

Microcrystallization and Active Applications of some Novel Glasses

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East China University of Science and Technology
(ECUST)



Passive and Active Applications

Passive applications

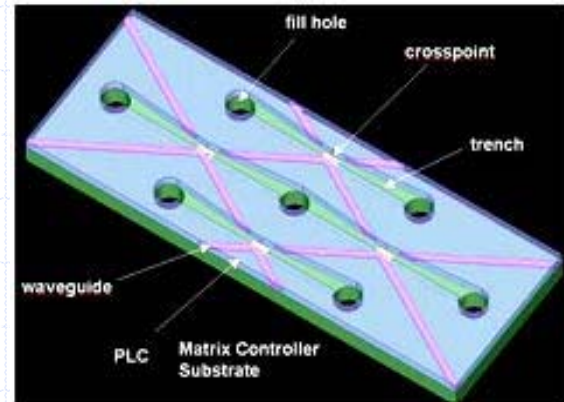
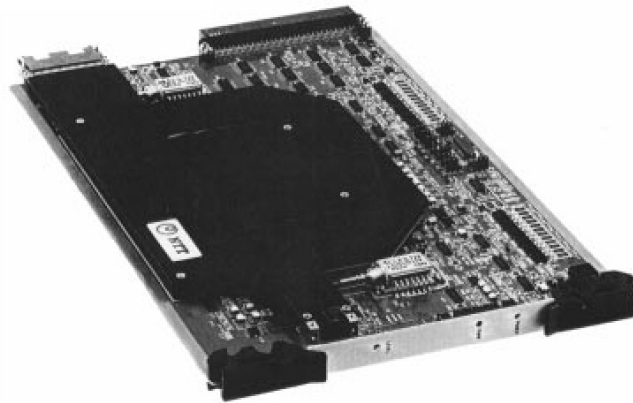
Without changing the optical properties, other than that due to scattering, absorption and end face reflection losses, etc.

Active applications:

The initial light propagating being modified by a process. Examples include fiber lasers, amplifiers, all-optical devices, etc.



Passive and Active Applications



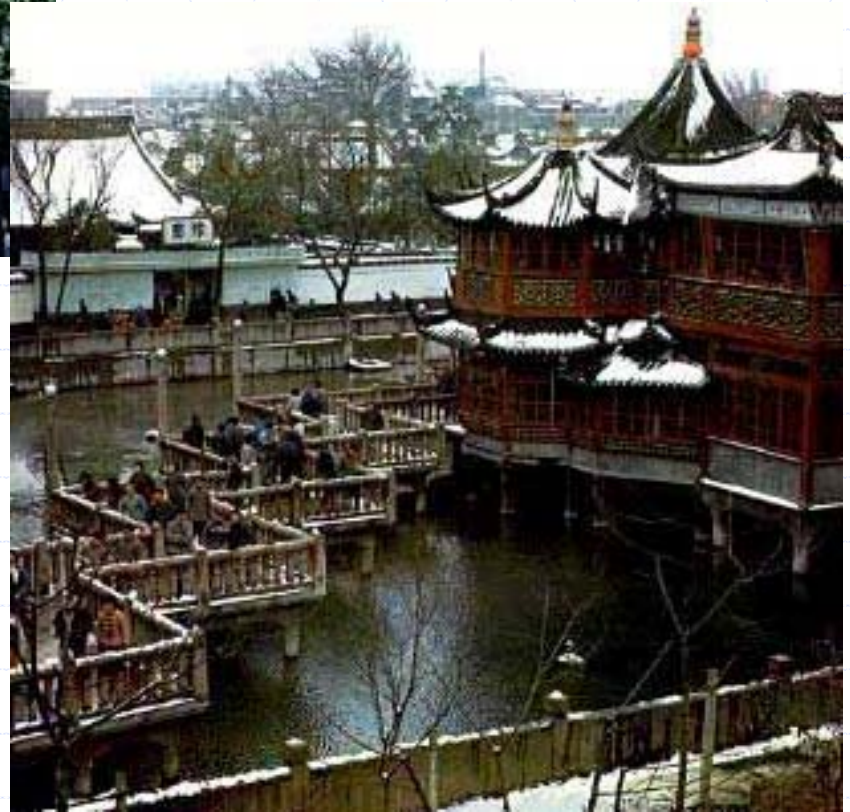


Shanghai



ECUST









3500 employees
1000 professors
15000 undergraduates
4000 graduates

52 B.Sc.
72 M.Sc.
12 Eng. M.
26 Ph. D.
5 Postdoc.

14 Schools

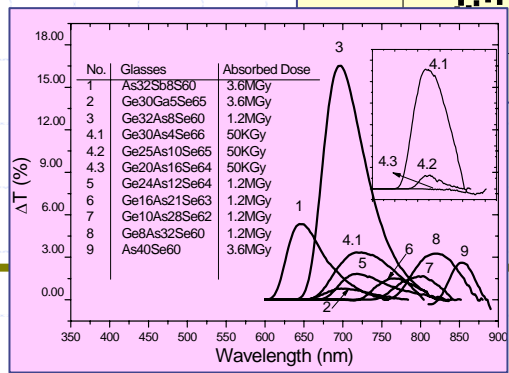
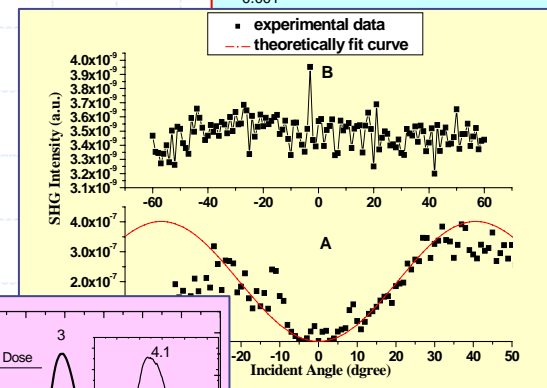
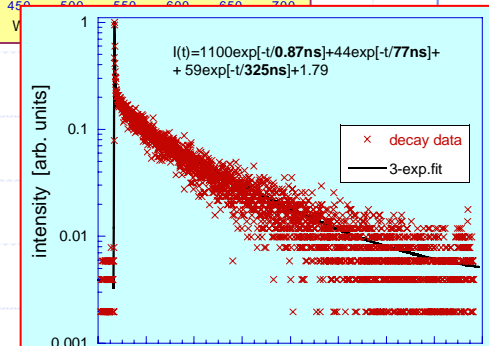
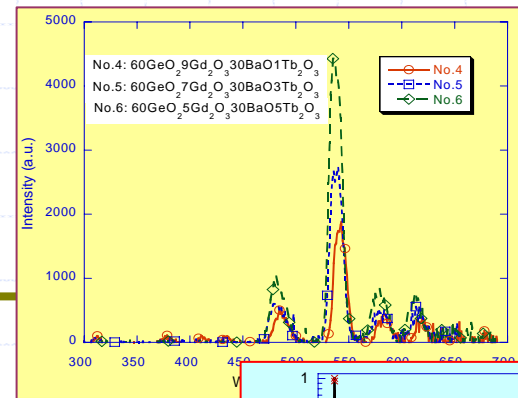
- Pharmacy
- Biotechnology
- Chemical Engineering**
- Chemistry and Pharmaceutics
- Materials Science and Engineering**
- Resources and Environmental Engineering
- Information Science and Engineering**
- Mechanical and Power Engineering**
- Science (Maths and Physics)**
- Culture and Arts
- Foreign Languages
- Philosophy and Politics
- Business and Economics
- Public & Social Administration



Researches

Novel Functional Glasses

- Oxide Glasses
 - ◆ Rare earth doped
 - ◆ ZnO-activated
- Chalcogenide Glasses
 - ◆ Micro-crystallization
 - ◆ IR luminescence
 - ◆ Non-linearity
 - ◆ Irradiation induced effects



Oxide Glasses

**Rare earth doping for scintillation
and white LED**

ZnO activating for fast scintillation

Internationally Collaborated with



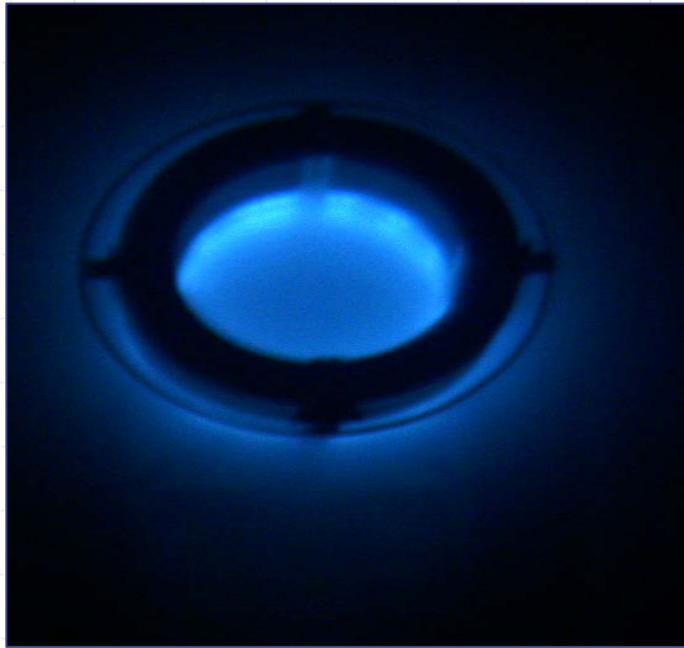
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Calliope ^{60}Co Source



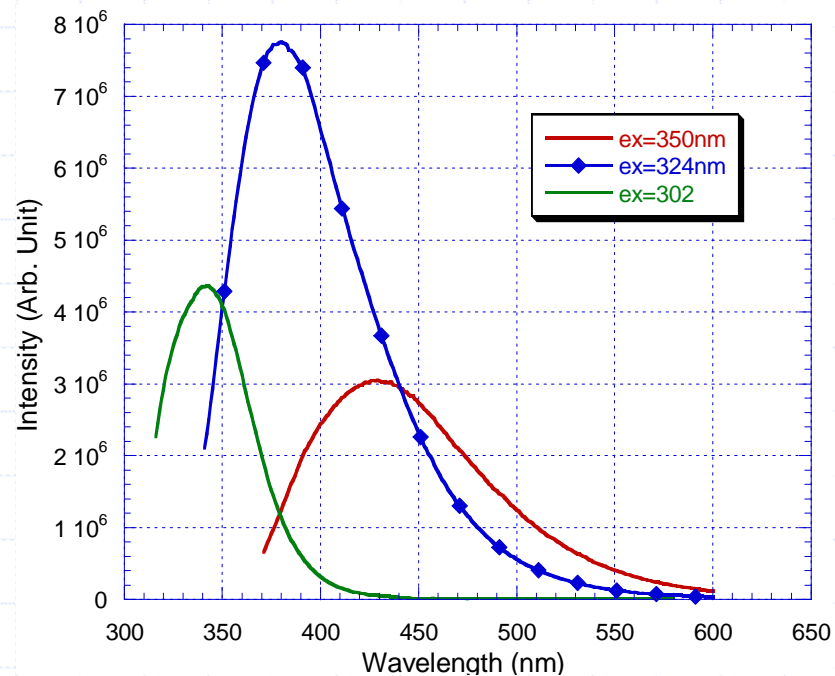
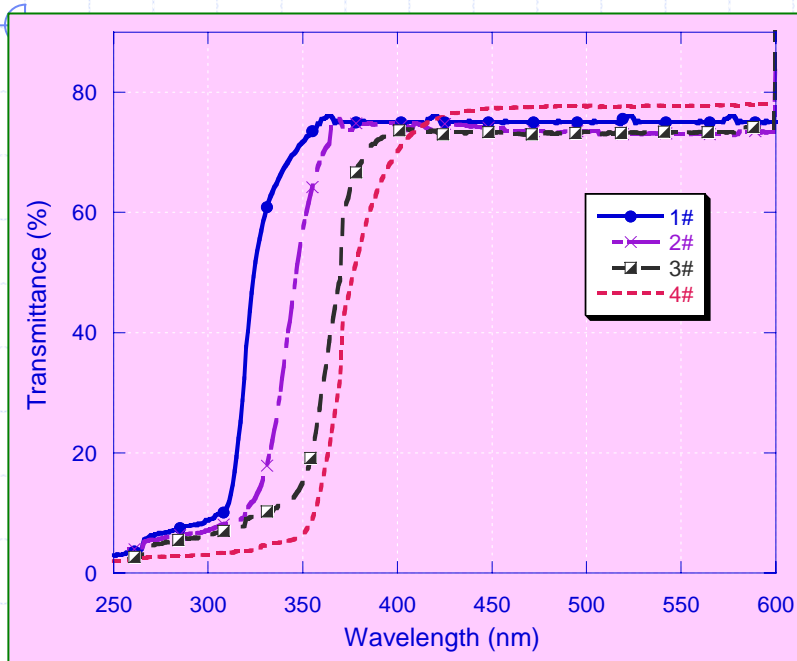
ENEA-Casaccia Center,
Rome, Italy

Background

A good alternative candidate as higher energy irradiation detector for dosimetry system due to:

