	0.2030	144.2
2 As, Se purified	0.0991	3.1
3 Glass distillated	0.0454	1.3
Ge-As-Se-Te system		
1 Unpurified	0.1814	103.4
2 Se purified	0.1160	66.7
3 As, Se purified	0.0893	17.4
4 As, Se, Te purified	0.0308	5.6
5 Glass (3) distillated	0.0209	0.8
6 Glass (4) distillated	0.0071	0.6

3 Thermal Treatment

- **Shortcoming of ChG:**
  weak bond strength

$$\upsilon = 2\pi\sqrt{\frac{\kappa}{\mu}}$$

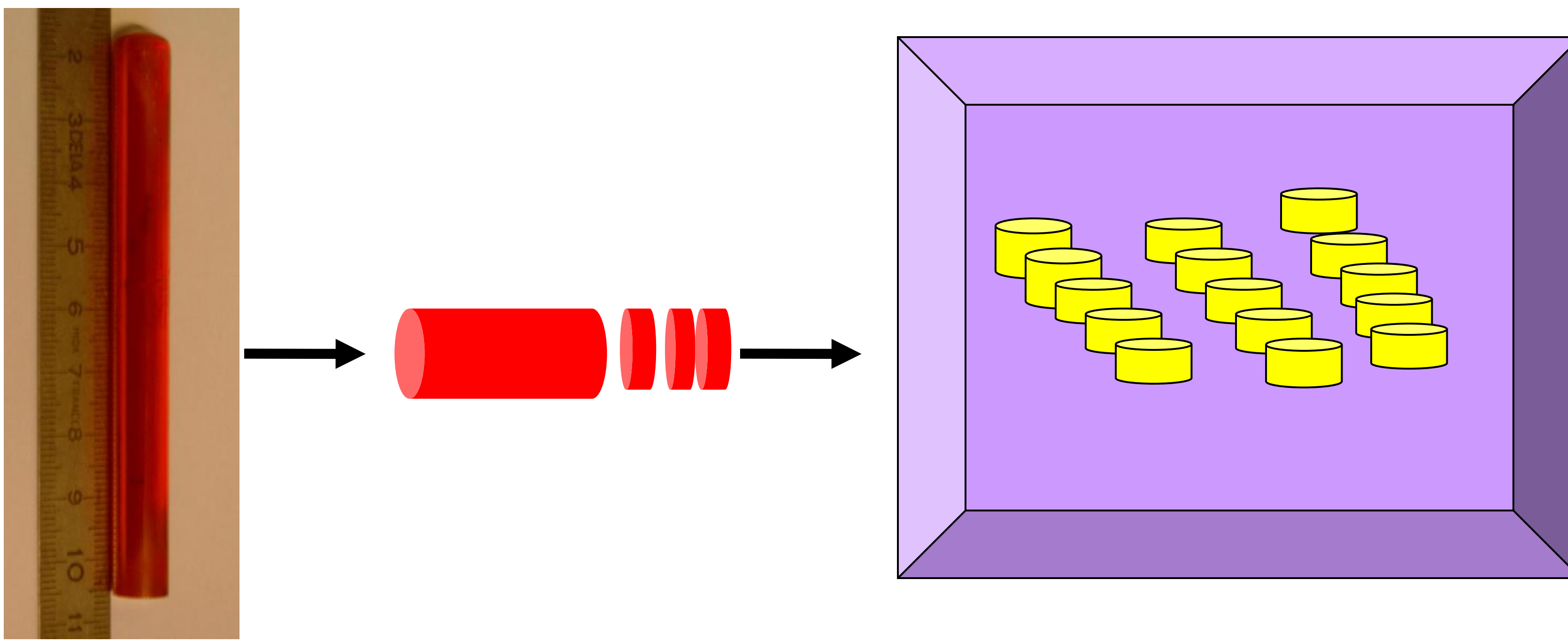


ν = vibration frequency
κ = force constant
μ = reduced mass of the vibrating ions
(μ = $m_c m_o/(m_c+m_o)$)

Controlled crystallization

Key points:

- **Glass composition**
- **Thermal treatment conditions**



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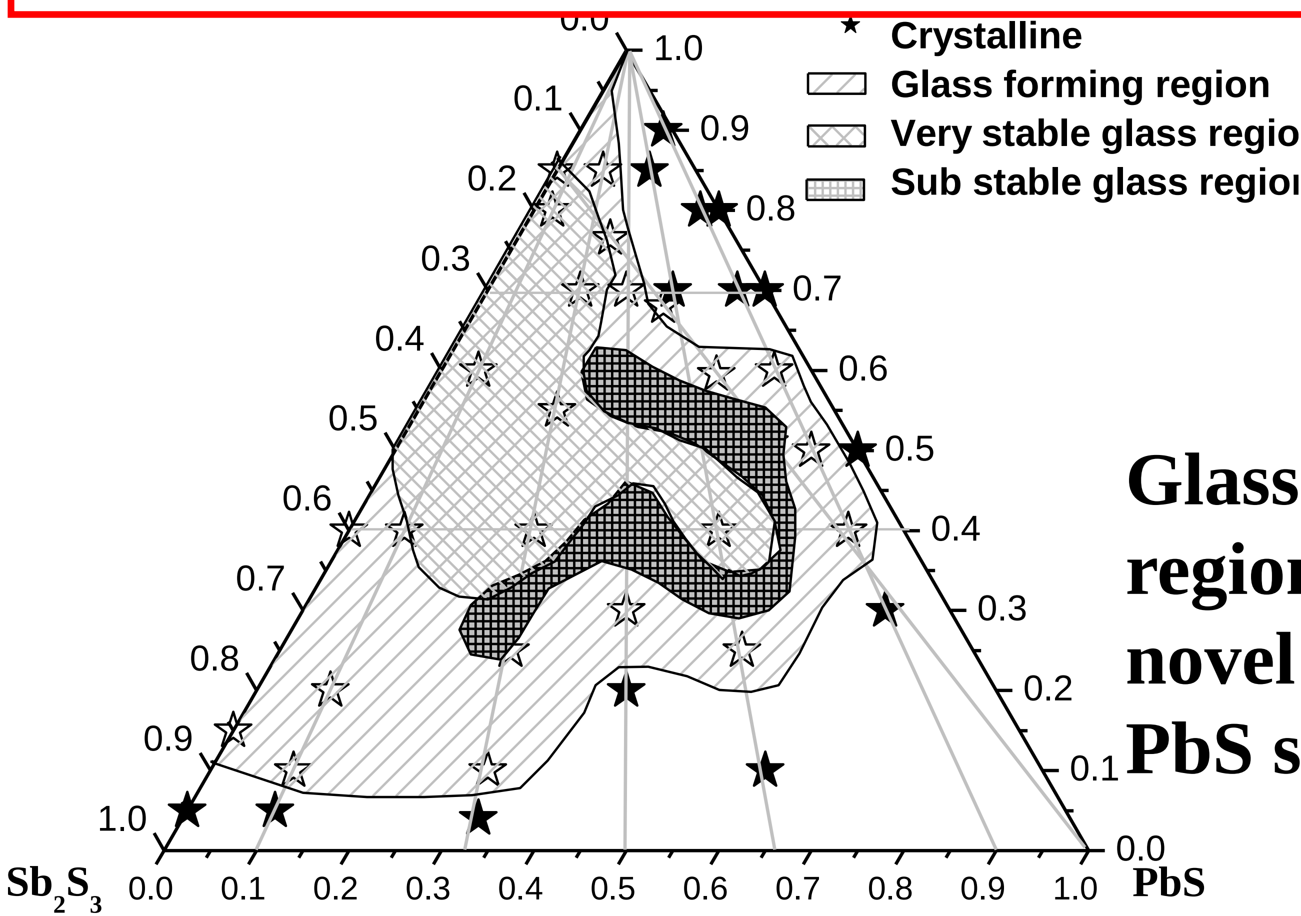


Glass forming region of the novel GeS_2-Sb_2S_3-PbS system

Fang Xia, et al., *J. Am. Ceram. Soc.*, 2006, 89(7) 2154-57

Crystallization ability

- **VSG region where glasses with larger ΔT (> 170℃, T_c- T_g), or no exothermal peak in DSC unable crystallized even for long time (>100 h) heating .**

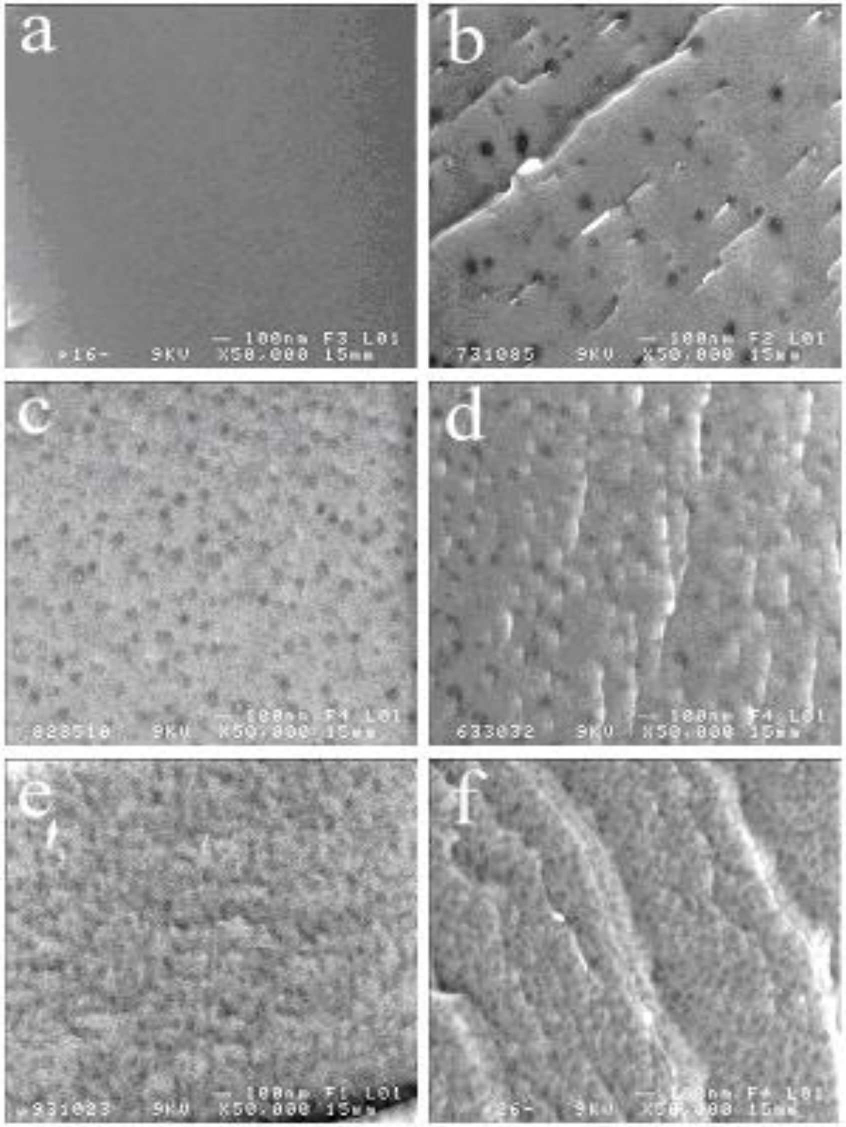
- **Glasses near the border of glass forming region not thermally stable and tended to crystallize but very difficult to control crystal growth thus affecting IR transmission of materials.**

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

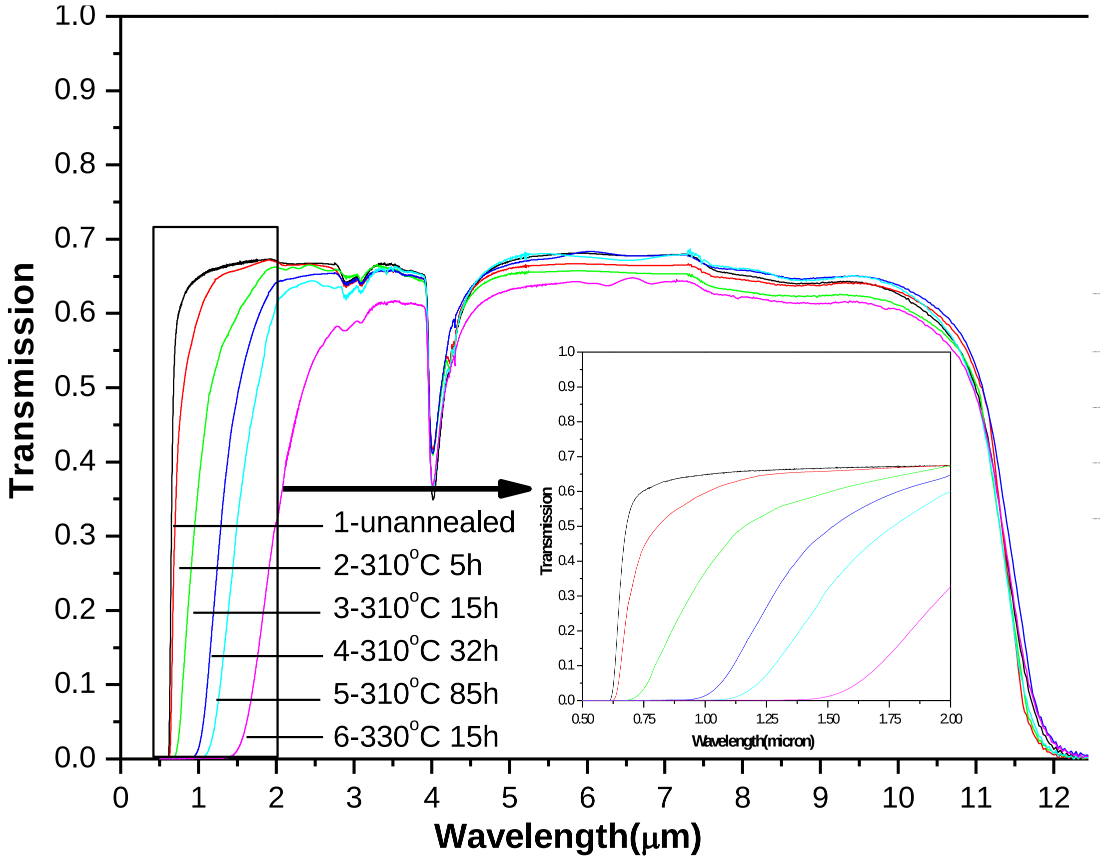


(a) P9 at 330°C for 163 h,
(b) P7 at 300°C for 5 h,
(c) P5 at 340°C for 15 h,
(d) P5 at 310°C for 15 h,
(e) P5 at 310°C for 32 h,
(f) P5 at 310°C for 85 h.

P5: $51GeS_2$-$9Sb_2S_3$-40PbS
P7: $30GeS_2$-$35Sb_2S_3$-35PbS
P9: $55GeS_2$-$30Sb_2S_3$-15PbS

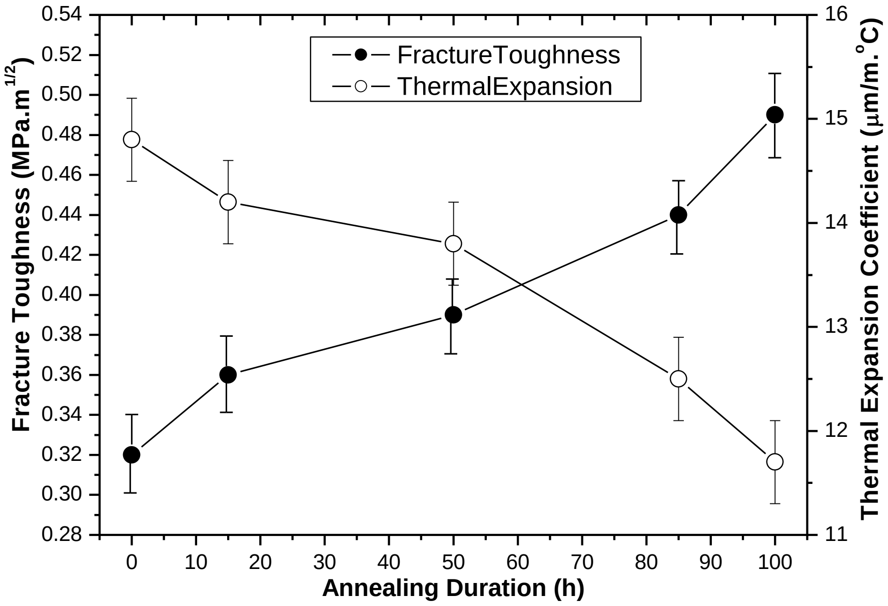
Crystal size: < 100 nm

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.

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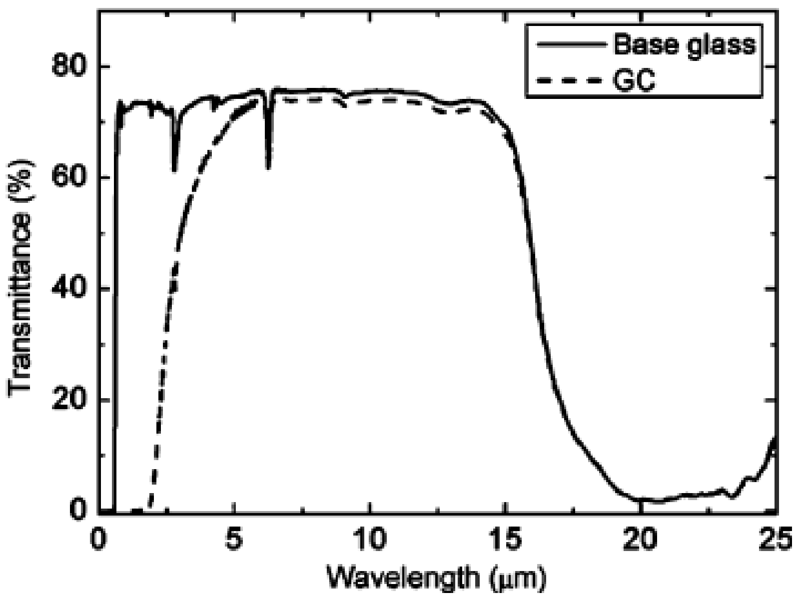
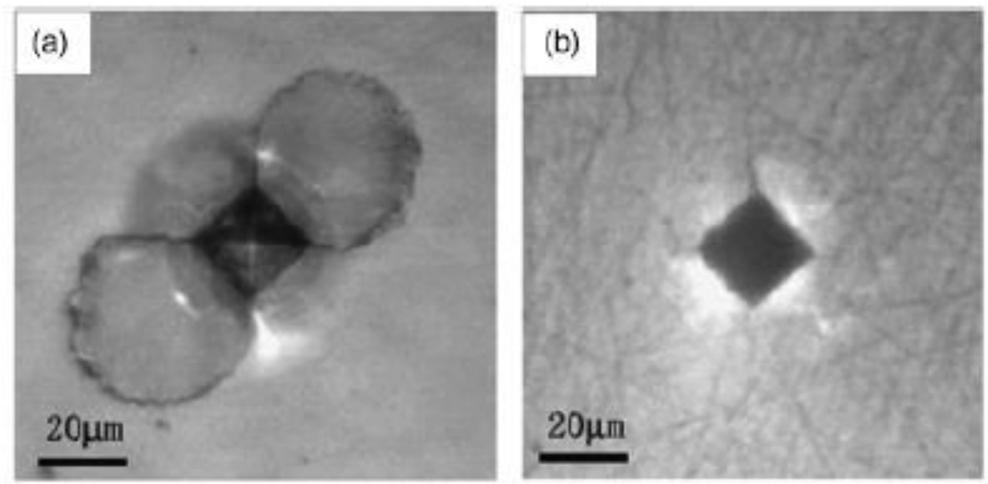




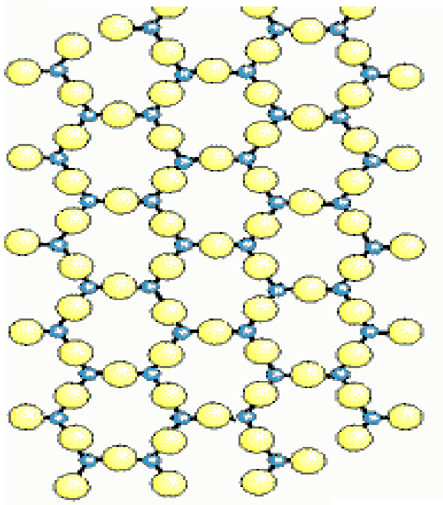
Controlled crystallization of $GeSe_2$-Ga_2Se_3-CsI ChGs during molding: (left) IR transmission spectra; (right) Resistance to crack propagation of (a) the base glass and (b) glass-ceramic

Wei Chen, et al., *J. Am. Ceram. Soc.*, 2008, 91, 2720

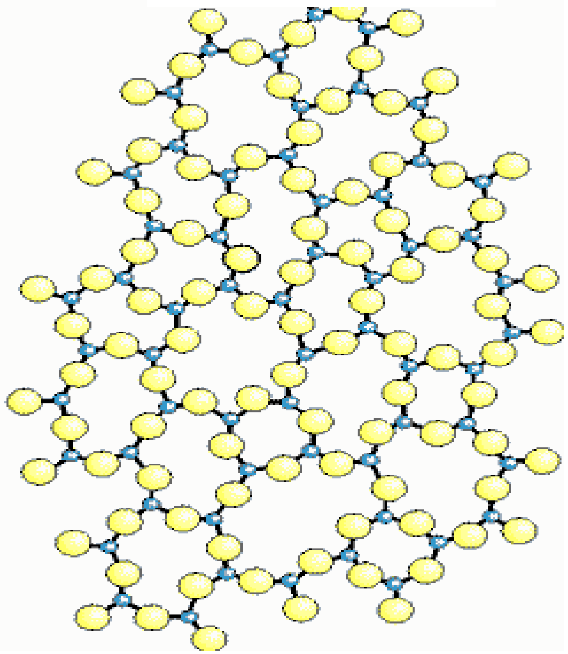
4 Structure and Properties

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

Crystalline



Glassy



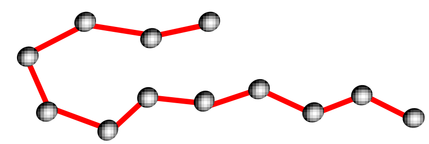
Feature of glass network:

Short-range in order, long-range disorder

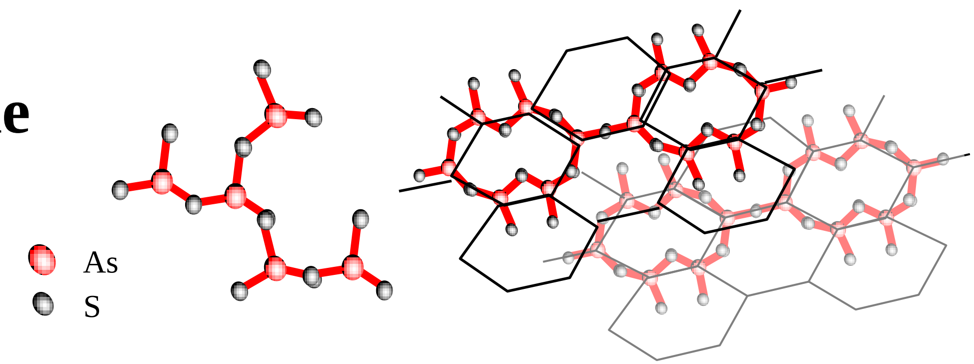
ChG: Structural models

ChG can be classified by reference to dimensionality

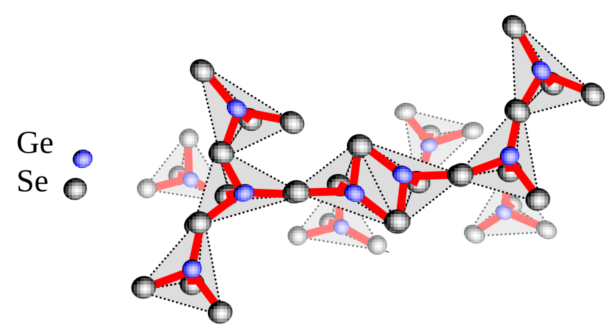
- **1D spaghetti-type, such as Se glass made of infinite chains**



- **2D distorted planar glasses such as As_2S_3 made from connections of 2 coordinated S atoms and 3 coordinated As atoms**



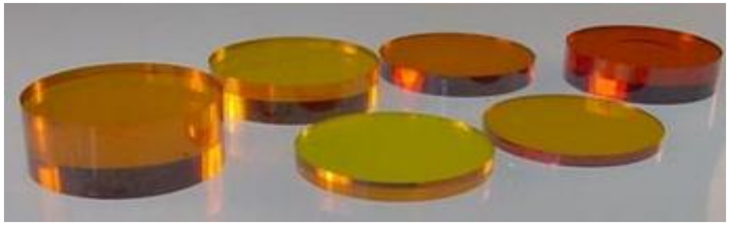
- **3D glasses, such as $GeSe_2$ being result of $GeSe_4$ tetrahedra connections**



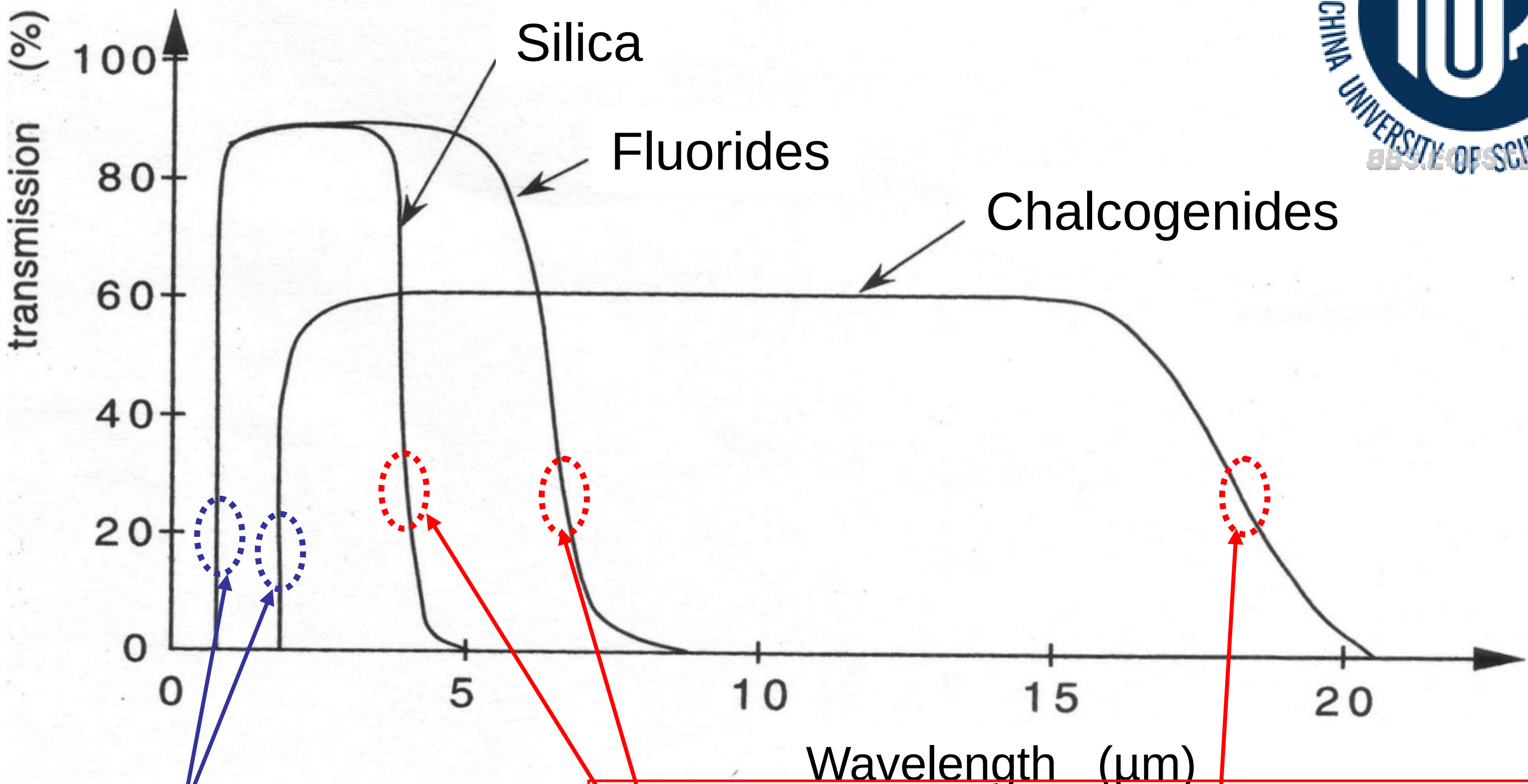
Properties

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:	Si–O : 1100 cm^{-1}
Fluorozirconates:	Zr–F : 580 cm^{-1}
Sulphides:	Ge–S : 350 cm^{-1}
Selenides, Tellurides	< 300 cm^{-1}