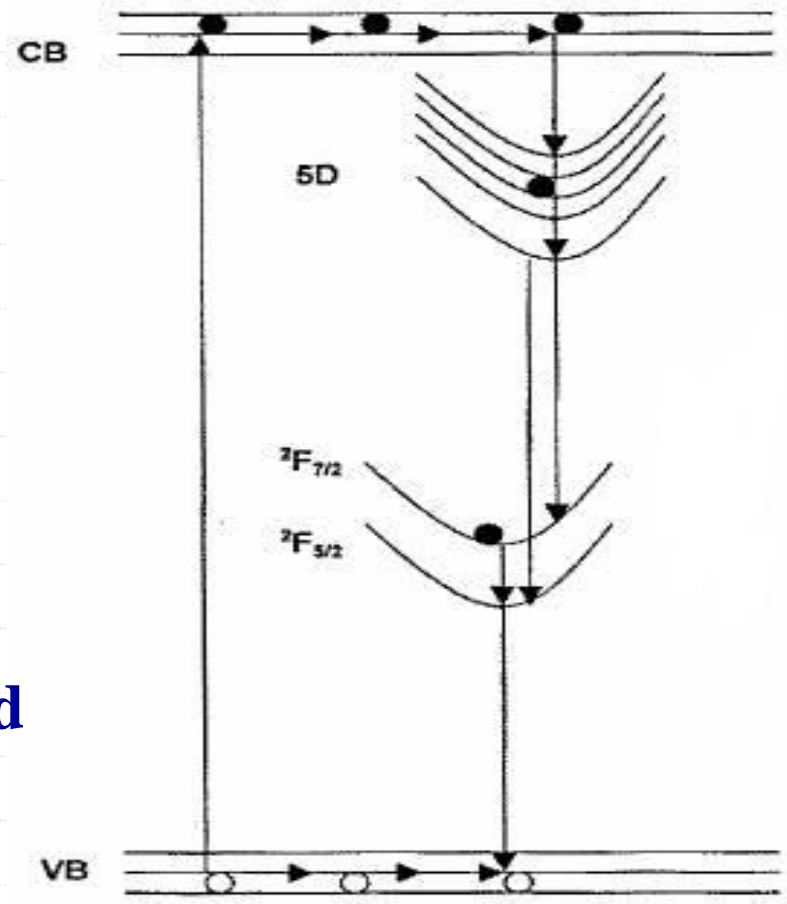
- A low barrier of information bleaching temperature (<350 °C)
- The higher energy irradiation detection (> 5MGy)

Optical properties of Ce^{3+} doped glasses



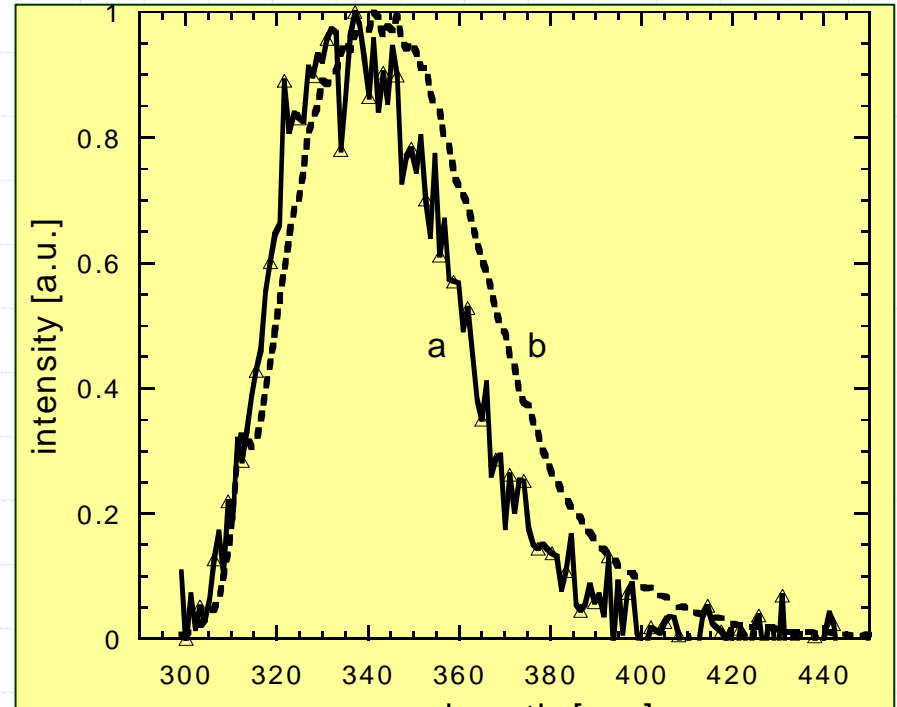
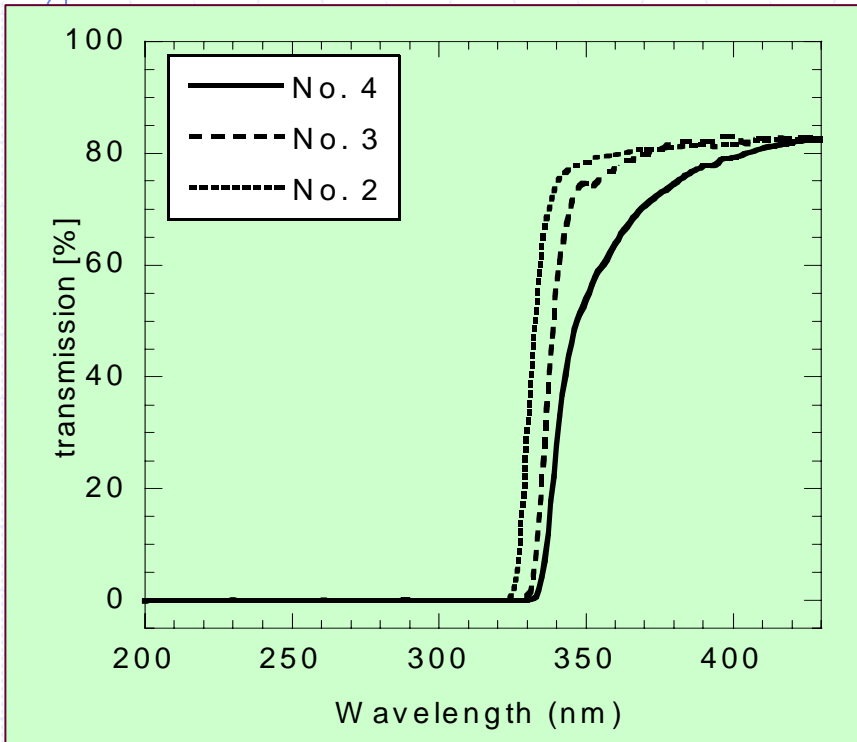
Transmitting and emission spectra of Ce^{3+} doped oxide glasses with different optical basicity - **the electron donor power of the oxides**

- Fast decay time of 20–50 ns suitable for scintillation
- Advantages of glasses: good matrix for rare earths, lower cost, stable properties etc.
- Disadvantages: Non-shielded 5d orbit sensitive to matrix; lower quantum efficiency



Energy levels diagram of Ce³⁺ 4f-5d electrons transitions

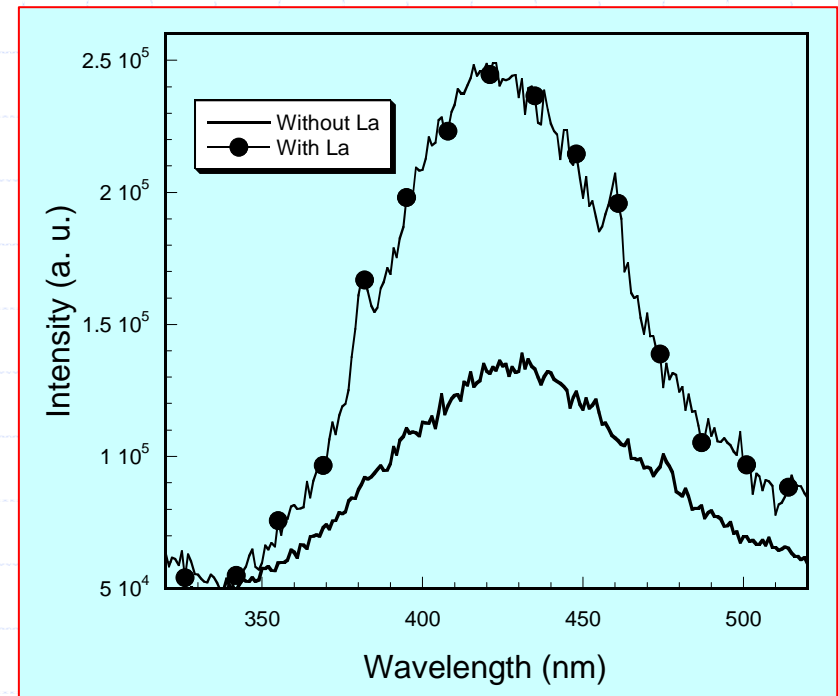
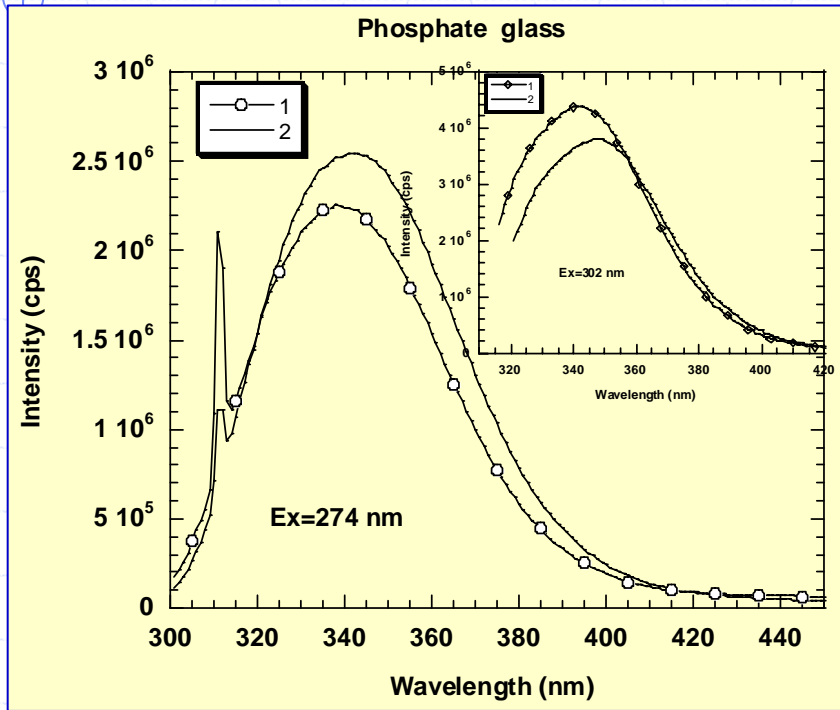




**Transmittance and emission spectra
 of Ce³⁺ doped oxide glasses with different alkali content**

Enhanced emissions due to energy

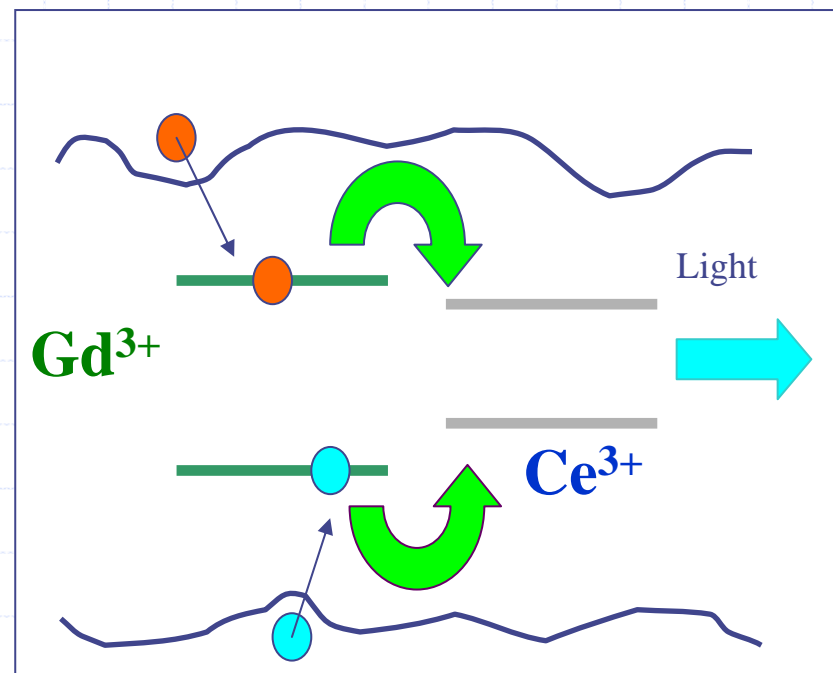
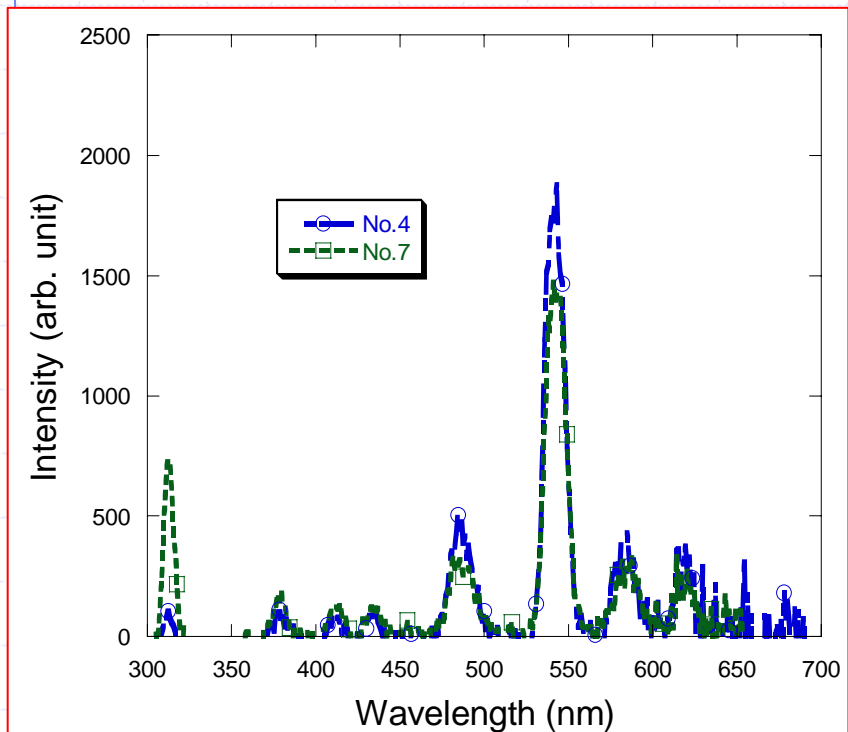
transfer from Gd^{3+} or partitioning role of La^{3+}



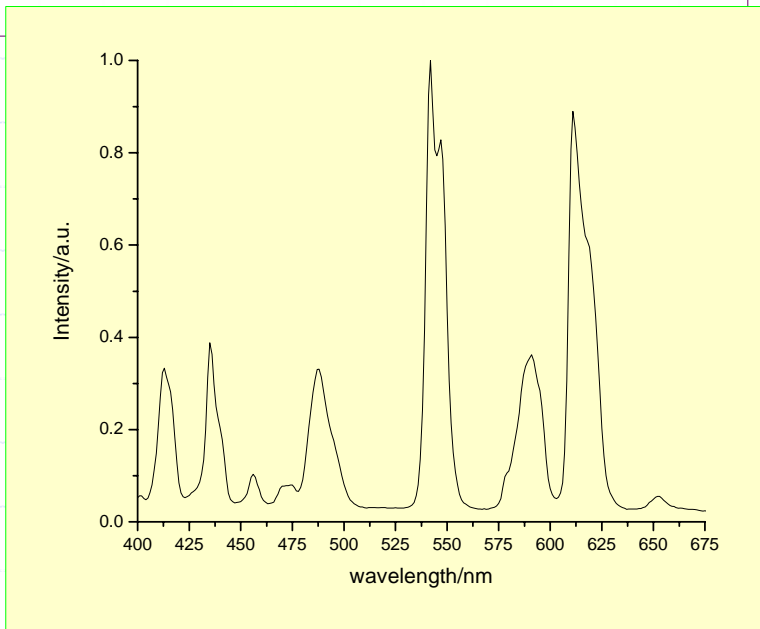
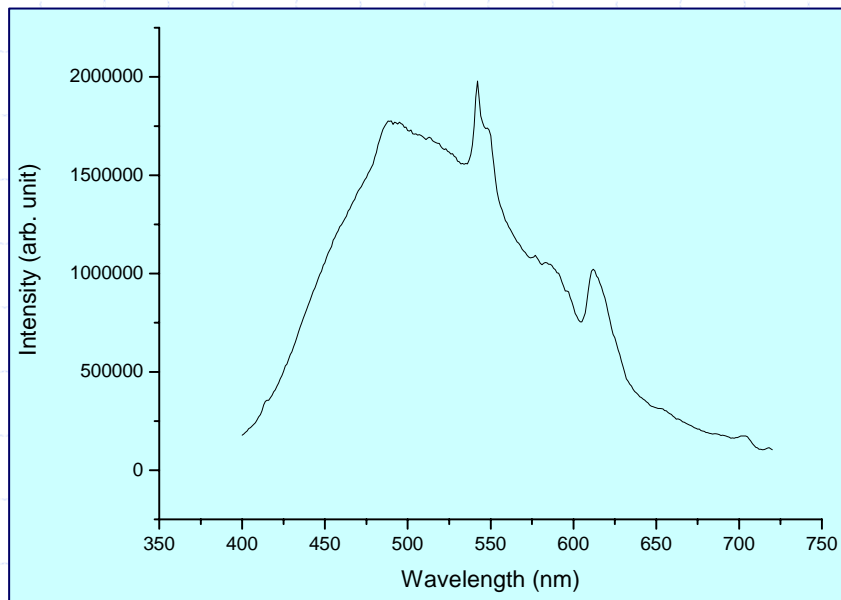
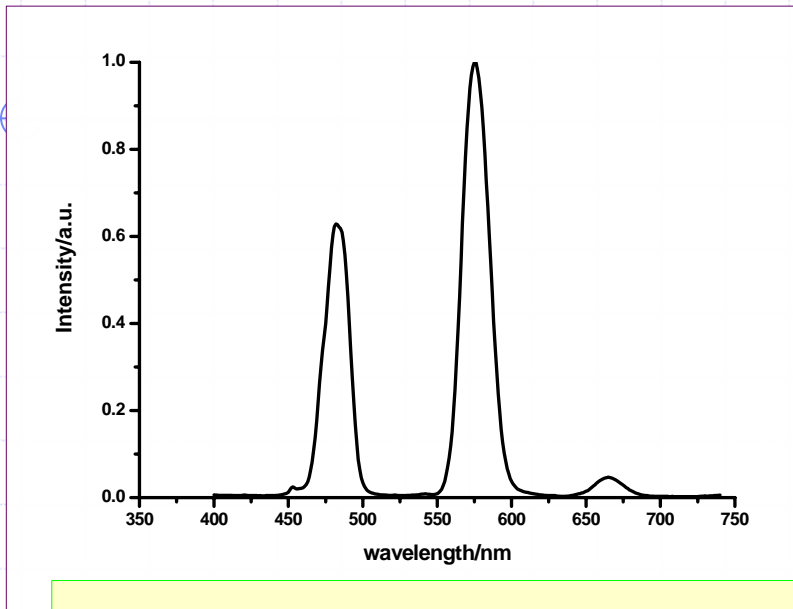
Mater. Res. Bull. (2006), doi:10.1016/j

J. Am. Ceram. Soc., 88(2) (2005) 293-296

Enhanced emissions due to energy transfer from Gd^{3+} or partitioning role of La^{3+}

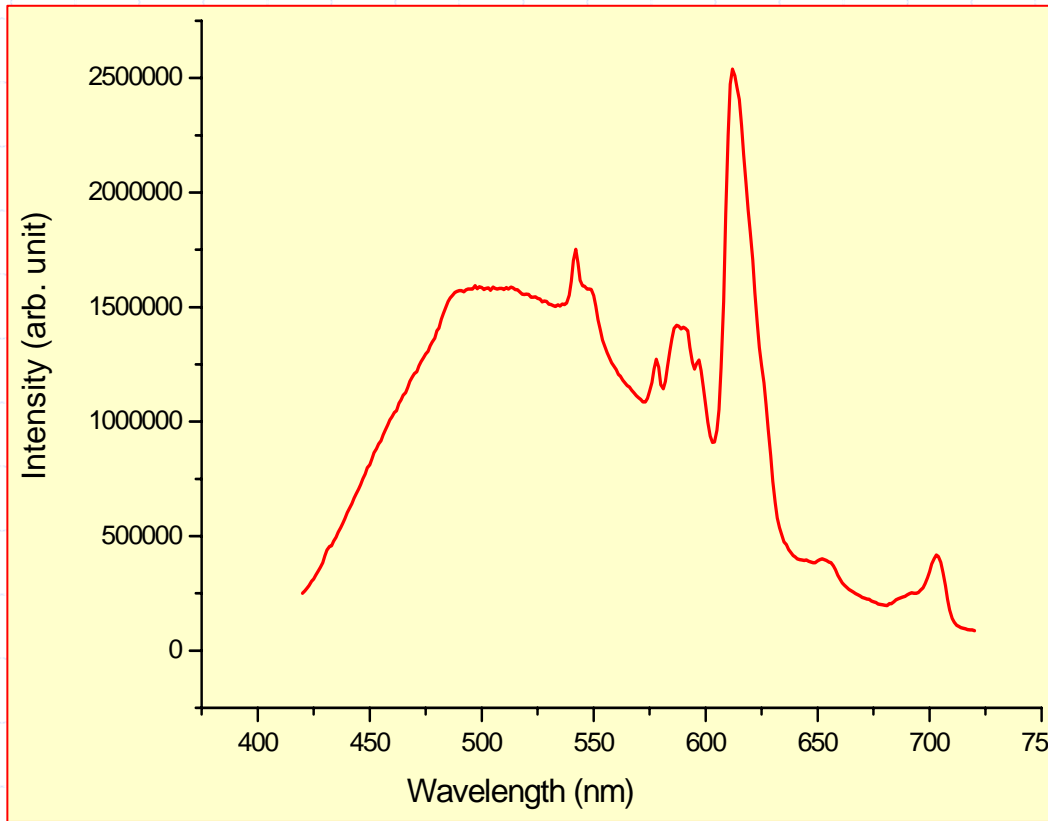


Luminescent Glasses for White LED Lighting



**Emission spectra
of Dy³⁺ doped (left above) ,
Tb³⁺/Eu co-doped (left below)
and Ce³⁺/ Tb³⁺/Eu co-doped
glasses excited at UV wavelength**

Luminescent Glasses for White LED Lighting



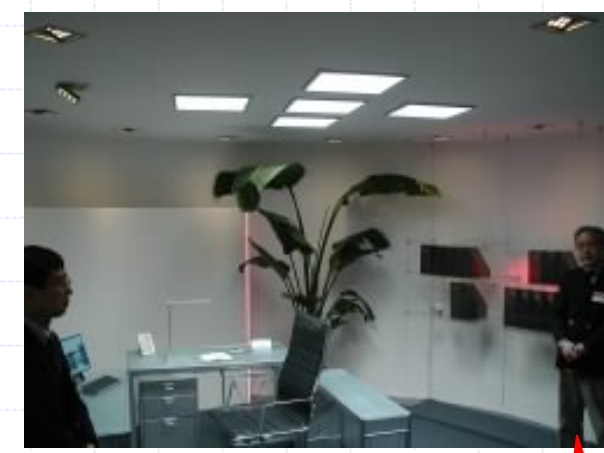
White-Light-Emitting diodes (W-LEDs)



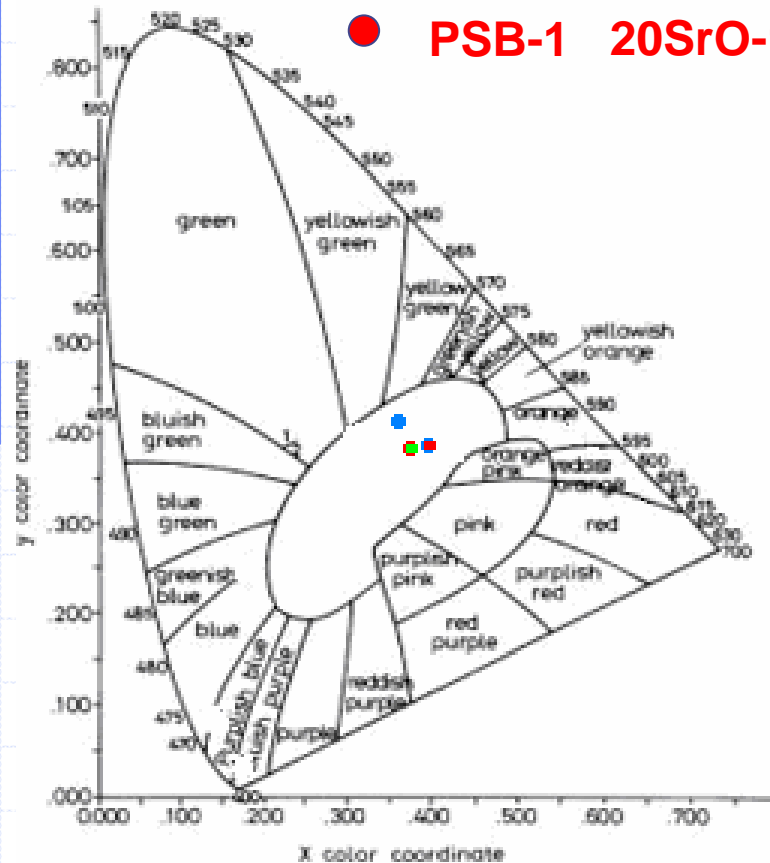
An important class of lighting devices for replacement of conventional lighting sources of incandescent and fluorescent lamps

Advantage: long lifetime, lower energy consumption, and environmental-friendly characteristics

Glasses: lower production cost, simpler manufacture procedure, free of halo effect, etc, feasible to replace phosphors for W-LED