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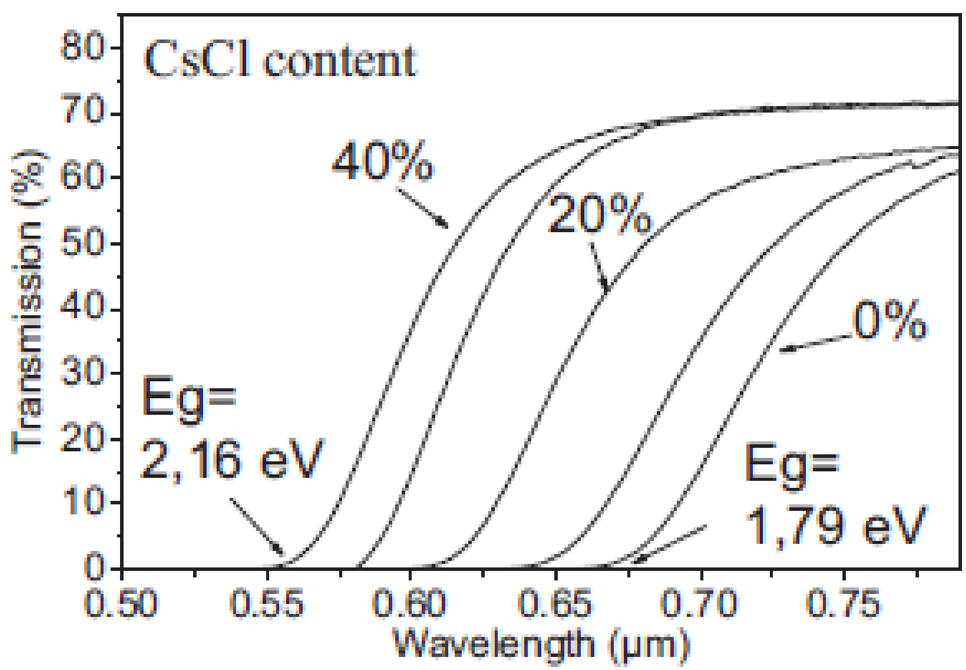
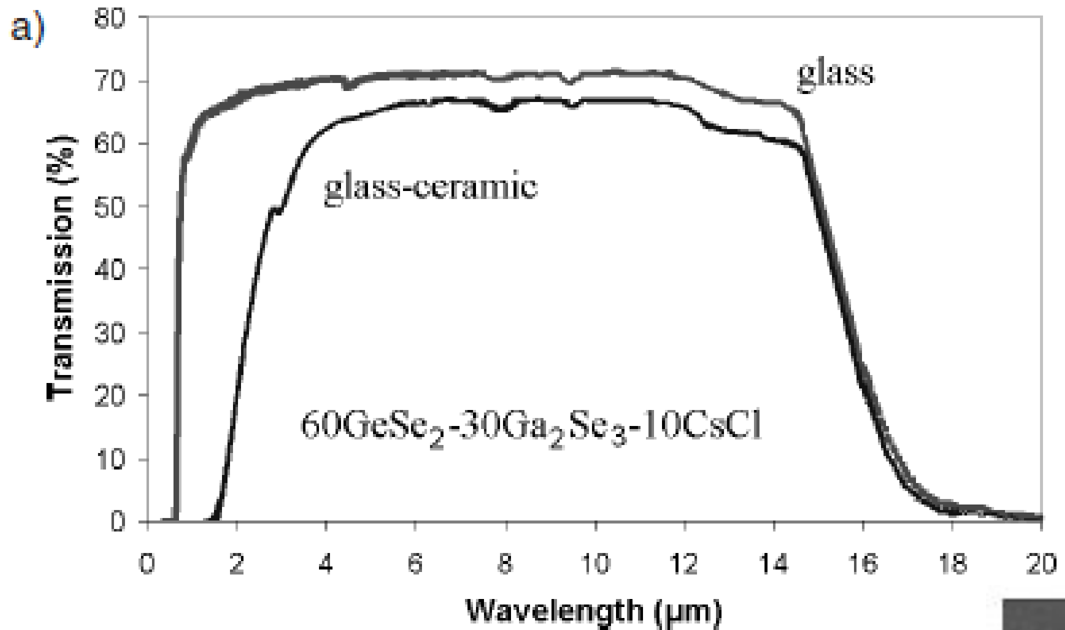
An example

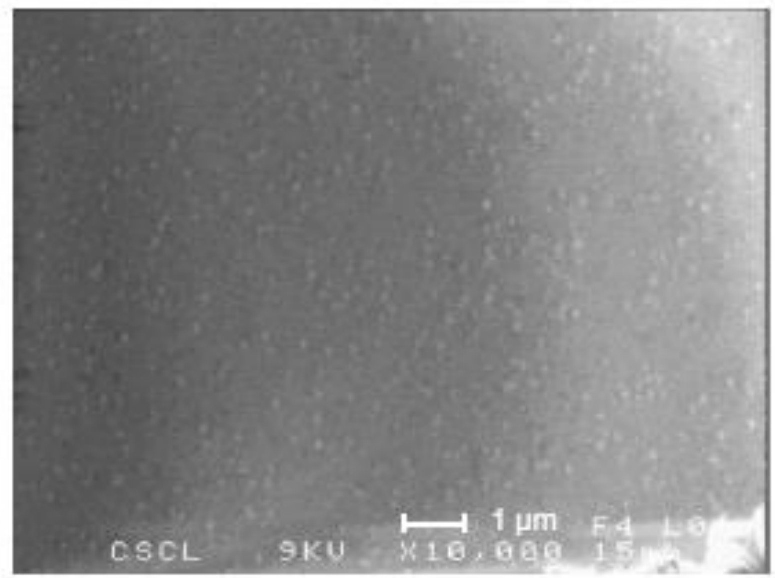


Evolution of the bandgap energy for $GeSe_2$-Ga_2Se_3 -CsCl glasses with 0, 10, 20, 30, and 40 mol% CsCl.

L. Calvez, et al., *Adv. Mater.* 2007, *19*, 129

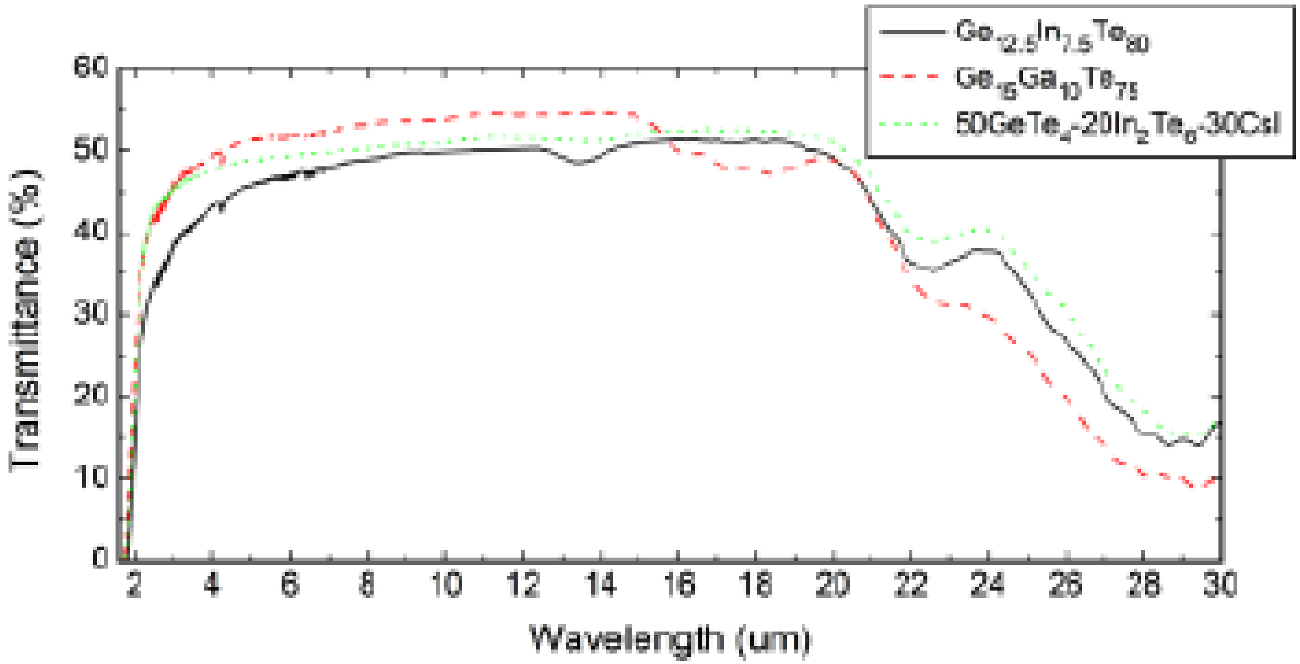


Grains homogeneous (ca. 100 nm) with uninfluenced FIR transmittance and the same *a*, and almost doubled toughness from 0.227 to 0.425.



University of Arizona, USA

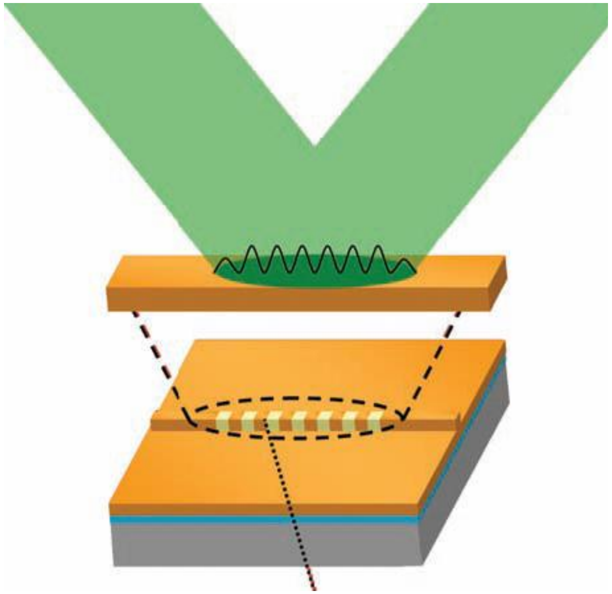
Tellurium based glasses have excellent transmission in 3-20 µm. Especially, Ge-As-Te system exhibits the best stability, more amenable for larger scale production.



P. Lucas, et al., *J. Am. Ceram. Soc.*, 2009, 92, 2920

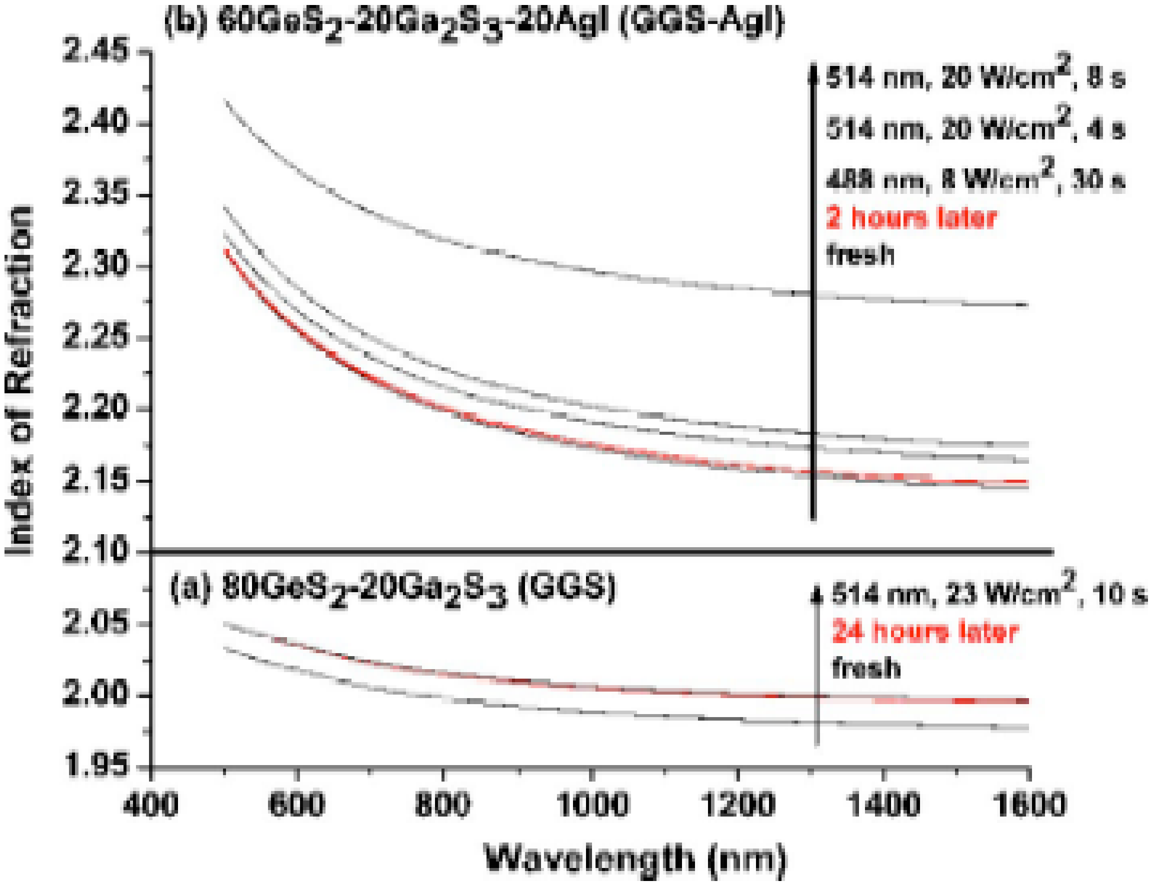
Photo-induced (PI) effects

- **PI dissolution (doping)**
- **PI refractive index (RI) change**
- **PI phase change**
- **PI bandgap energy change (darkening or bleaching)**
- **PI contraction**
- **……**