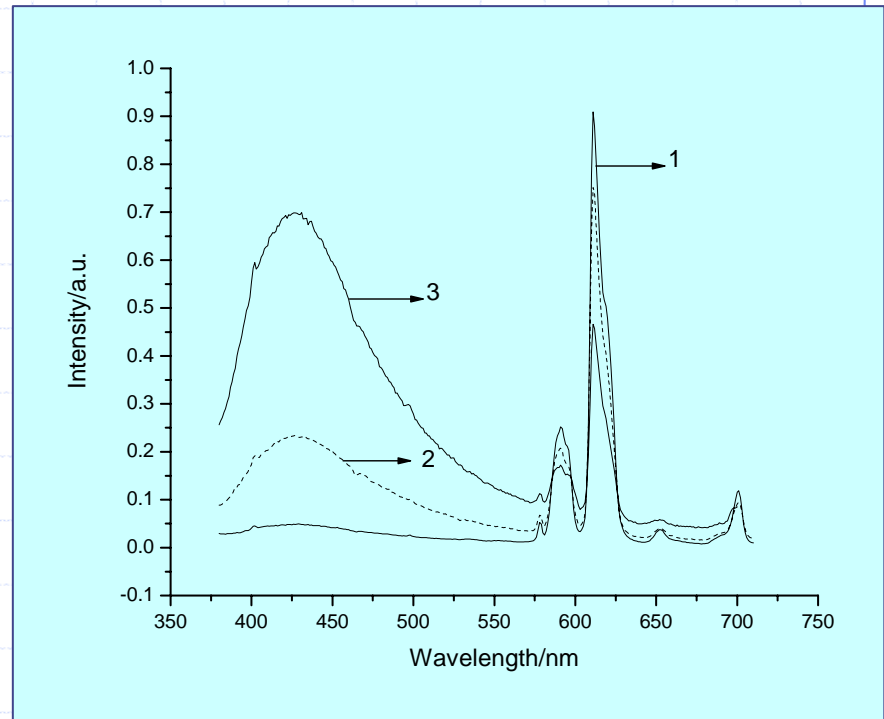
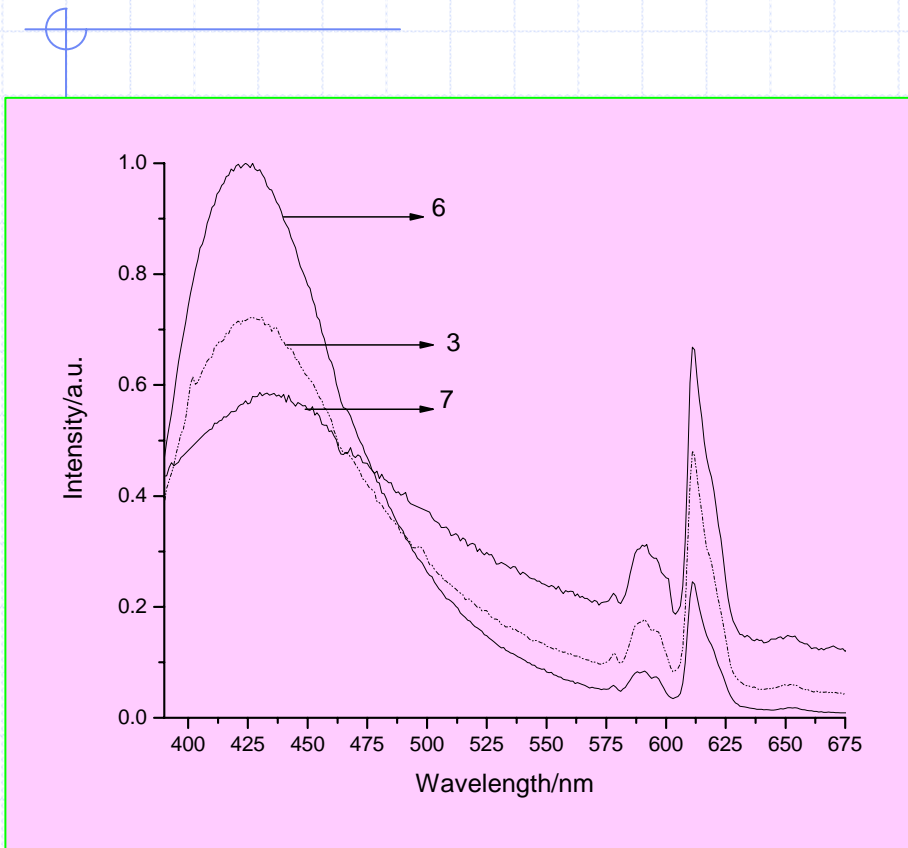


- SCB-4 $37\text{CaO}-13\text{BaO}-40\text{SiO}_2-10\text{B}_2\text{O}_3:0.5\text{Ce},0.25\text{Tb},1.5\text{Eu}$
- SCB-5 $37\text{CaO}-13\text{BaO}-50\text{SiO}_2:2\text{Dy}$
- PSB-1 $20\text{SrO}-15\text{BaO}-5\text{B}_2\text{O}_3-60\text{P}_2\text{O}_5:1\text{Eu},1\text{Tb}$

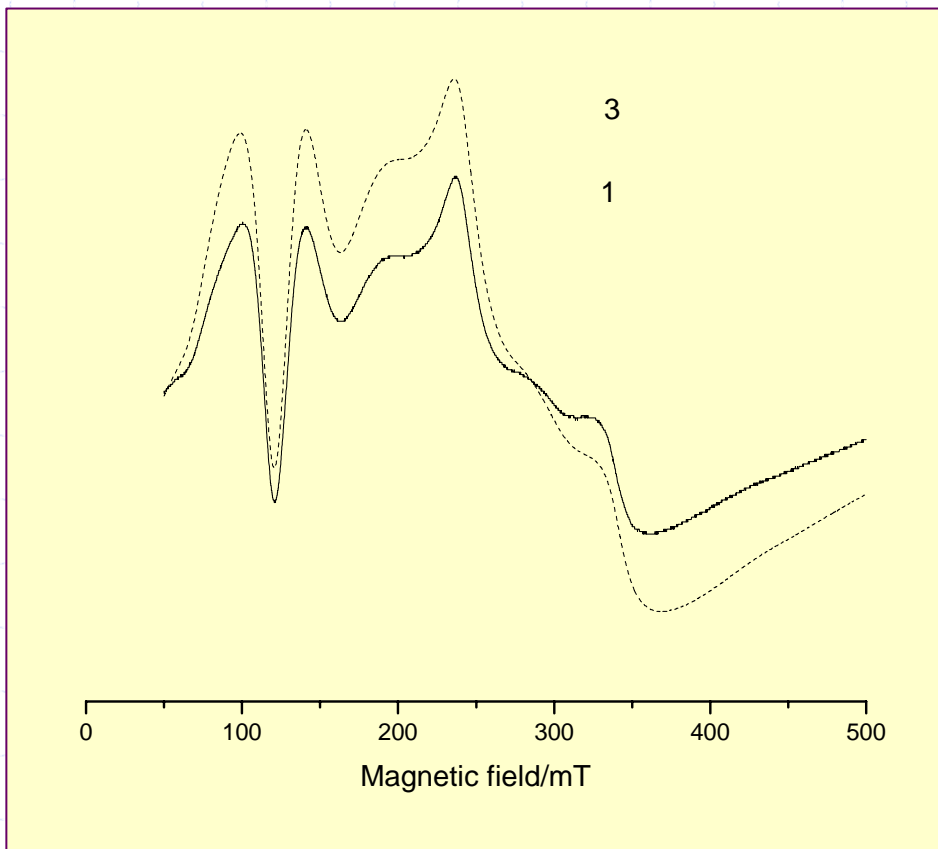


Sample No.	X	Y
SCB-4	0.3731	0.3828
SCB-5	0.4137	0.3684
PSB-1	0.4241	0.3578

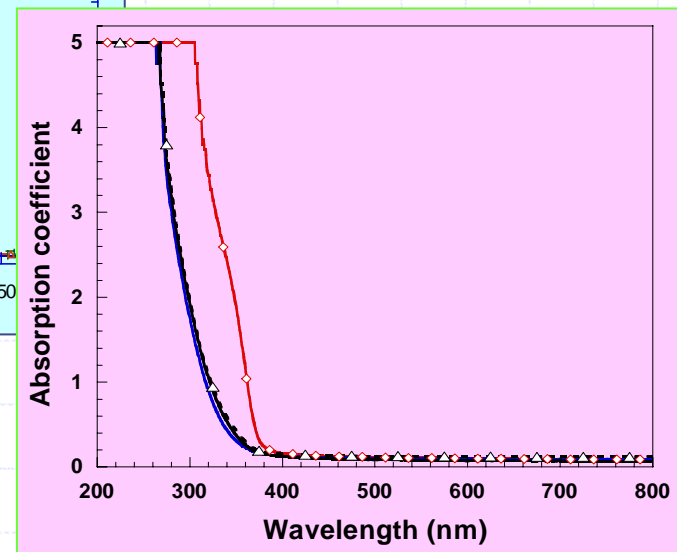
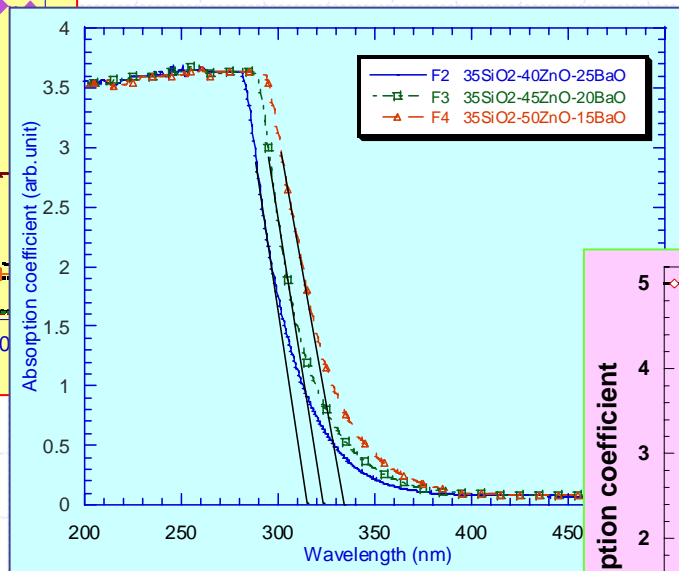
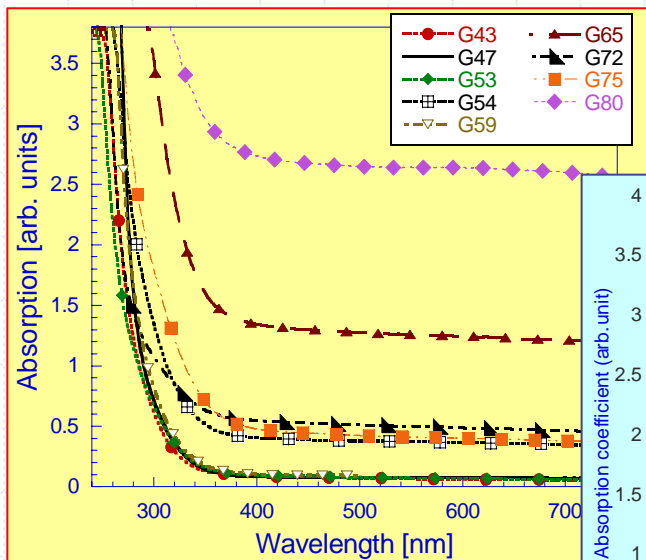
Color coordinate diagram of luminescence glasses



**Emission spectra
of Eu-doped glasses with different
B₂O₃ (above) and different type of
alkaline earth oxides**



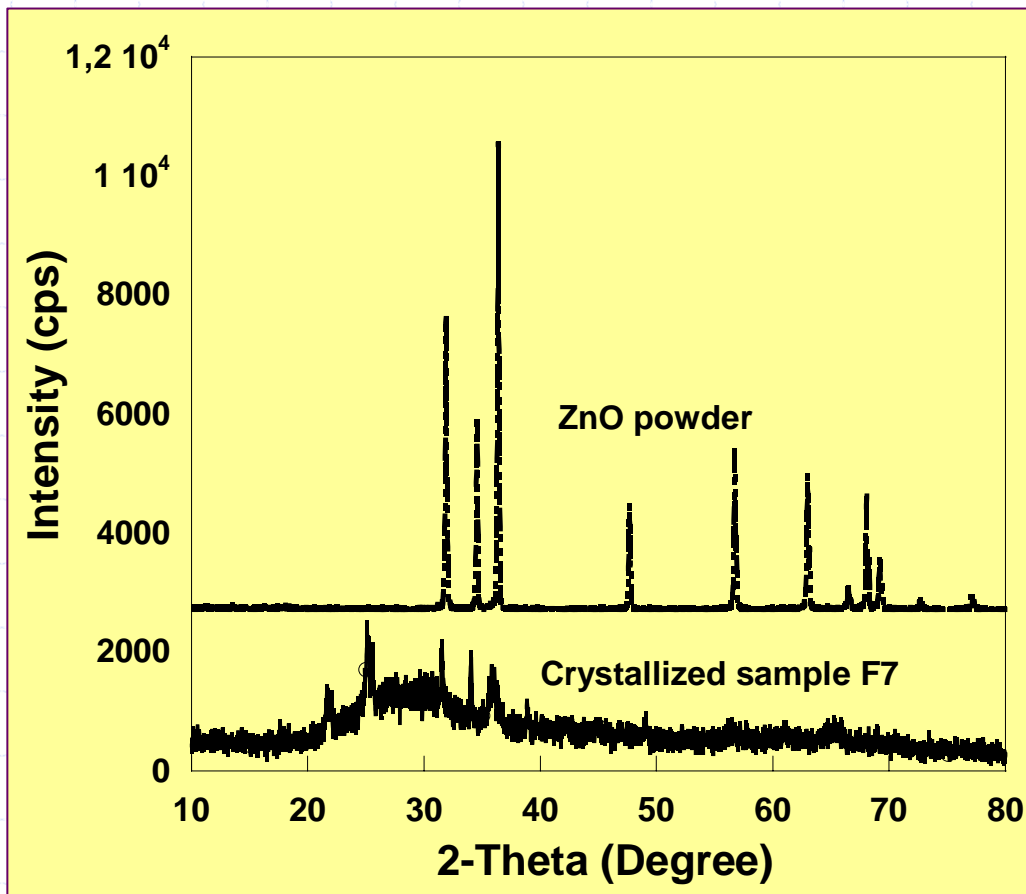
ZnO-Activated Oxide Glasses for Scintillation



Absorption spectra

of glasses with different compositions (left),
different ZnO/BaO ratios (middle) and different
thermal treating conditions.