University of Pardubice, Czech

△n > 6%

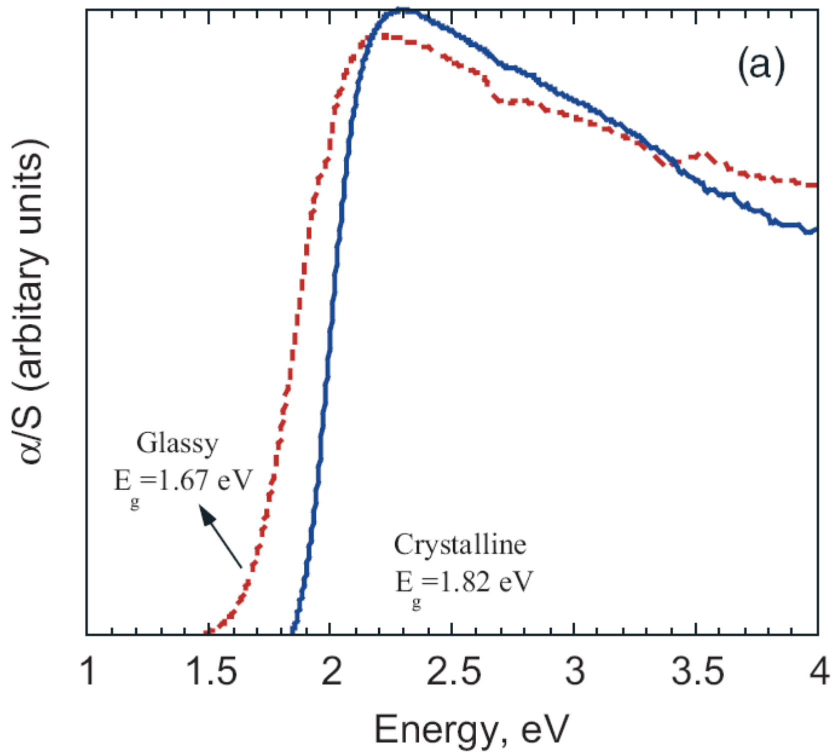


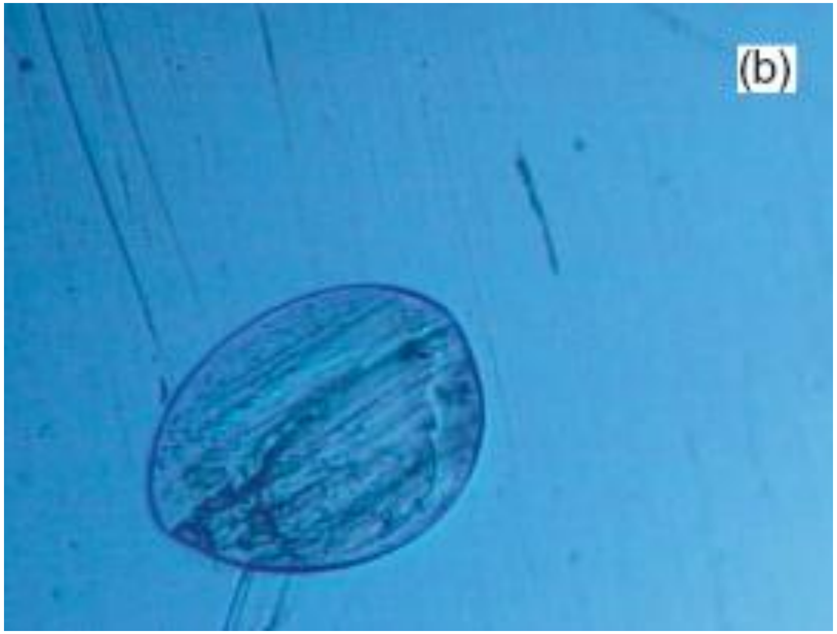
Changes of RIs of GeGaS (a) and GeGaS-AgI (b) before and after laser exposing. The red curves are obtained 24 h and 2 h later after the laser exposing

T. Wagner, et al., *Appl. Phys. Lett.*, 92 (2008)011114

Michigan State University, USA
Aristotle Univ.of Thessaloniki, Greece

1.82 eV ⇄ 1.67 eV

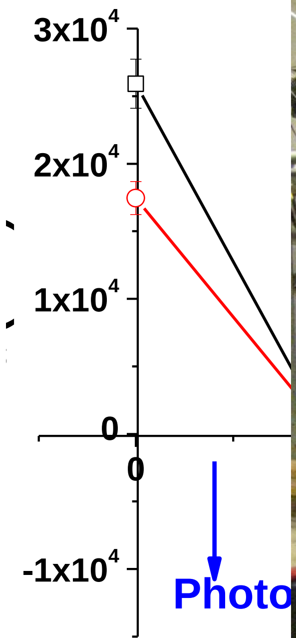


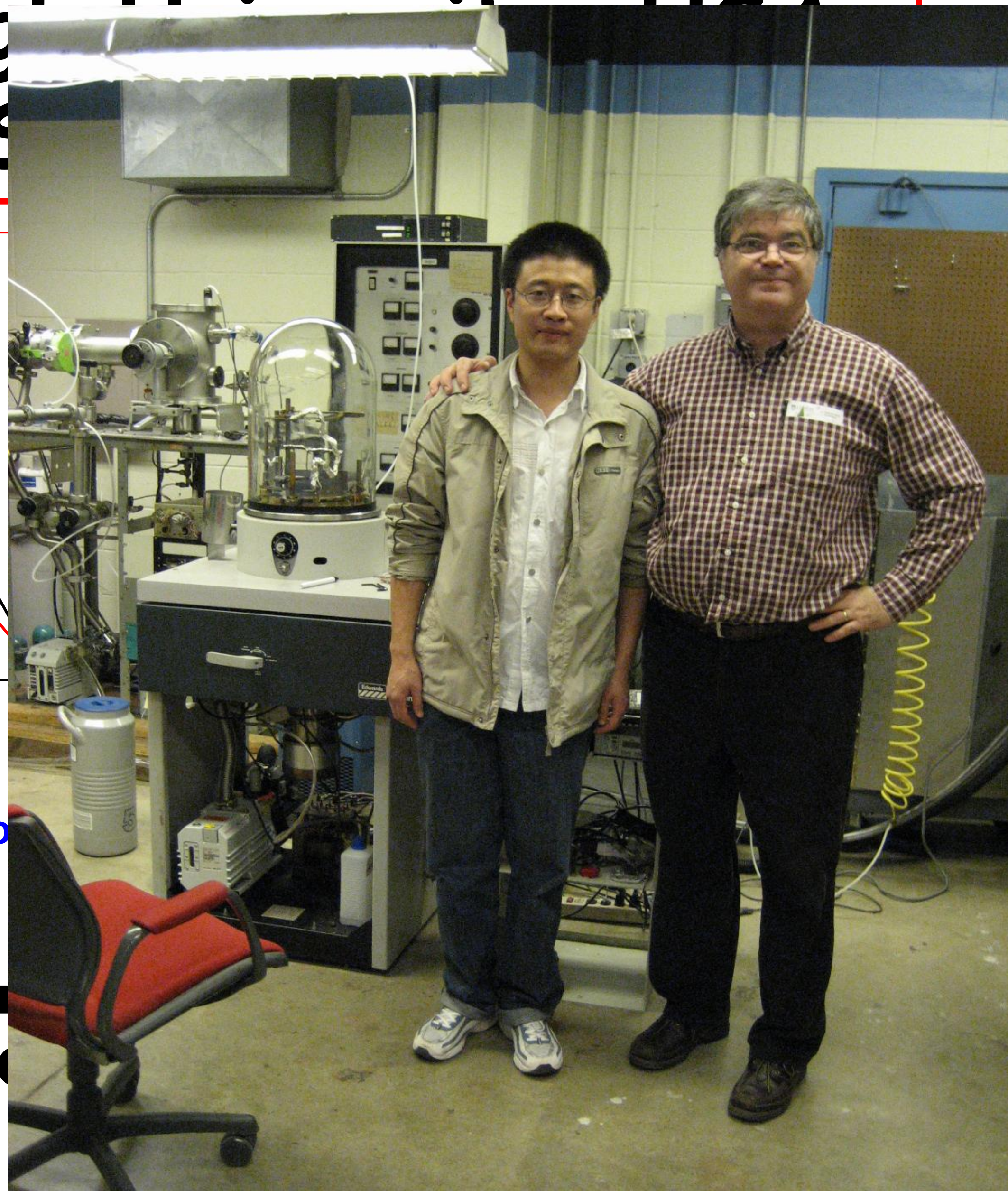


Schema of photo-induced phase change material KSb_5S_8

T. Kyratsi, et al., *Adv. Mater*., 2003,15(17):1429

Lehig
ECUS





oto-stable
Se_{55} films

Variatio
(Δα) vs.
system

2008,16:10565

University of Arizona, USA
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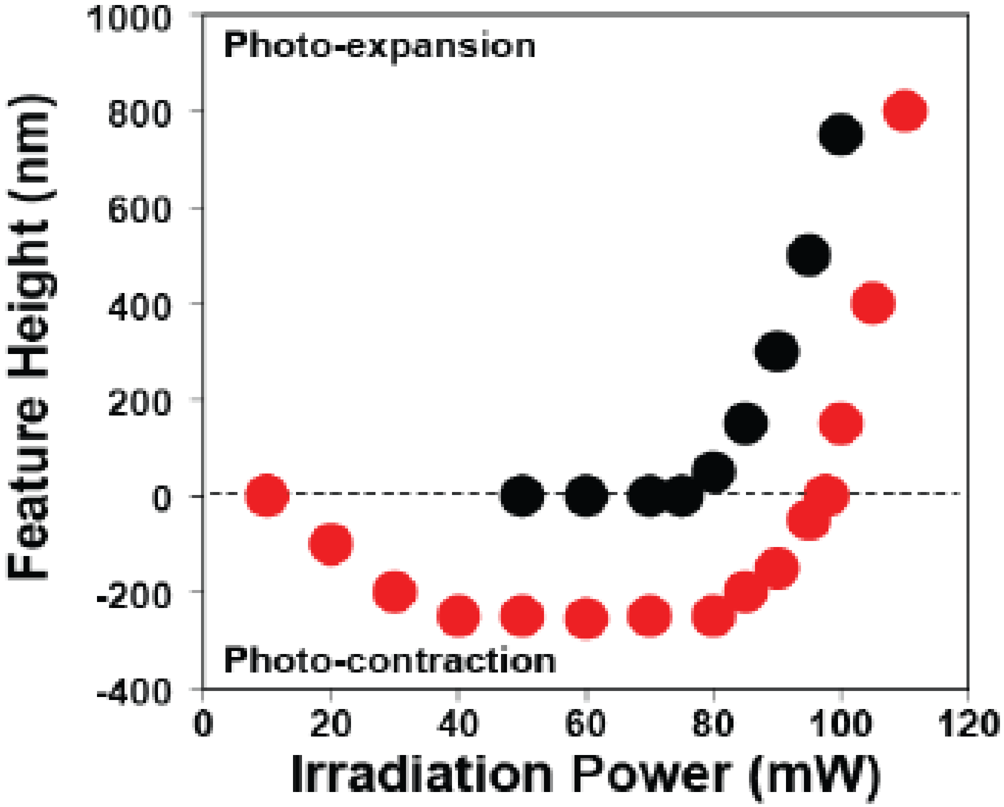
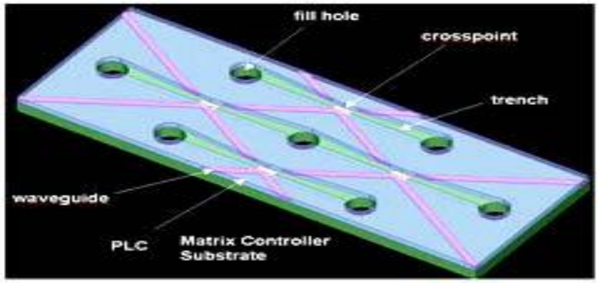


Effect of intensity on PI volume change in $GeAsSe_{13}$ glass. The annealed glass (black) shows PE, the quenched (red) PC. For large intensity, the latter eventually expansion.

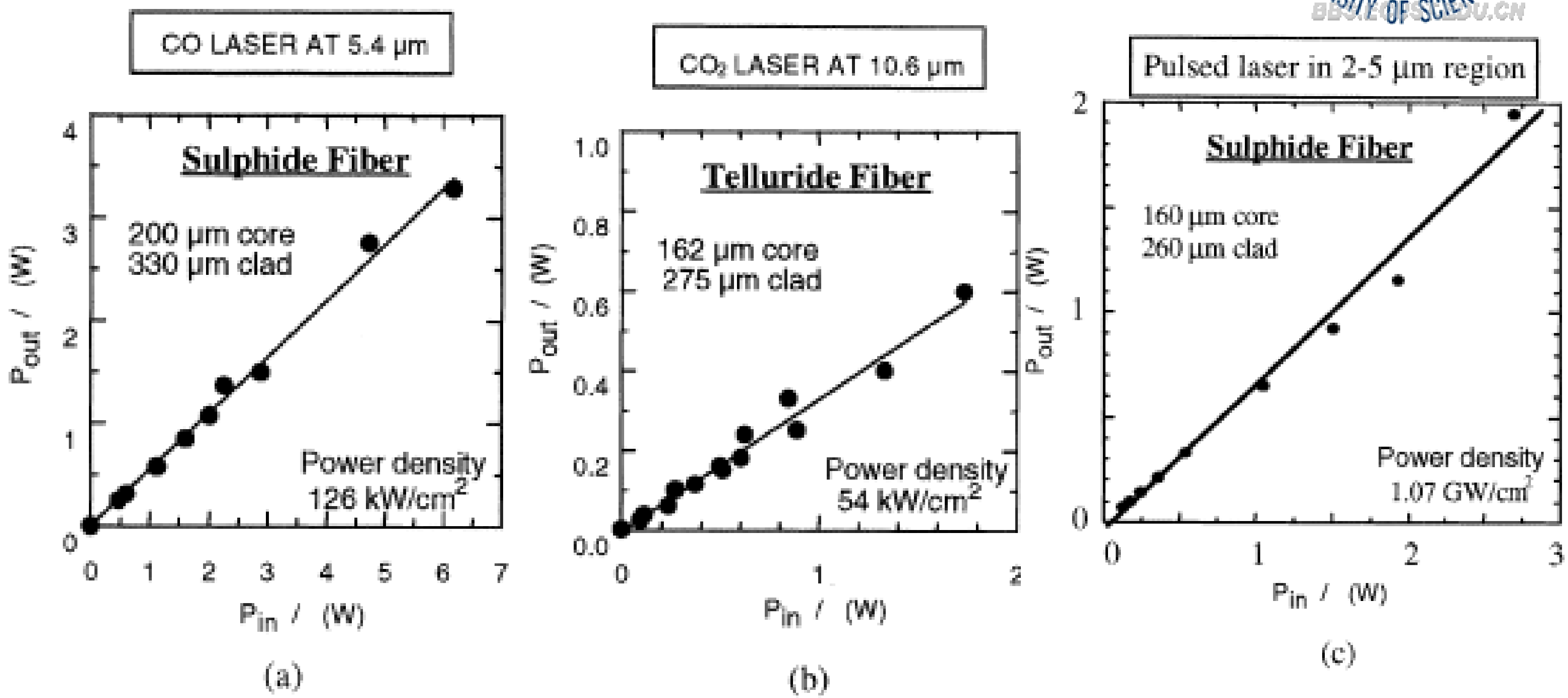
L. Calvez, et al., *Opt. Express*, 2009,17:18581

5 Main applications

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



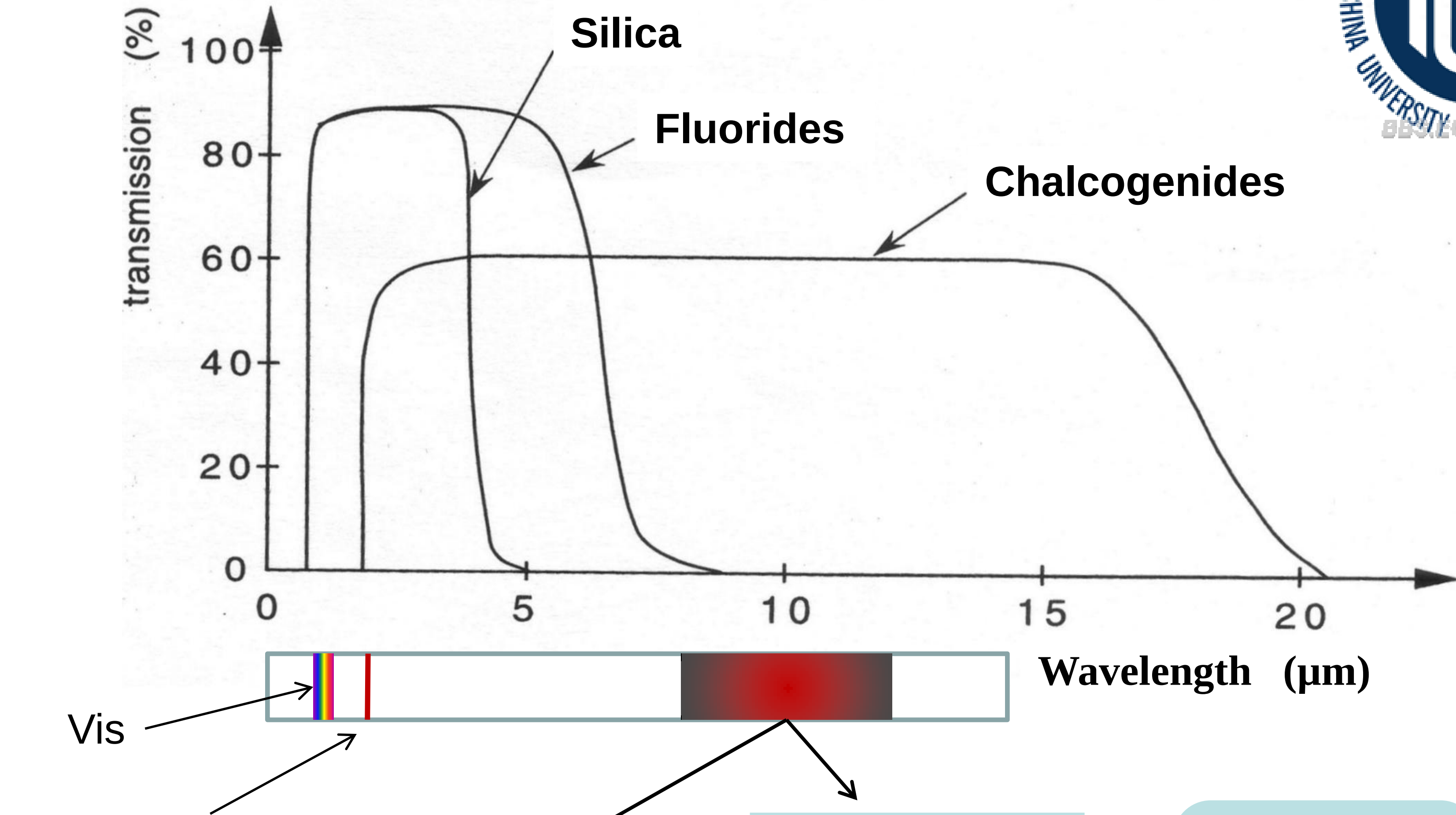
Laser power delivery



(a)CO laser transmission, (b) CO_2 laser transmission and (c) pulsed high energy laser transmission in the 2-5 µm region (±0.01 mW)

J. S. Sanghera, *J. Non-Cryst. Solids*, 1999, 256-257:6

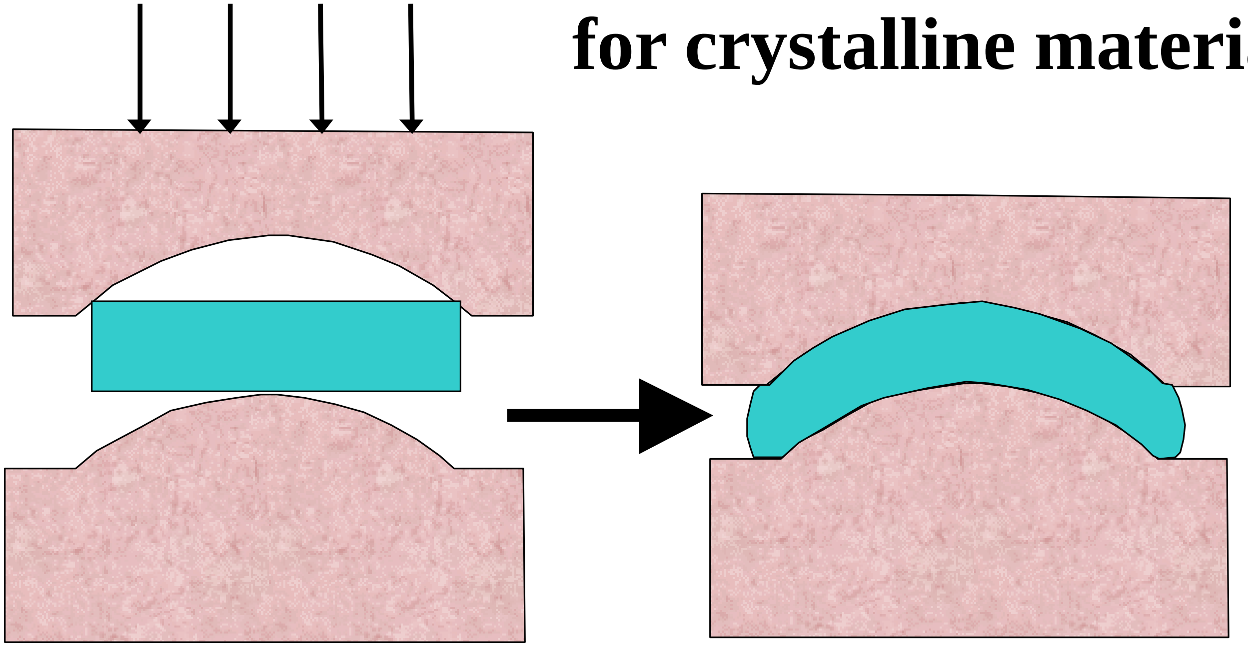
Thermal imaging



Transparence 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 equiped with IR night-vision system with molded chalcogenide glass optics

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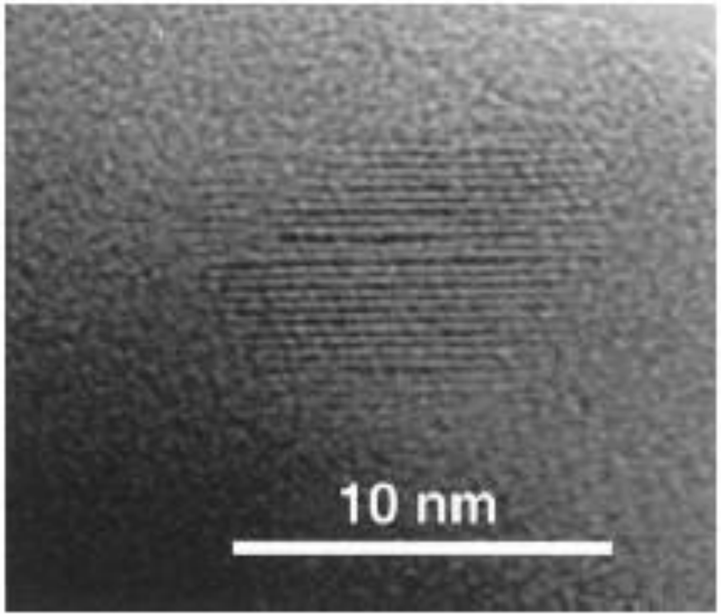
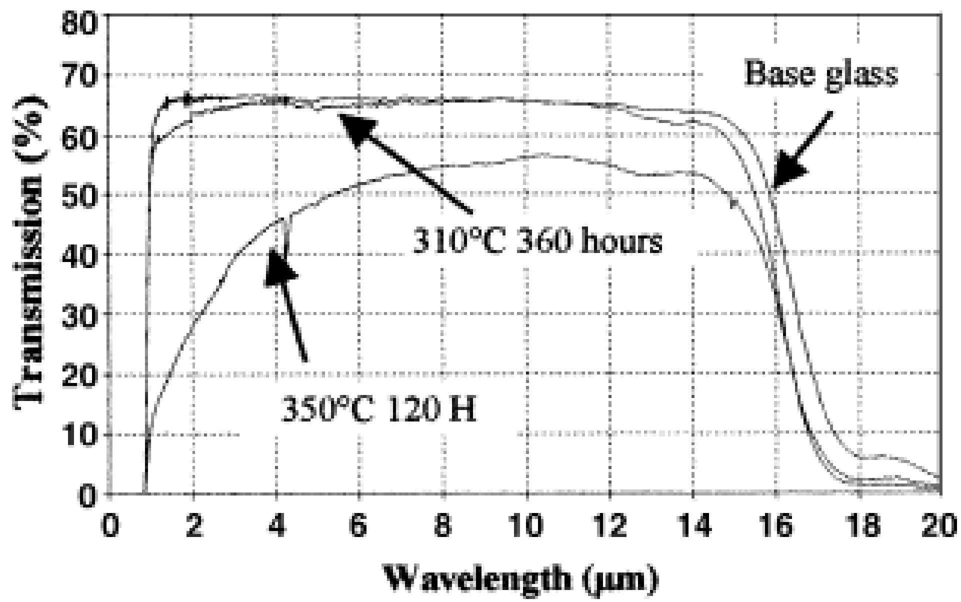


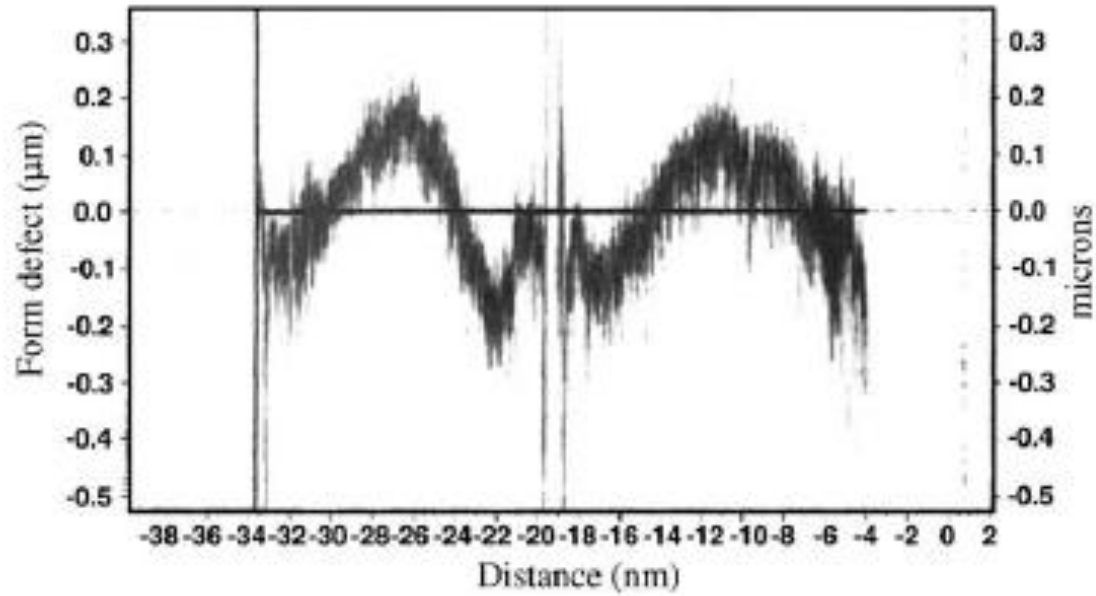


Crystal size: ~ 10 nm

IR transmission of GCs compared with $Ga_5Sb_{10}Ge_{25}Se_{60}$ glass

X. Zhang, et al., *J. Non-Cryst. Solids*, 2004, 336: 49

Molded lens

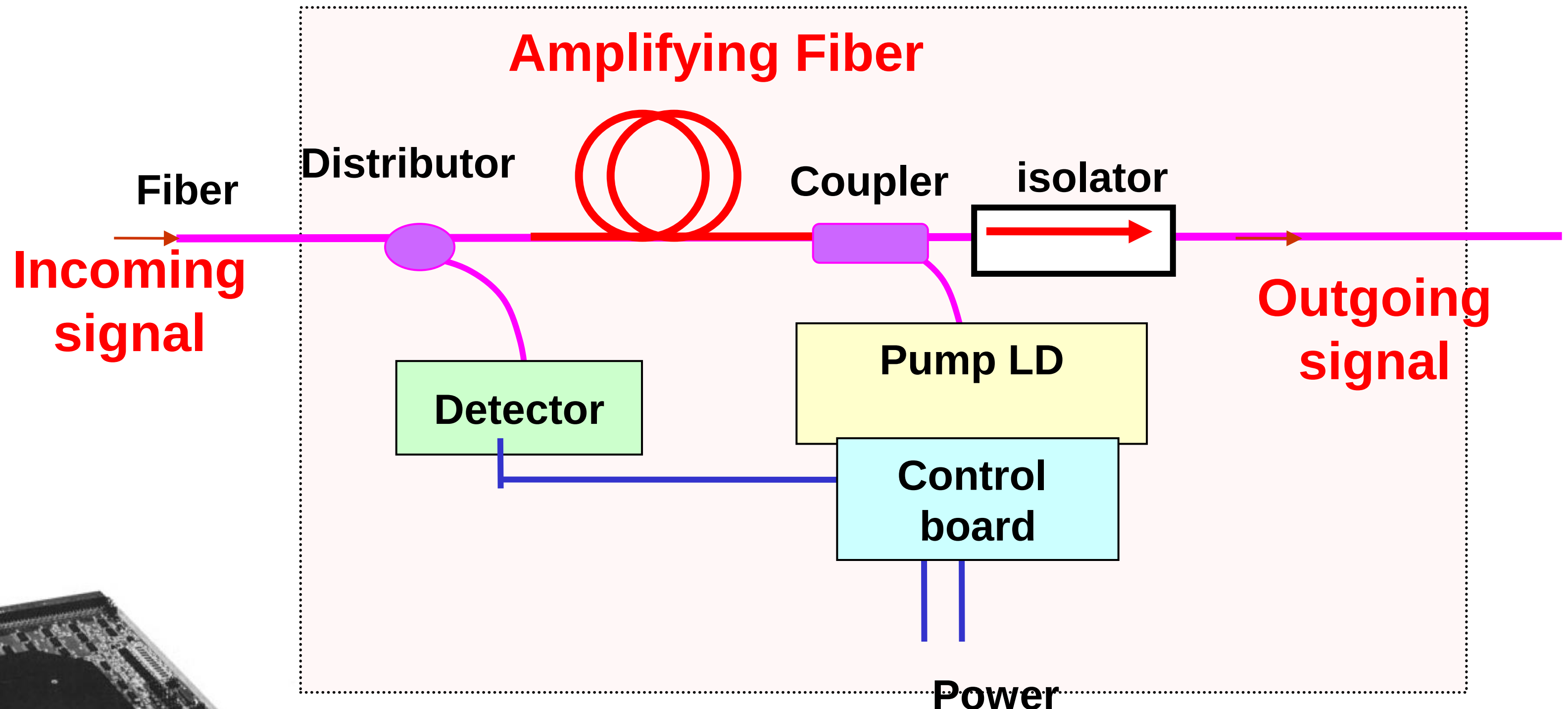


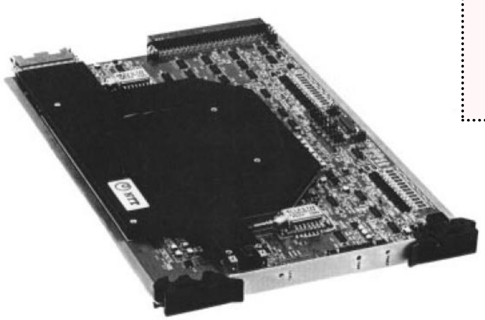
A molded GC lens (D=30 mm)