ZnO-Activated Oxide Glasses for Scintillation

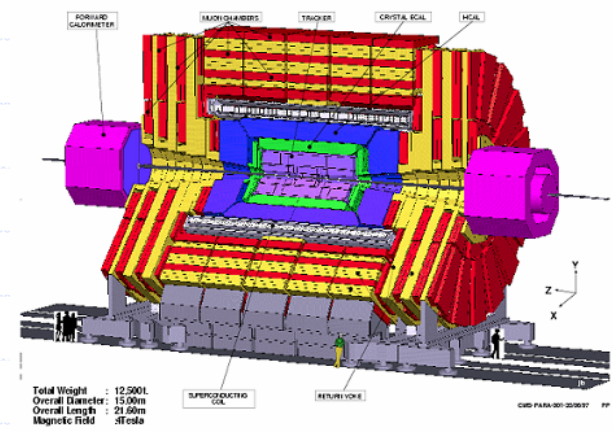


Luminescence ZnO

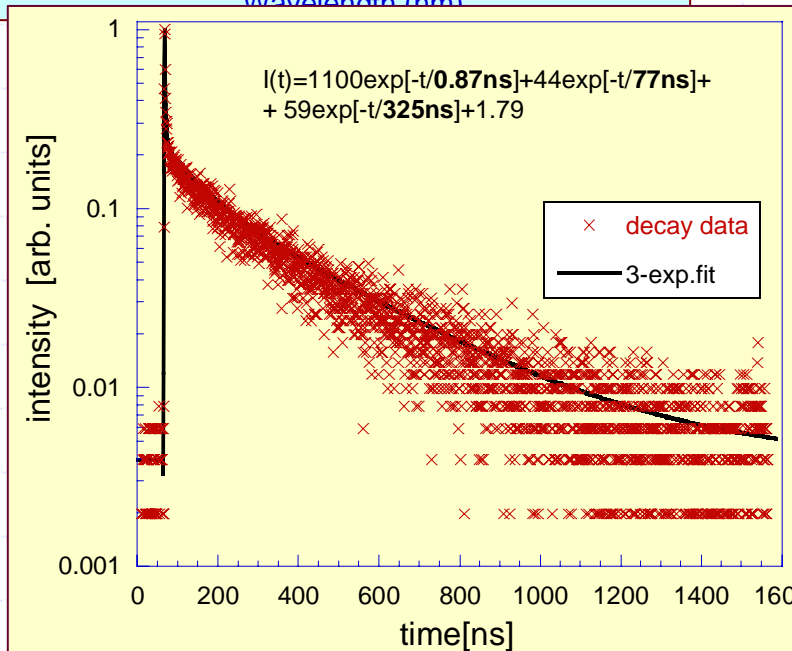
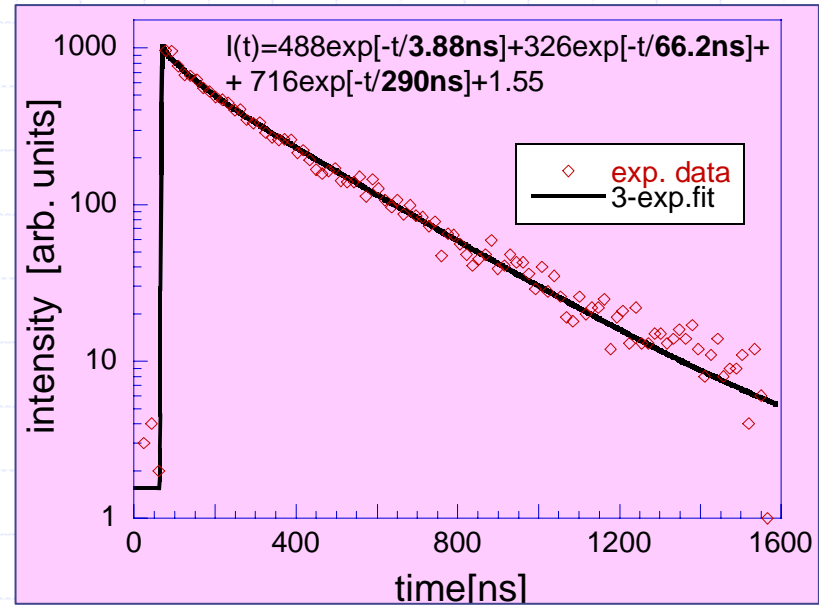
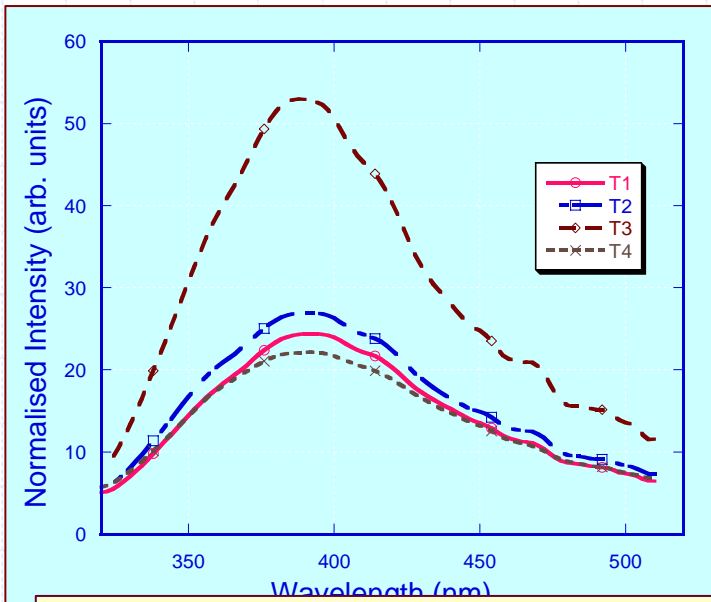
Applications in optoelectronic devices: vacuum fluorescent and field emission displays, blue and ultraviolet emitters and detectors.

Near band-gap excitonic emission from ZnO at around 380 nm with the subnanosecond lifetime.

It appears of interest for developing novel superfast scintillating materials with ZnO as activator.

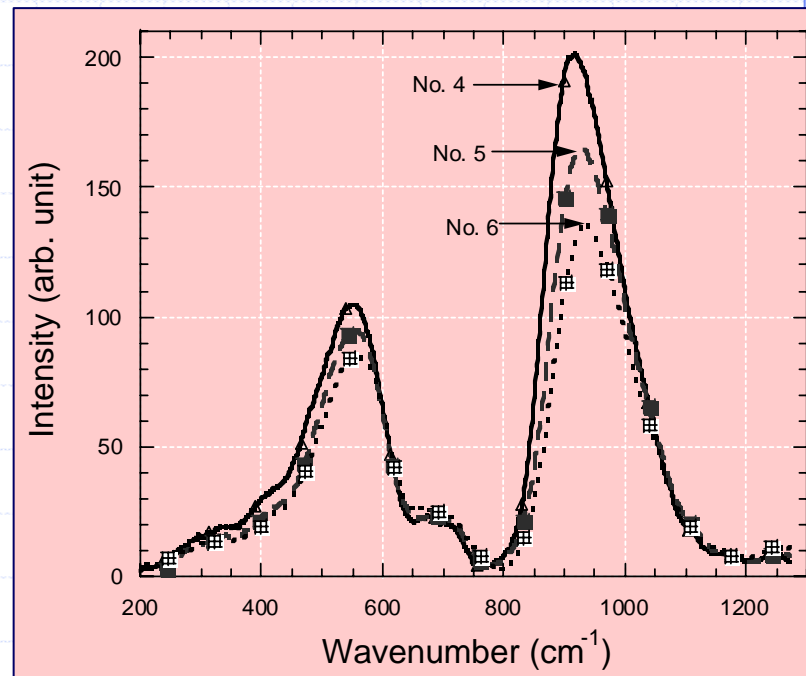
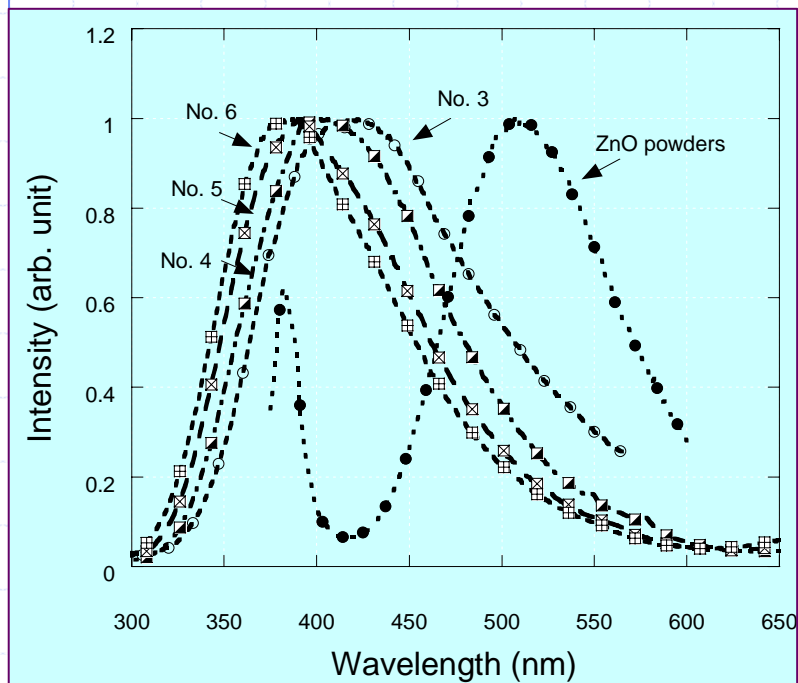


Photoluminescence



**Emission spectra
 of glasses annealed at different
 temperatures (left) and decay curve
 of glasses with different compositions**

Emission spectra (below) and Raman spectra (right) of glasses with and without F⁻ ions



Chalcogenide Glasses (ChG)

Novel systems for crystallization

IR luminescence

Second Harmonic Generation (SHG)