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

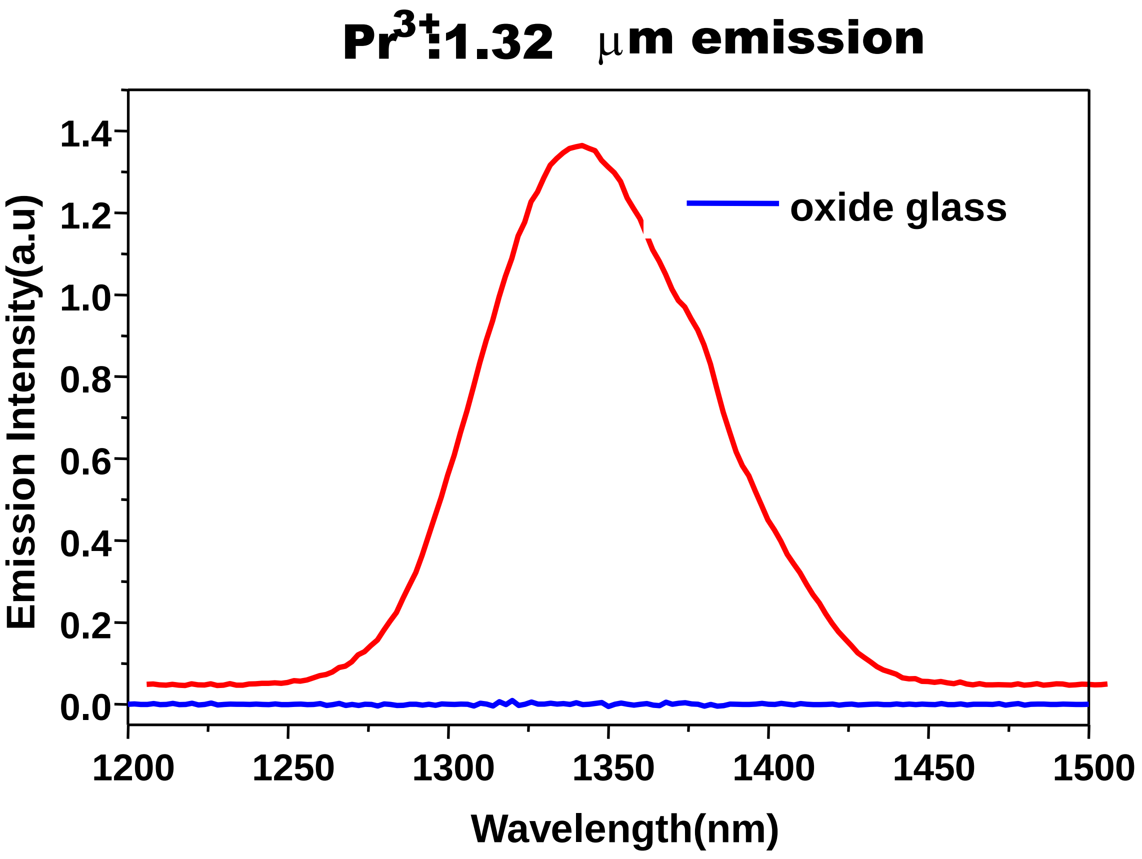
light/fiber/amplifier/fiber/light





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

Multiphonon relaxations (MPR)

- **Total probability of de-excitation:**

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

Radiative (W_{rad}) **Multiphonon** (W_{MP}) **Energy Transfer** (W_{ET})

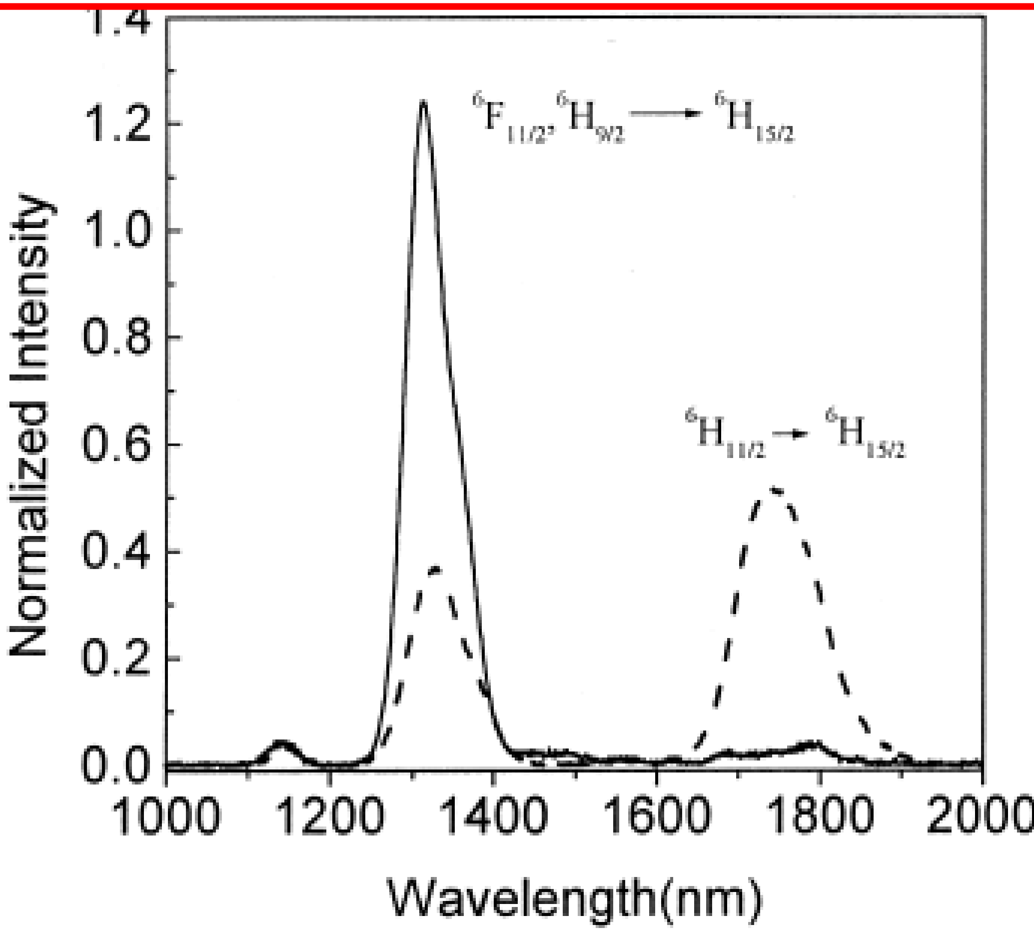
- **Quantum efficiency:**

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

$W_{MP}\uparrow$ with $\uparrow$phonon energy of the host

$W_{mp} \downarrow$ 1/1000 → **Higher quantum efficiency in chalcogenide glasses**

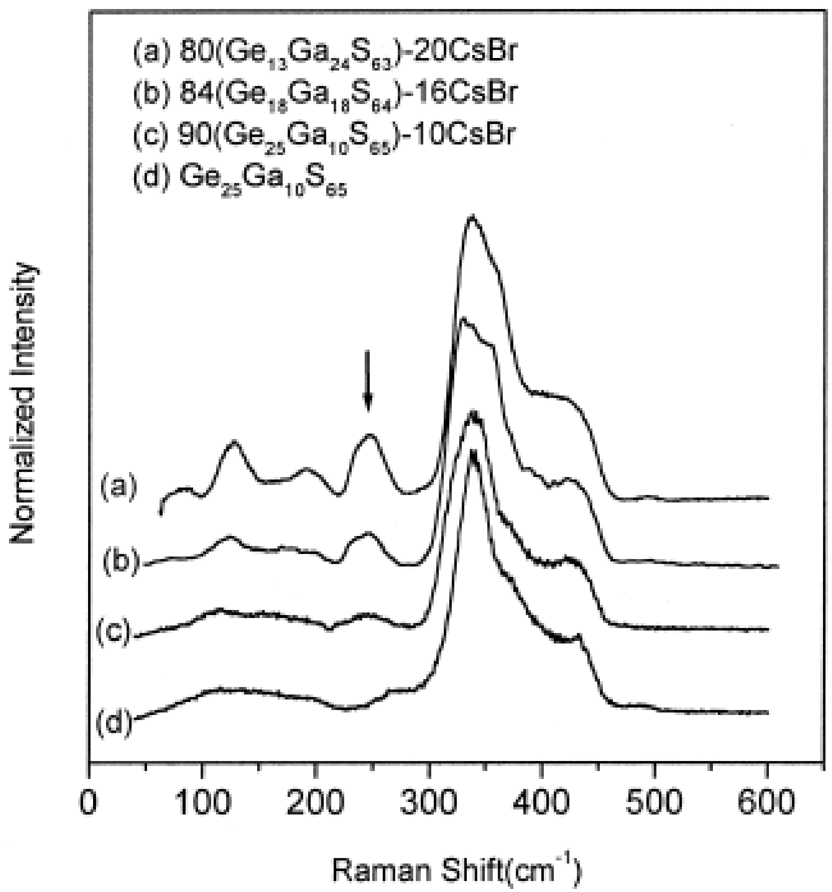
Pohang University of Science and Technology, Korea



Emission Spectra of Ge-Ga-S (dashed) and Ge-Ga-S-CsBr glasses doped with Dy^{3+} ions

J. Heo et al., *Chem. Phys. Lett.*, 2000, 317: 637

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.

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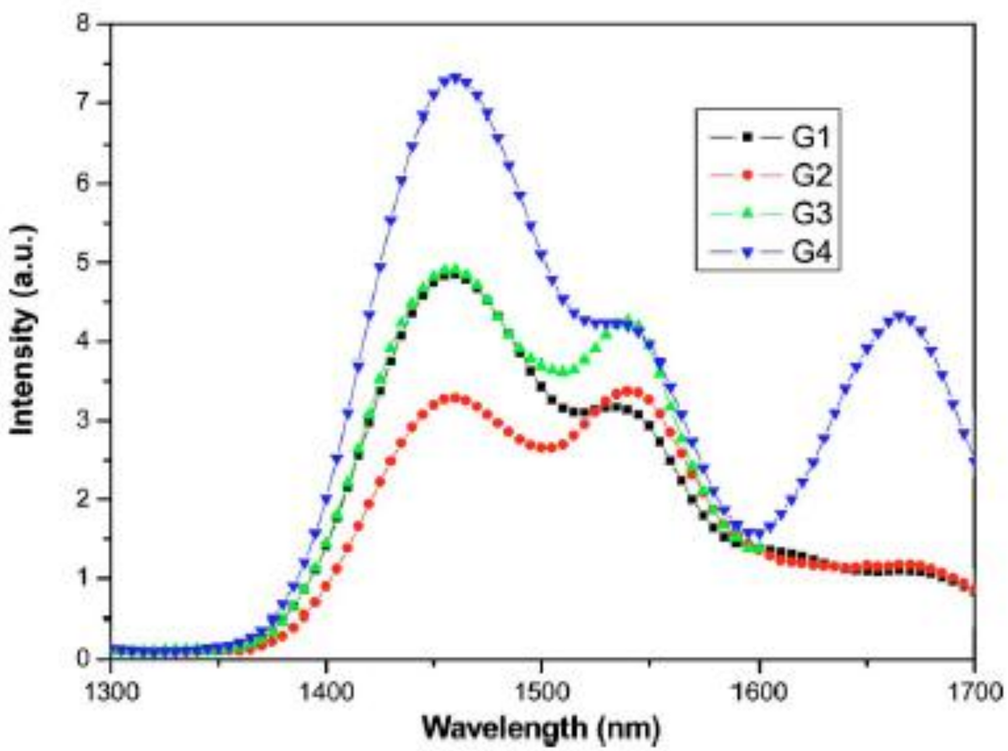
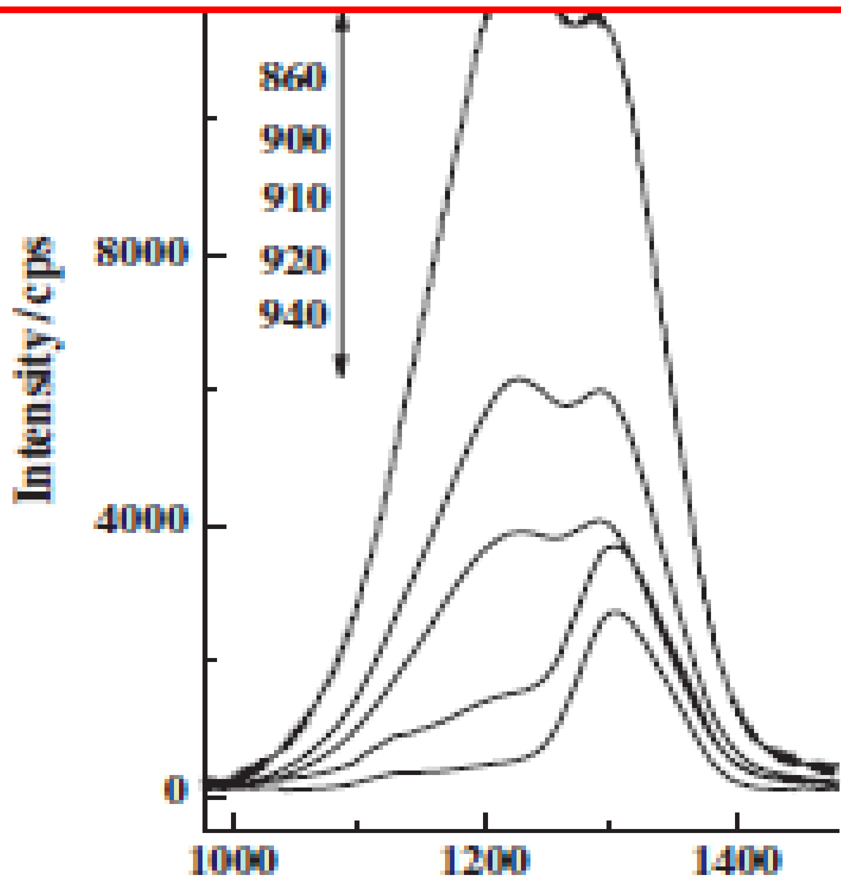
ECUST, China