γ -irradiation induced effects

Internationally Collaborated with

ENEA

Centro Ricerche Casaccia

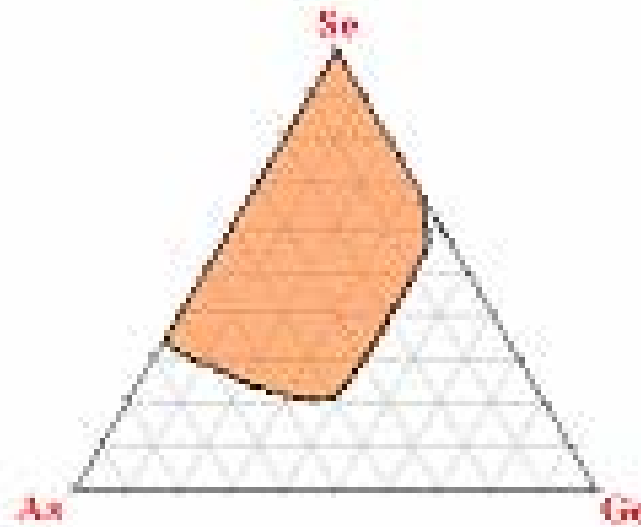
ENTE PER LE NUOVE TECNOLOGIE, L'ENERGIA E L'AMBIENTE



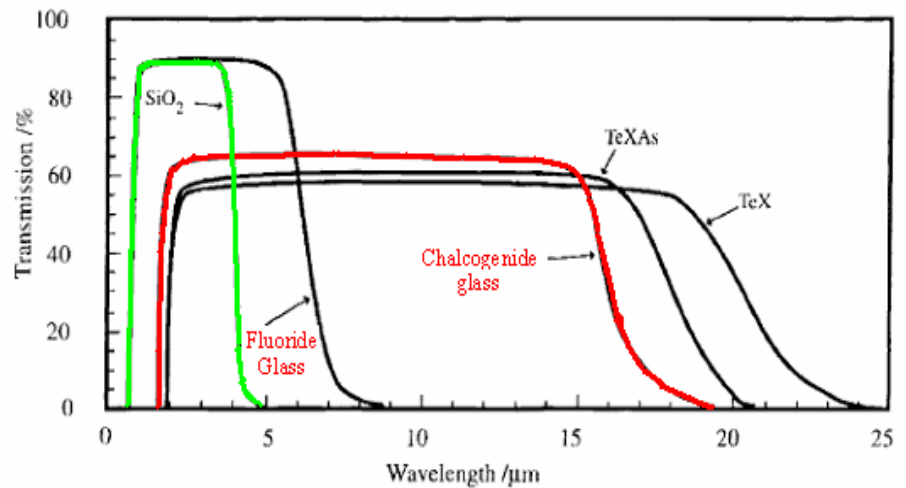
**UNIVERSITE
DE RENNES I**

Typical Chemical Elements used in chalcogenide glass

C	N	O	F
Si	P	S	Cl
Ge	As	Se	Br
Sn	Sb	Te	I
Pb	Bi	Po	At

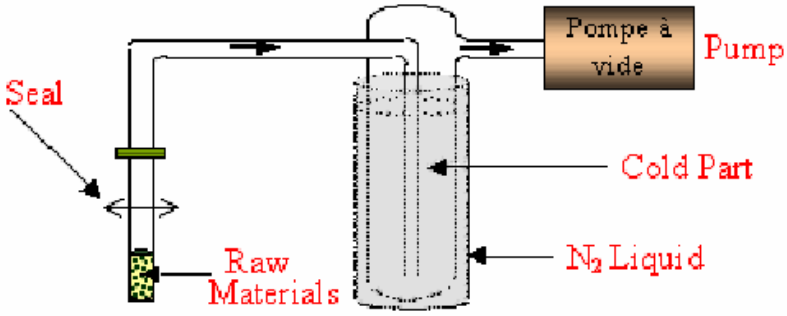


Se-Ge-As chalcogenide glass systems

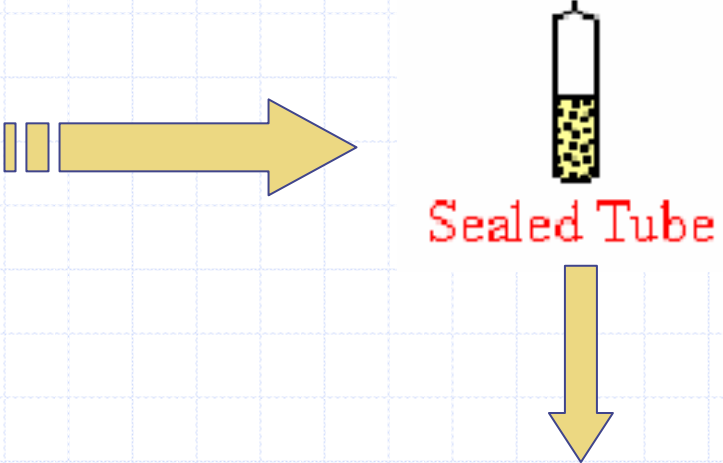


Optical transmission spectra of chalcogenide glasses

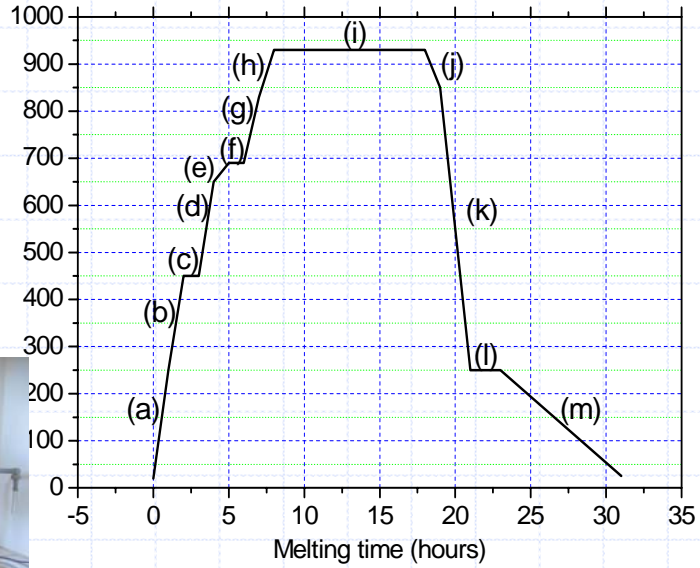
Sample Preparation



Vacuum Sealing



Prepared Samples

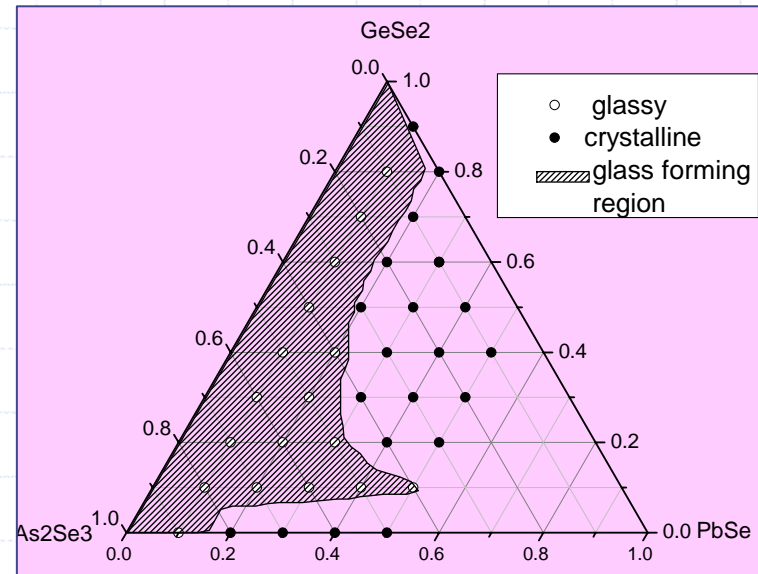
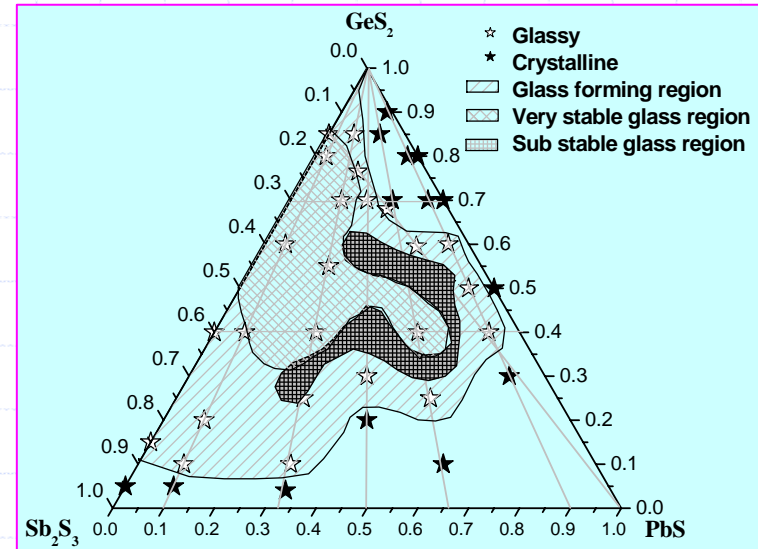
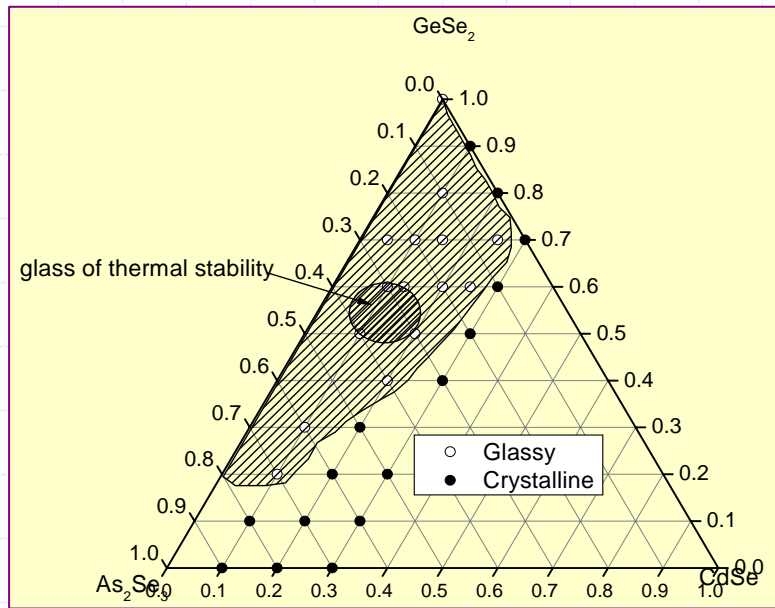


Melting in Rocking Furnace

Novel Chalcogenide Glass Systems

Novel glass forming regions:

GeSe₂-As₂Se₃-CdSe (below),
GeSe₂-Sb₂S₃-PbS (right above)
GeSe₂-As₂Se₃-PbSe



J. Am. Ceram. Soc., **88** (2005) 3143-3146

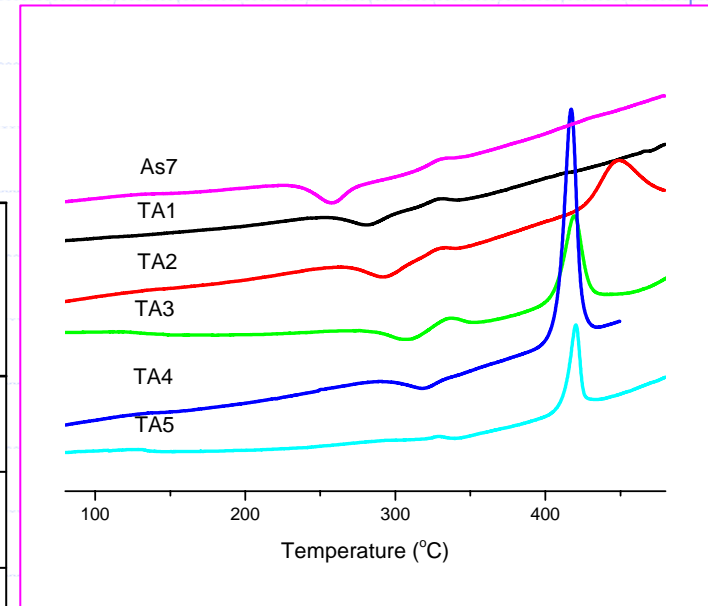
J. Am. Ceram. Soc. **89** (2006) 2154-2158

J. Am. Ceram. Soc. (2007) (accepted)

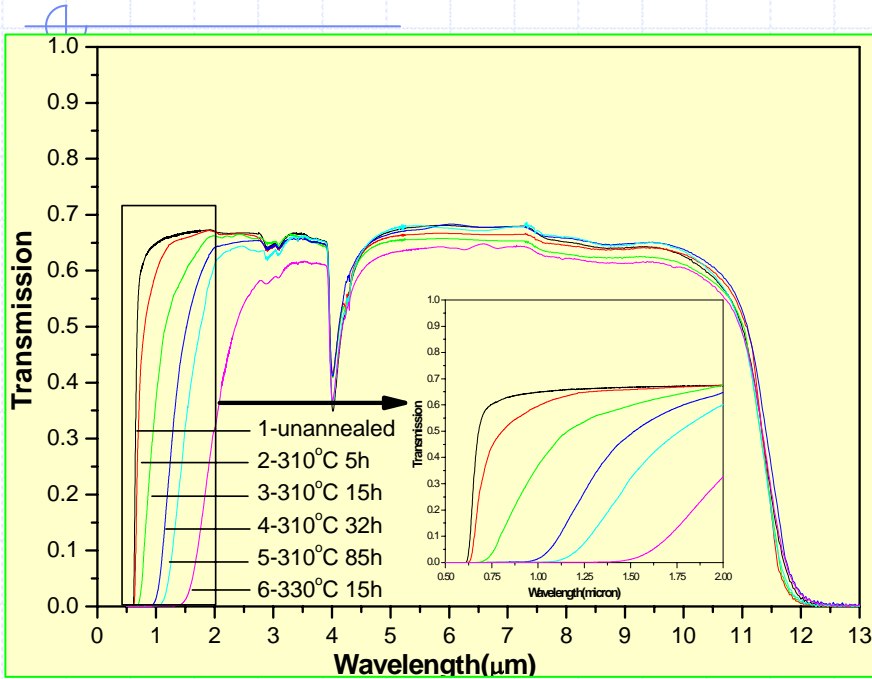
Crystallization Process

Properties of some glasses in the (1-x) (0.85GeS₂+0.15Sb₂S₃)-xPbS Group

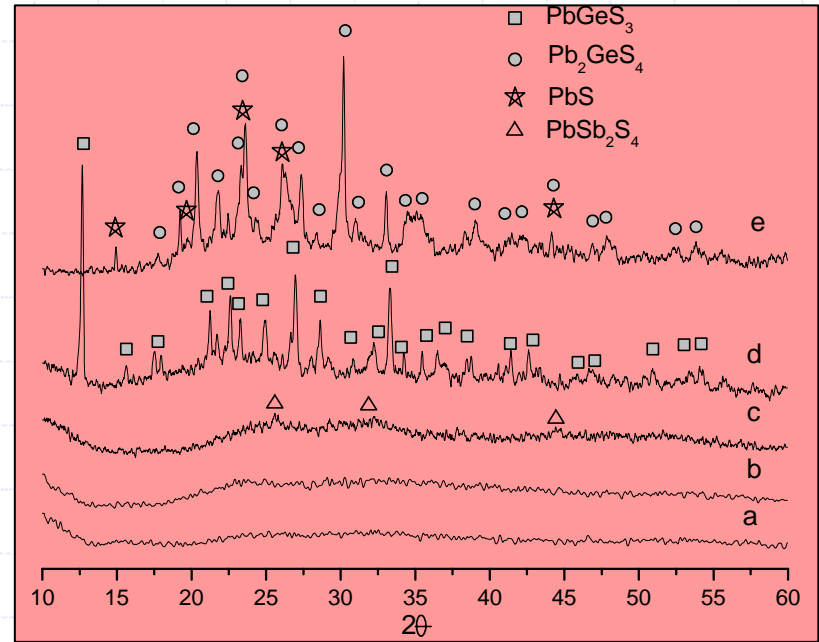
Sample code	ρ (kg/m ³)	Molar Volume (cm ³ /mol)	H _v (kg/mm ²)	K _c (MPa·m ^{1/2})	T _g (°C)	T _c (°C)	ΔT (°C)
P1	3.1299	53.42	185.2	0.2379	336	537	201
P2	3.6110	48.30	184.2	0.2090	312	505	193
P3	3.8481	47.19	166.6	0.1937	293	467	174
P4	4.2197	44.75	169.6	0.1920	293	458	165
P5	4.4352	44.20	169.6	0.1913	295	437	142



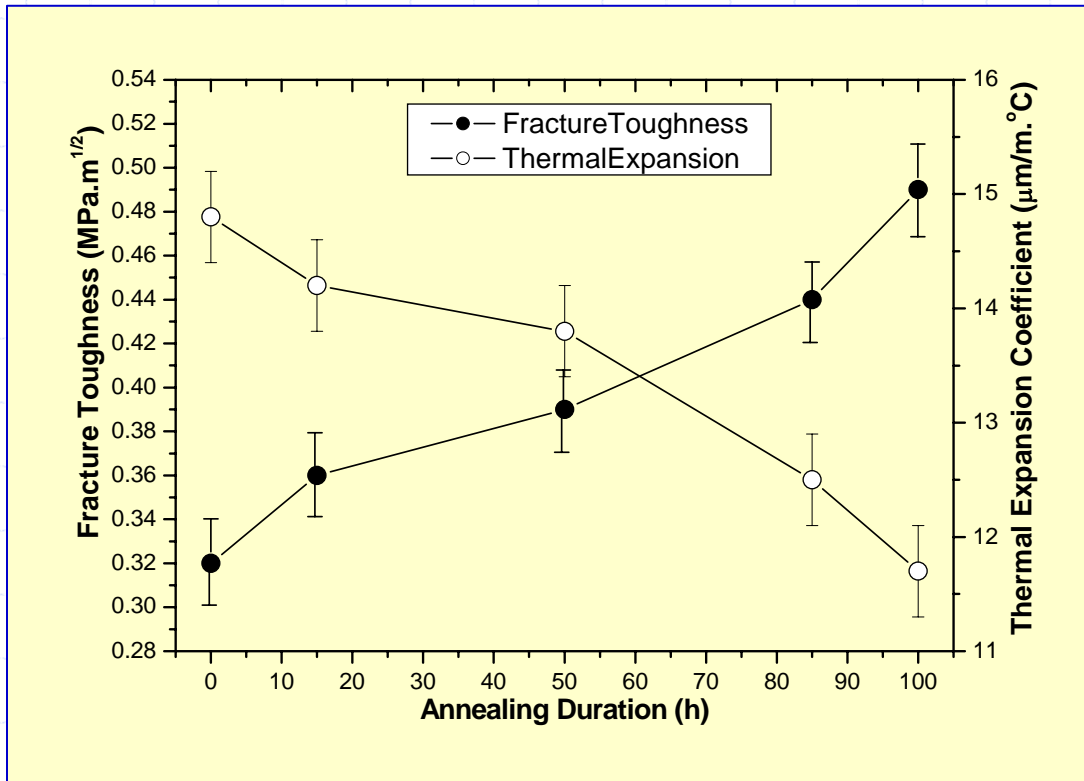
DSC curves of GeSe₂-As₂Se₃-CdSe chalcogenide glasses



**IR transmitting spectra of P5
 (51GeS₂-9Sb₂S₃-40PbS) glass**

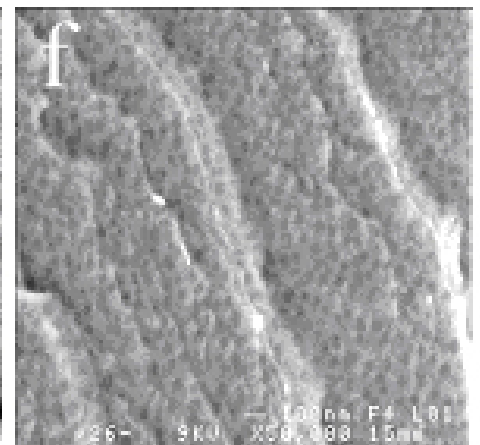
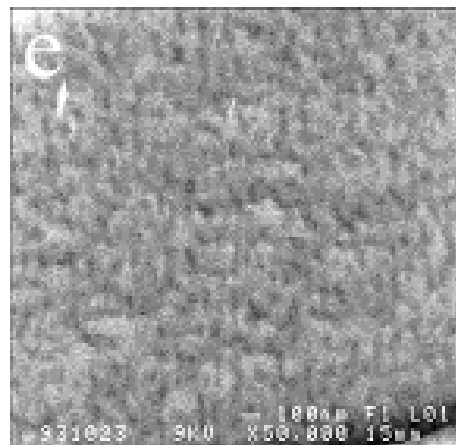
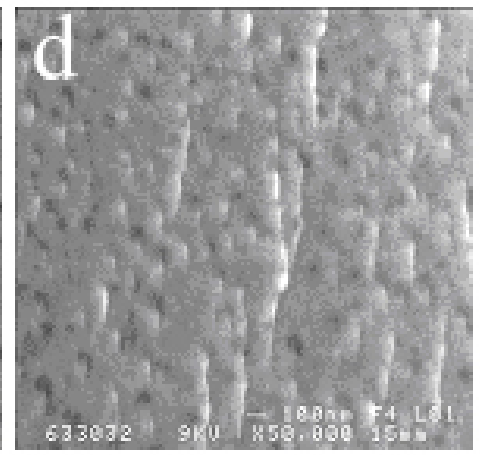
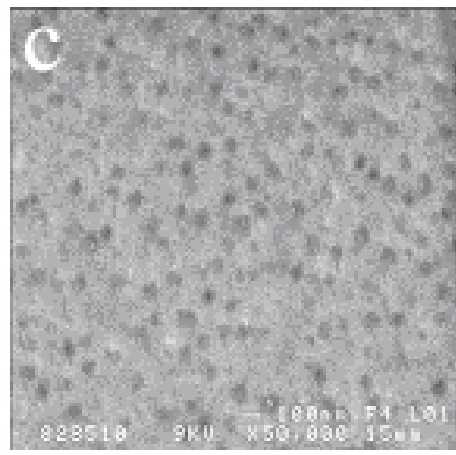
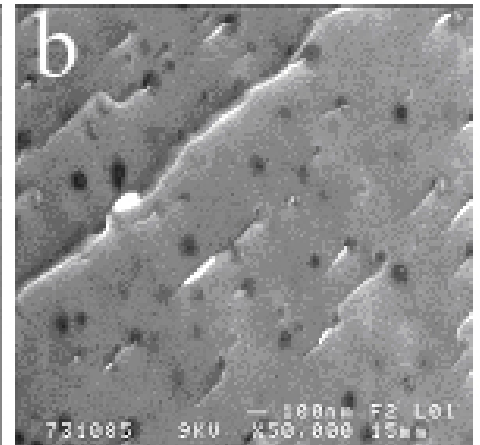
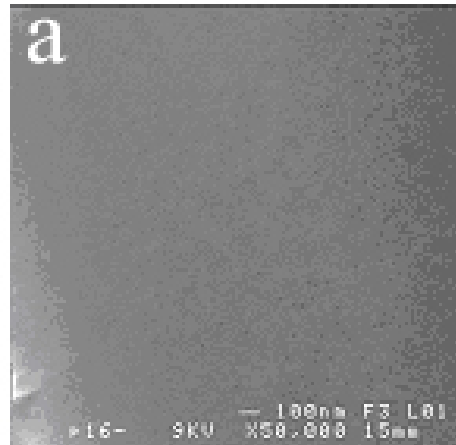


**XRD patterns of (a) P5 ; (b) P5
 after annealing at 340°C for 15h;
 (c) P7 at 300 °C for 5h; (d) P5 at
 310 °C for 85h; (e) P6 at 330 °C
 for 12h**

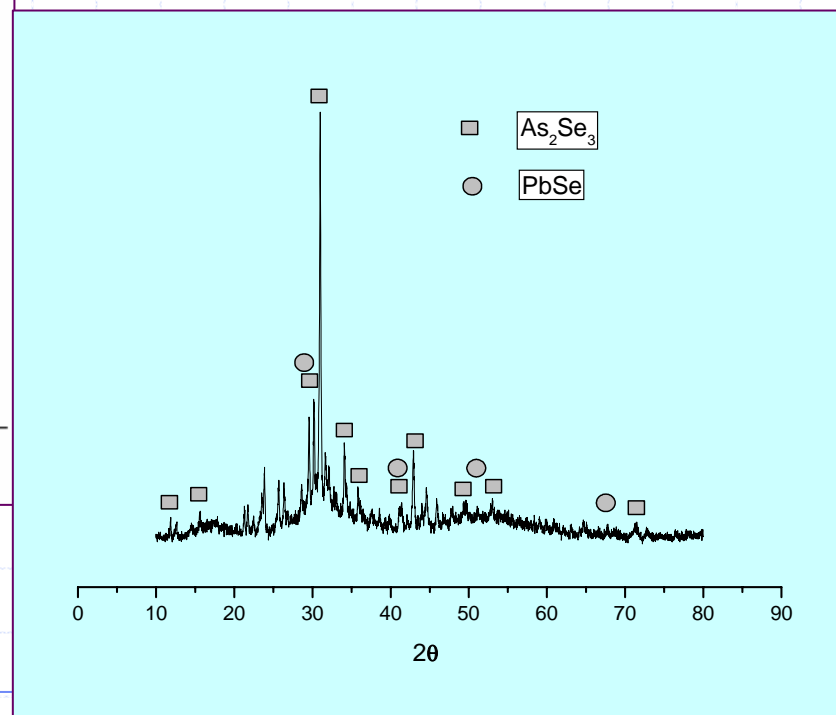
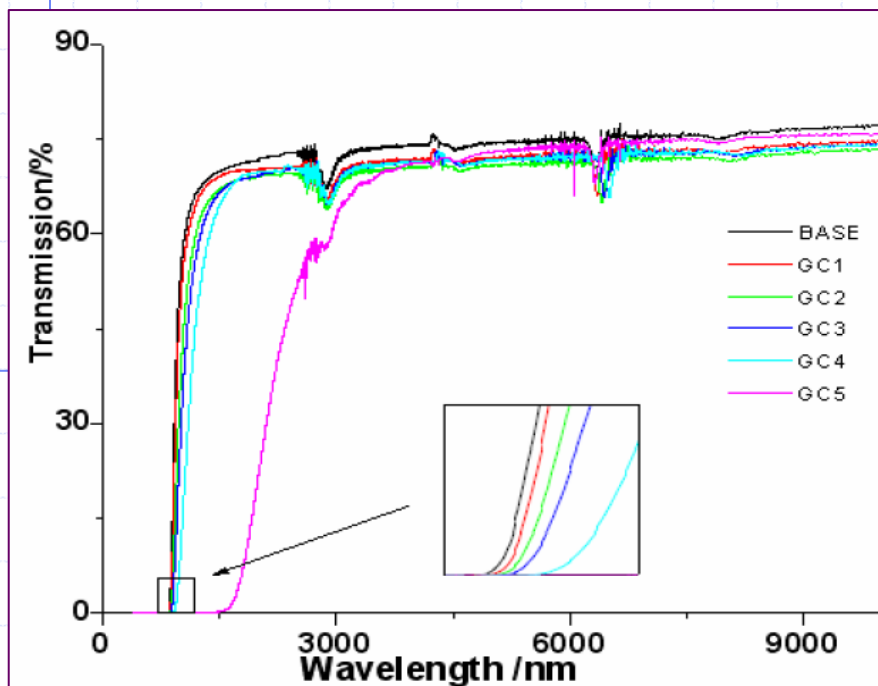


SEM Observations:

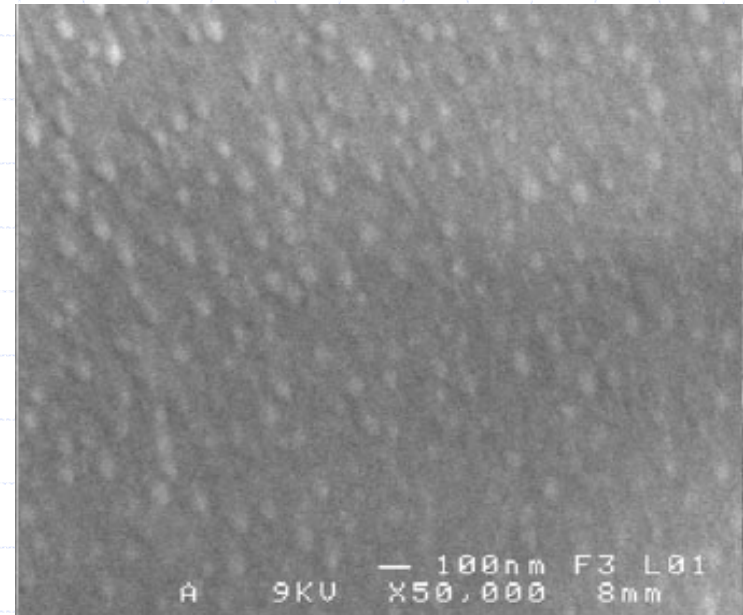
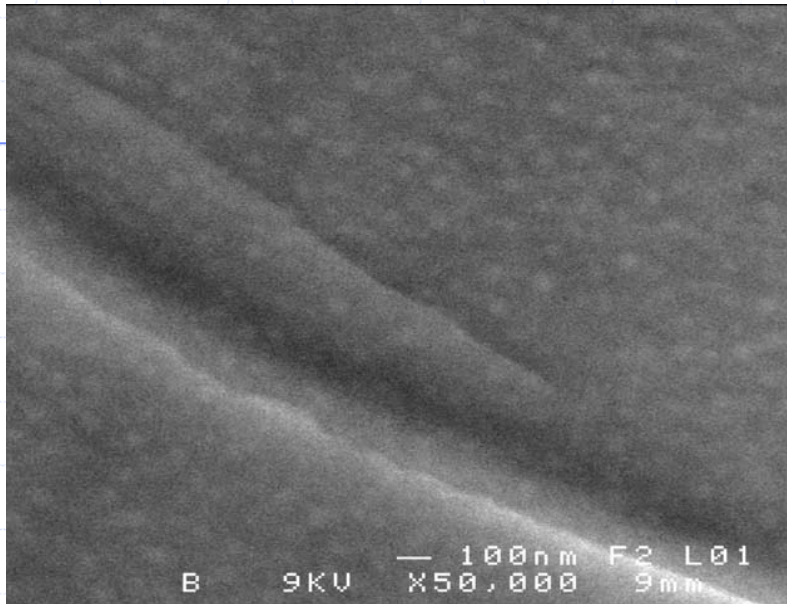
- (a) P9 at 330°C for 163h,
- (b) P7 at 300°C for 5h,
- (c) P5 at 340°C for 15h,
- (d) P5 at 310°C for 15h,
- (e) P5 at 310°C for 32h
- (f) P5 at 310°C for 85h



Sample	Base	GC1	GC2	GC3	GC4	GC5
$\alpha(\mu\text{m}/\text{m}\cdot^{\circ}\text{C})$	12.93	12.13	11.94	11.7	9.41	8.79

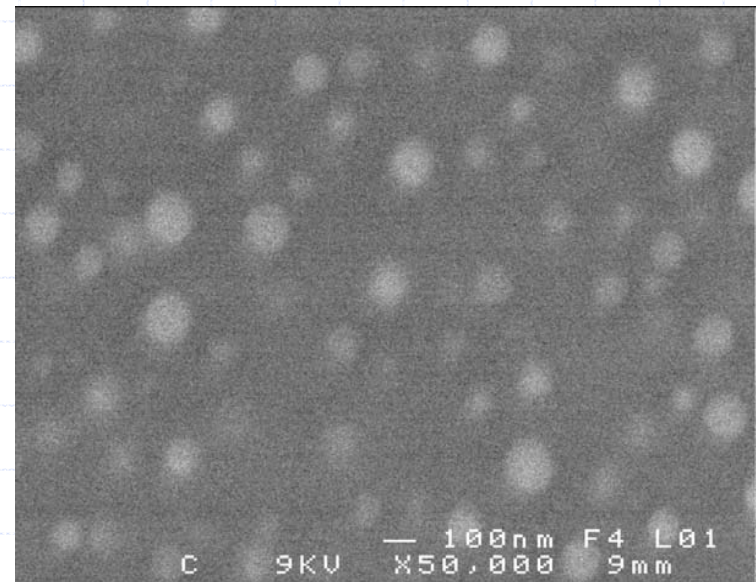


Transmission spectra and XRD patterns of sample 40GeSe₂-50As₂Se₃-10PbSe after different thermal treatments