Broad NIR emission from Er^{3+}-Tm^{3+} co-doped $70GeS_2$-$20In_2S_3$-10CsI glasses

Yinsheng Xu et al., *Opt. Lett.*, 2008, 33(20):2293

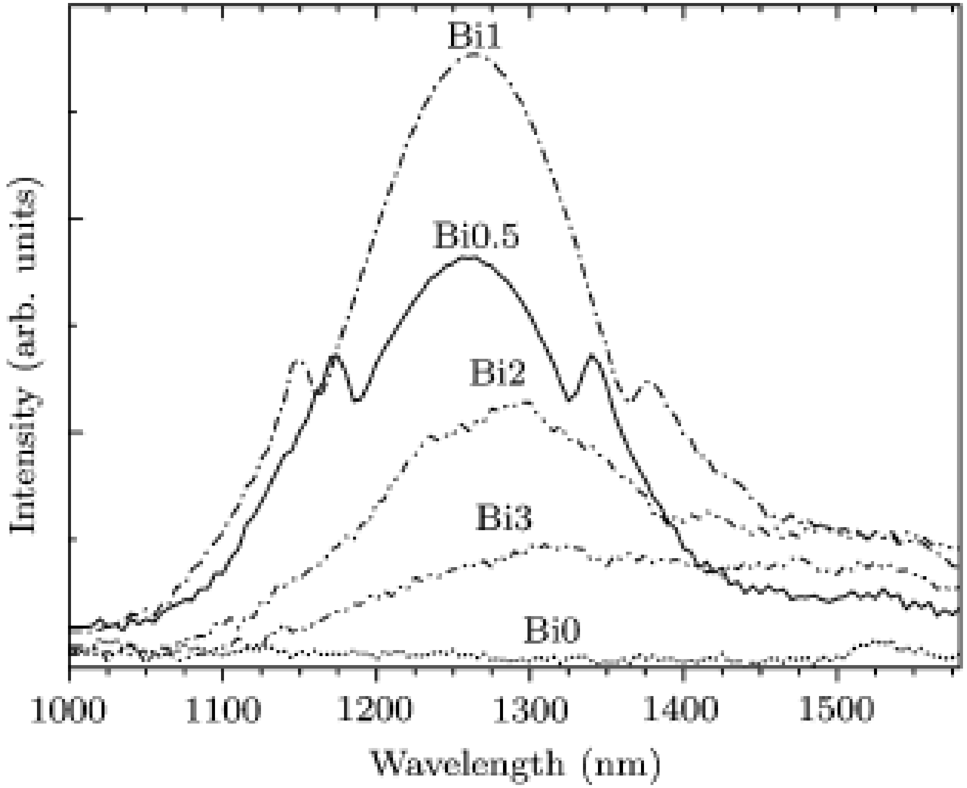
Shanghai Institute of Optics and Fine Mechanics,China
ECUST, China



Emission spectra of Bi-Dy co-doped $70GeS_2$-$9.5Ga_2S_3$-20KBr chalcohalide glasses melted at the different temperature

Guang Yang, et al., *J. Am. Ceram. Soc.*, 2007, 90, 3670

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

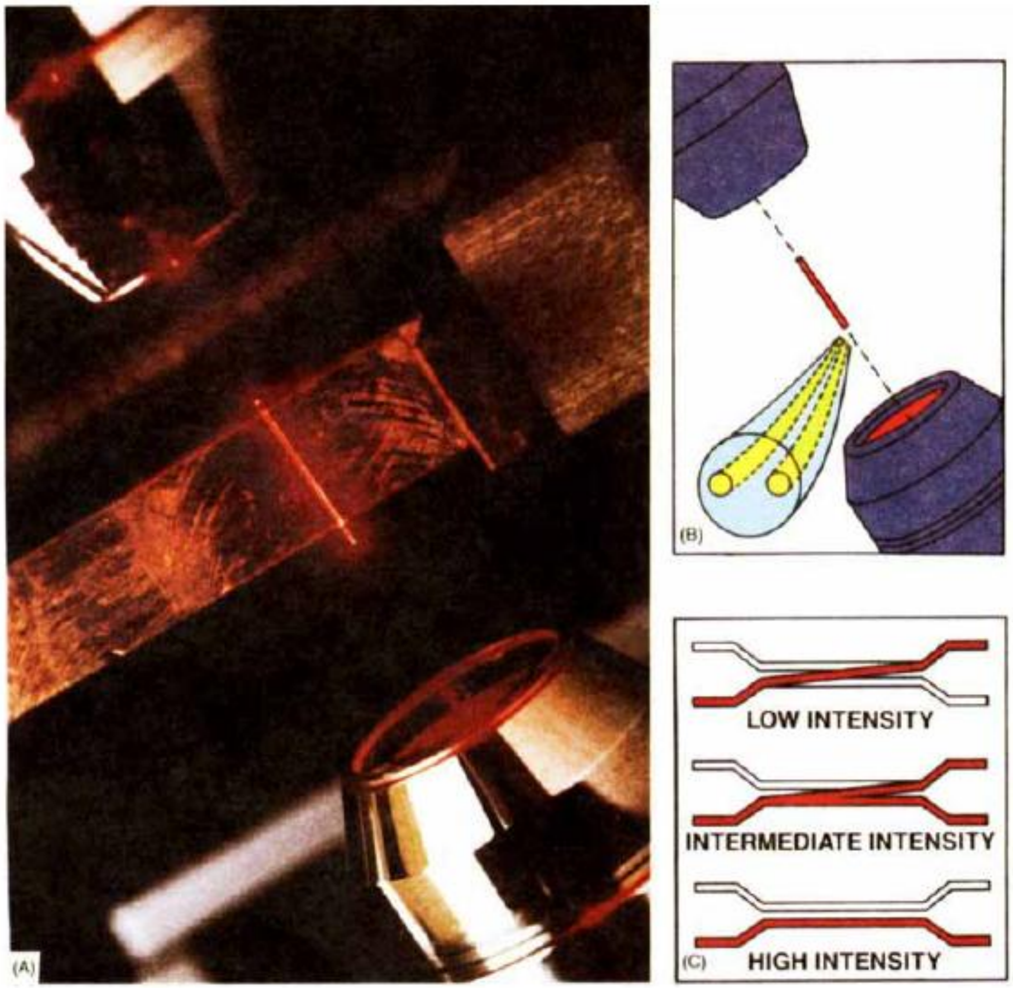


Emission spectra of Bi-doped $80GeS_2$-$20Ga_2S_3$ chalcogenide glasses

FWHM ~ 200 nm

Jianrong Qiu, et al., *Chin. Phys. Lett.*, 2008, 25:1891

All-optical device (AOD)

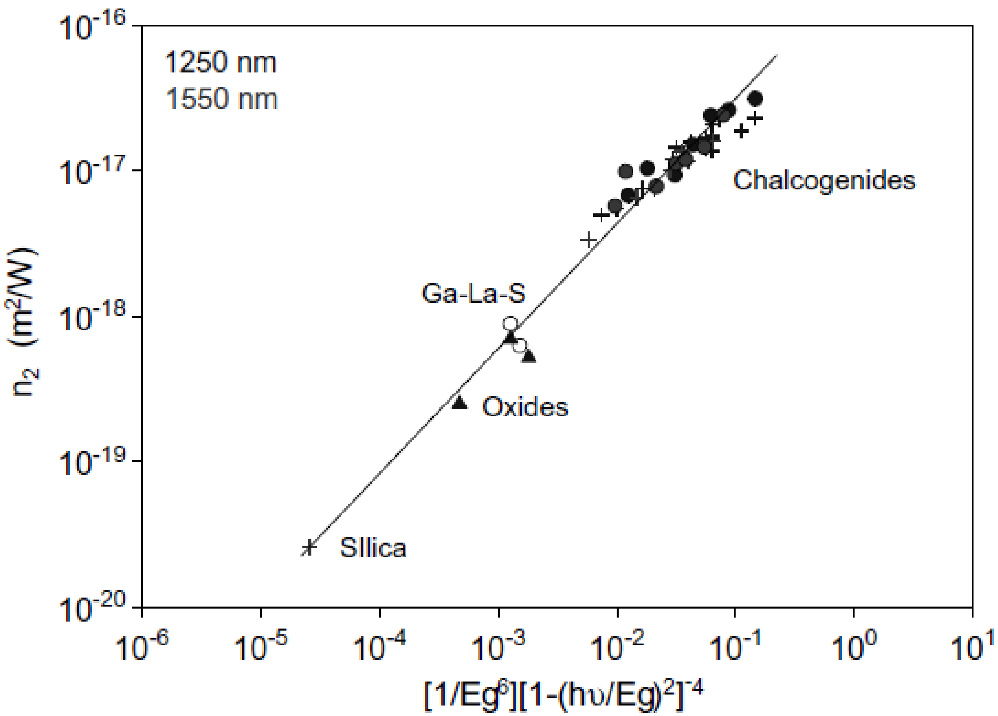


All-optical dual core coupler (A) setup, (B) schematic dual core SiO_2 fiber, (C) two single-mode cores as waveguides.

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

Vogel E M, *J. Am. Ceram. Soc.*, 1989, 72(5):719

Optical nonlinearity

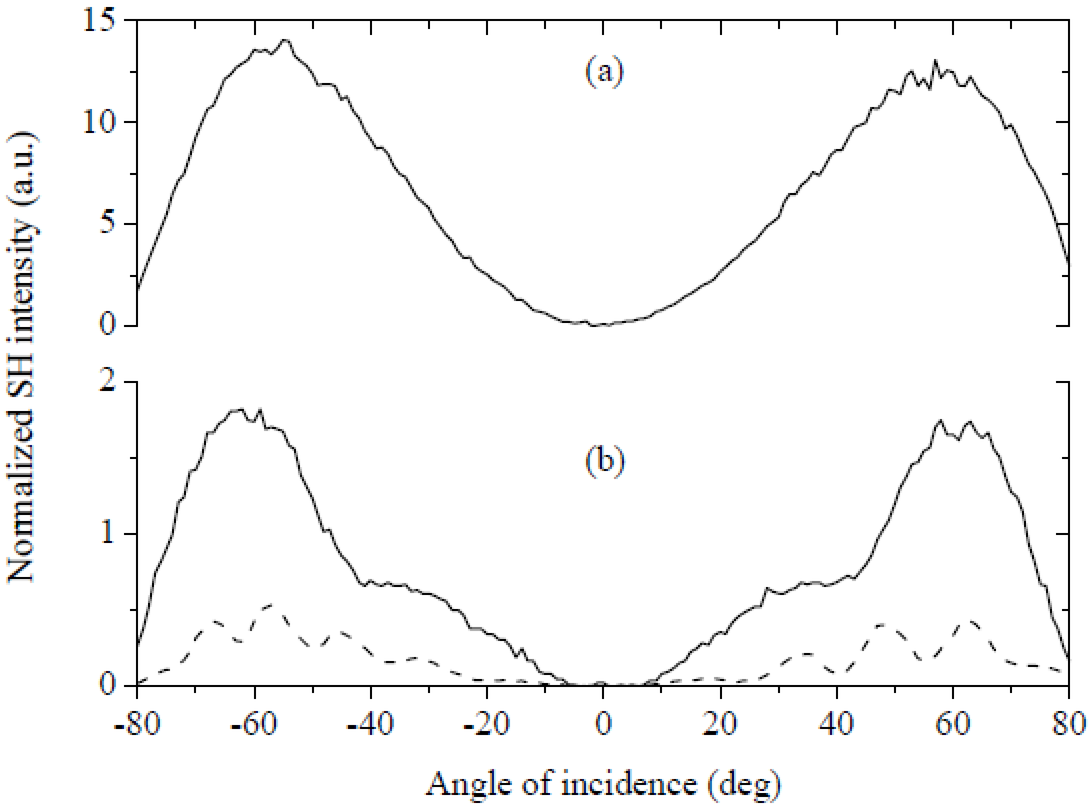


With the higher susceptibility $\chi^{(3)}$ and SHG $\chi^{(2)}$, ChG photonic chips allow all-optical signal processing.

Plot of n_2 versus the term containing the normalized photon energy

J. S. Sanghera, et al., *J. Non-Cryst. Solids*, 2008, 354:462

Université de Rennes 1, France

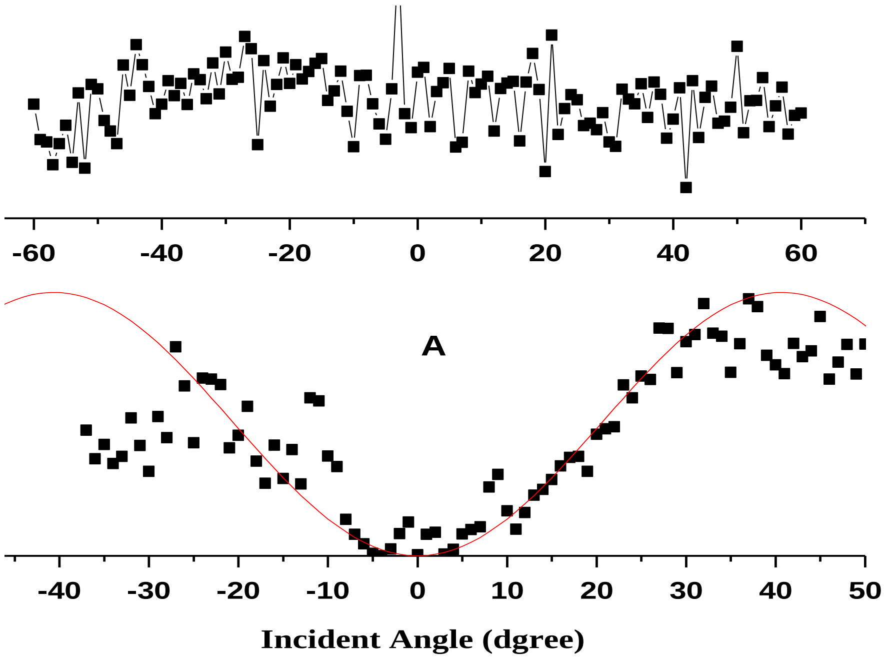


$n^{(2)}$ = 8.0 pm/V

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)

M. Guignarda, et al., *Opt. Express*, 2006 ,14(4) 1528

Kyoto University, Japan
ECUST, China

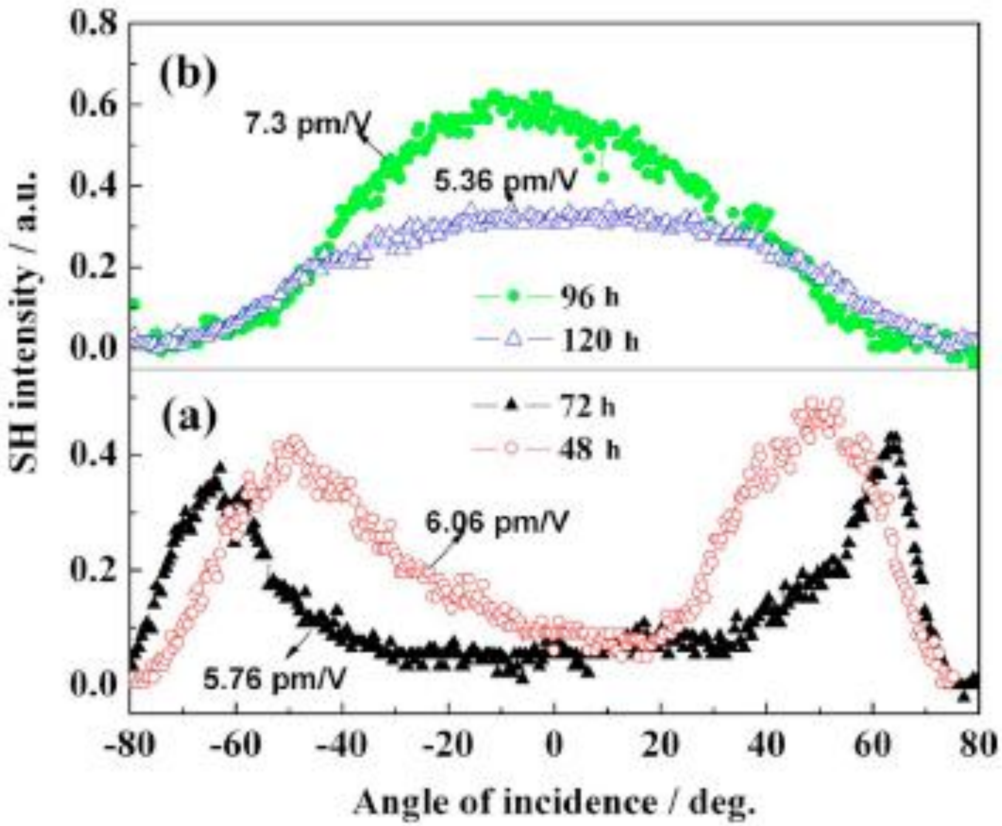


$n^{(2)} = 7.0$ pm/V

Maker fringe of $60GeS_2$-$20Ga_2S_3$-20KBr glass with higher alkali content after thermal poling

Jing Ren, et al., *Opt. Lett.*, 2006, 31(23):3492

Wuhan University of Technology,China

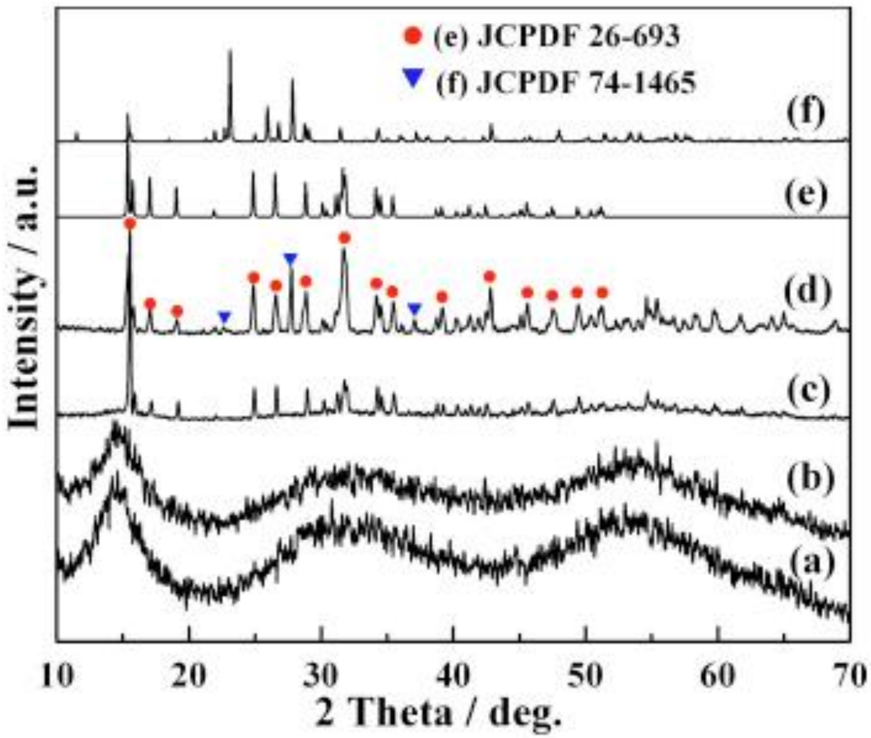


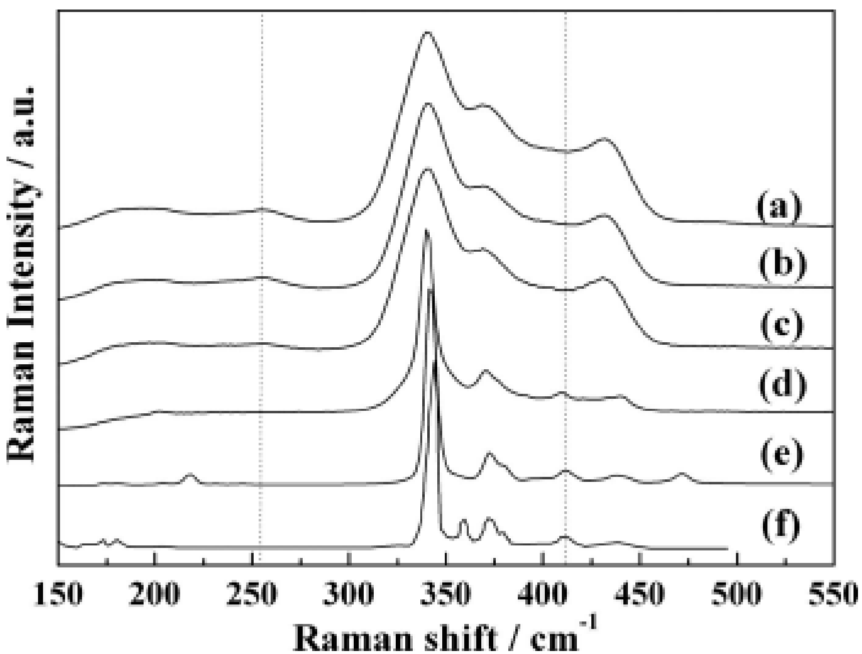
$n^{(2)}$ = 5.36-7.3 pm/V

Maker fringe patterns of the β-GeS_2 crystallized glasses without poling treatment

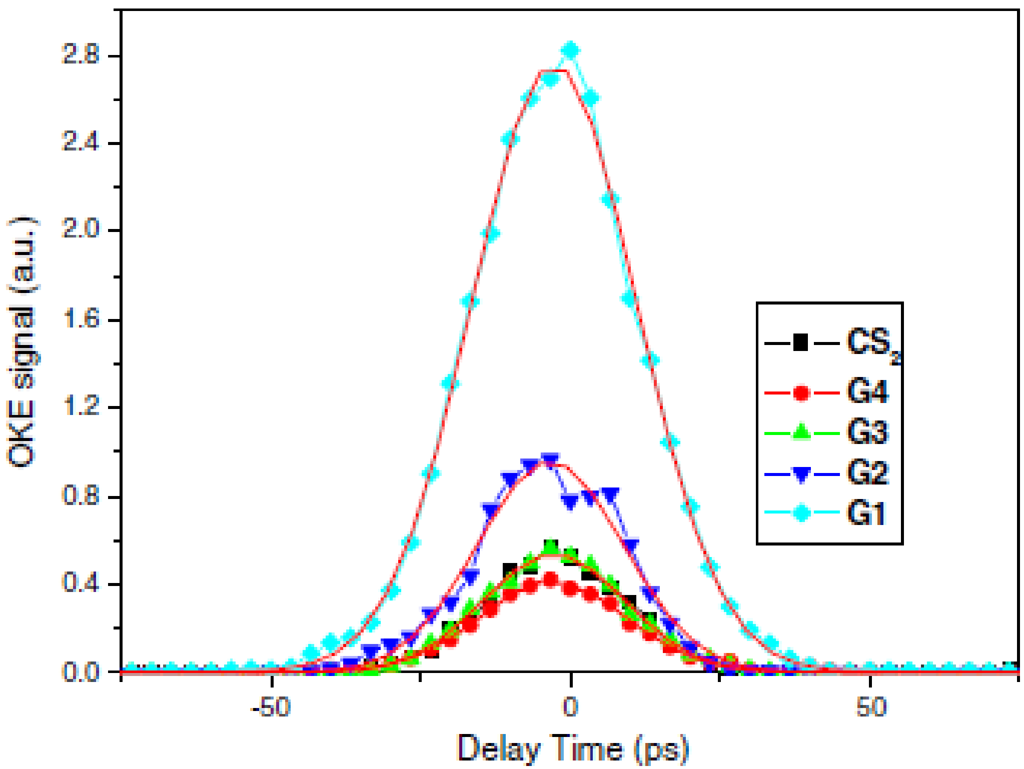
Xiujian Zhao, et al., *Opt. Lett.*, 2009, 34(4):437

XRD and Raman spectra





Fudan University, China
ECUST, China

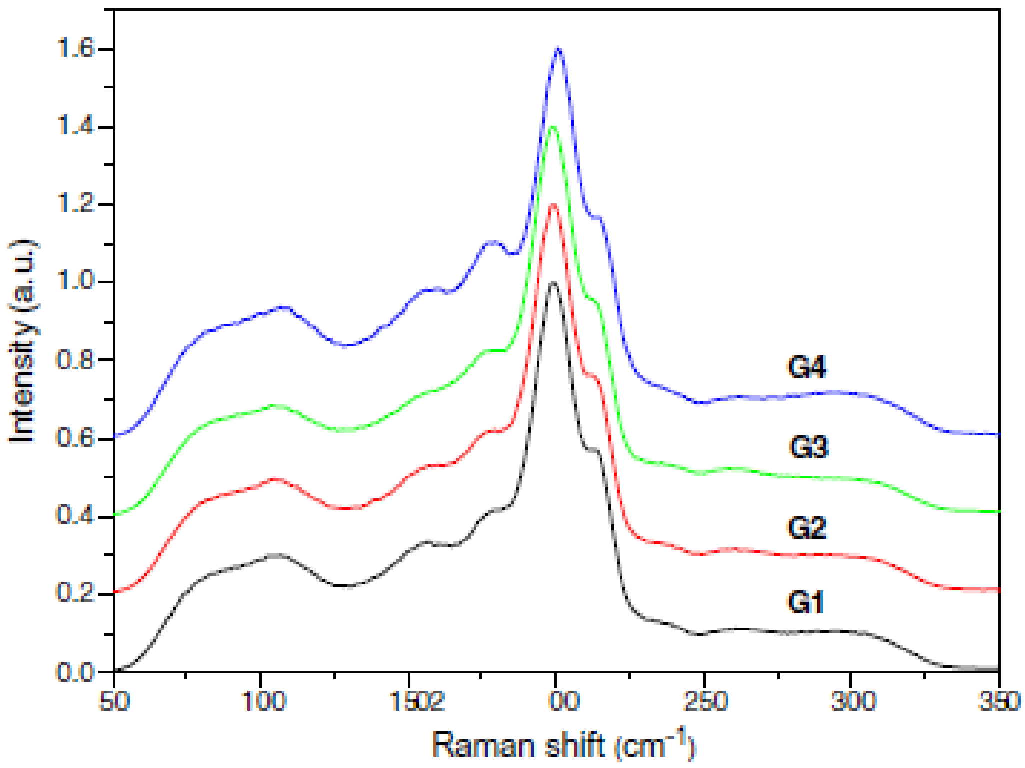


$\chi^3 = 10.07 \times 10^{12}$ esu

Optical Kerr Effect Siganl of $GeSe_2$-In_2Se_3-CsI glasses

Yinsheng Xu, *et al.*, *Phy. Chem. Lett.*, 2008, 462, 69-71

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

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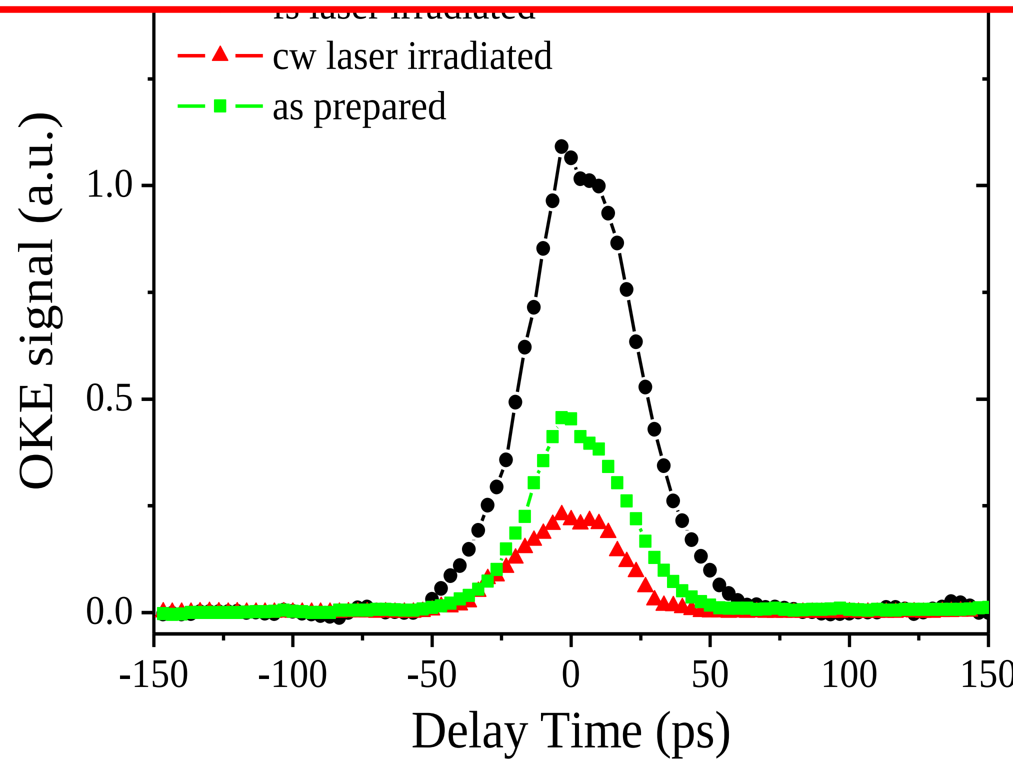
ECUST, China



Laser radiation induced enhancement of χ^3 on As_2S_3 glass

Optical Kerr Effect Siganl of As_2S_3 glass before and after laser radiation

Lei Xu, *et al.*, *Appl. Phy. Lett.*, 2007, 91, 181917

Summary

- **Purification is an important procedure for synthesis of high purity ChGs.**
- **Controlled crystallization is an effective way to improve mechanical and thermal properteis 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