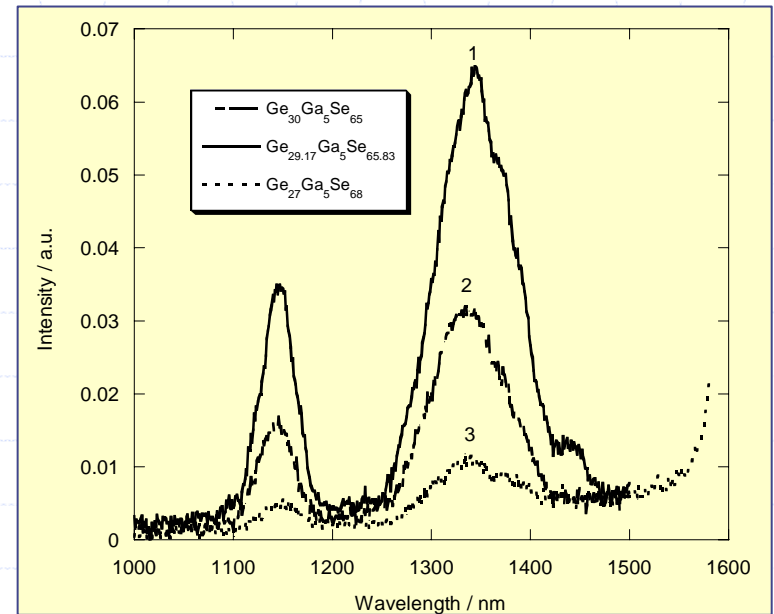
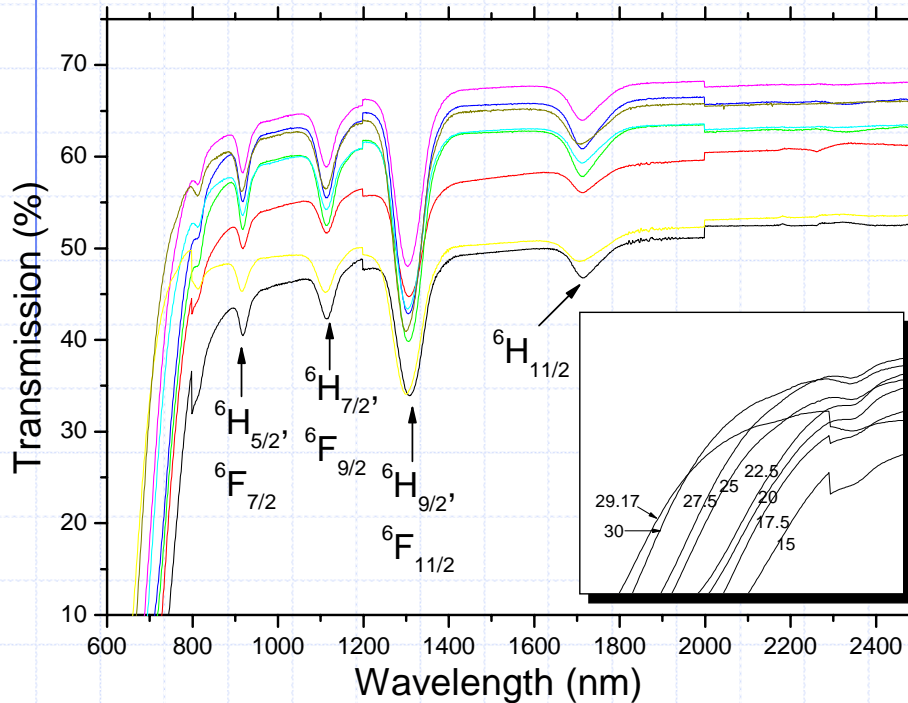
SEM observations

of sample annealed: (left)
230°C , 20h ; (right above)
250°C , 10h ; (right below)
270°C , 10h ;



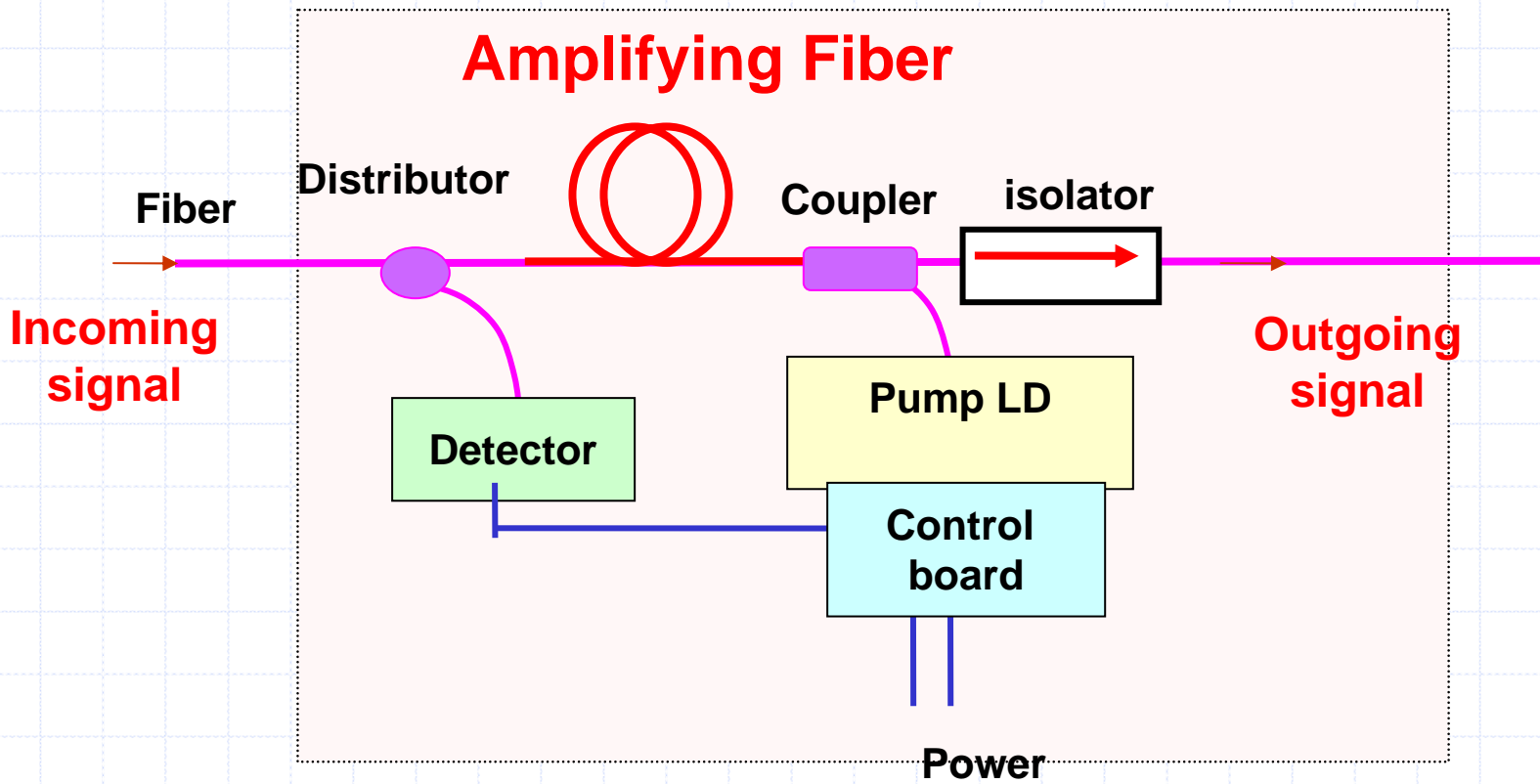
IR Luminescence

Average Coordination Number
 (ACN) > 2.67 $\tau = 440\text{-}530 \mu\text{s}$

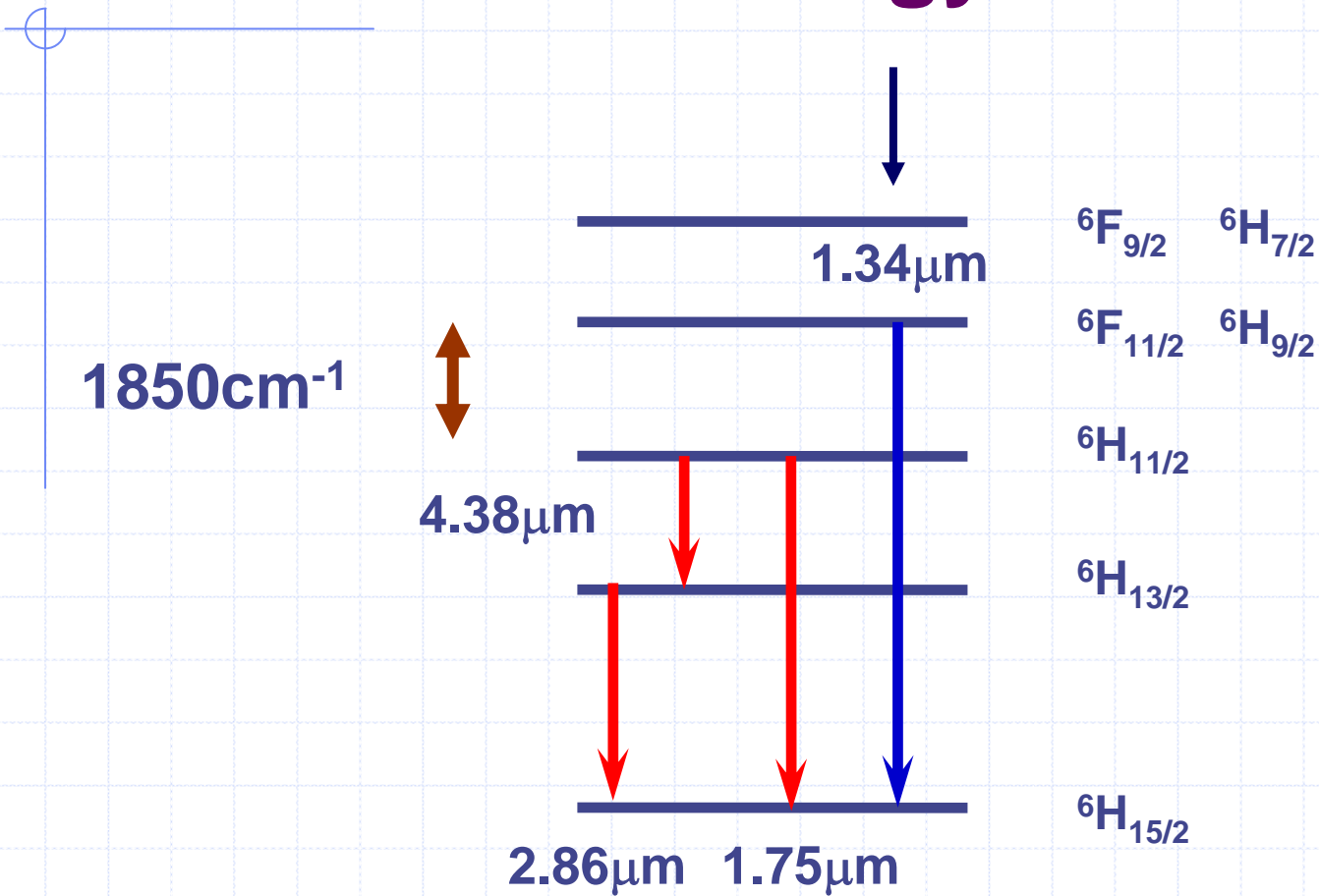


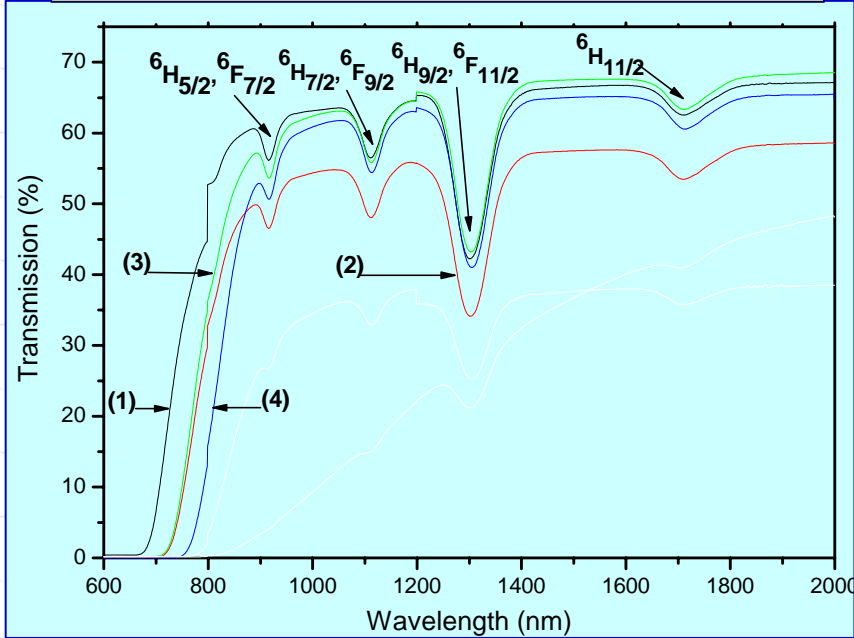
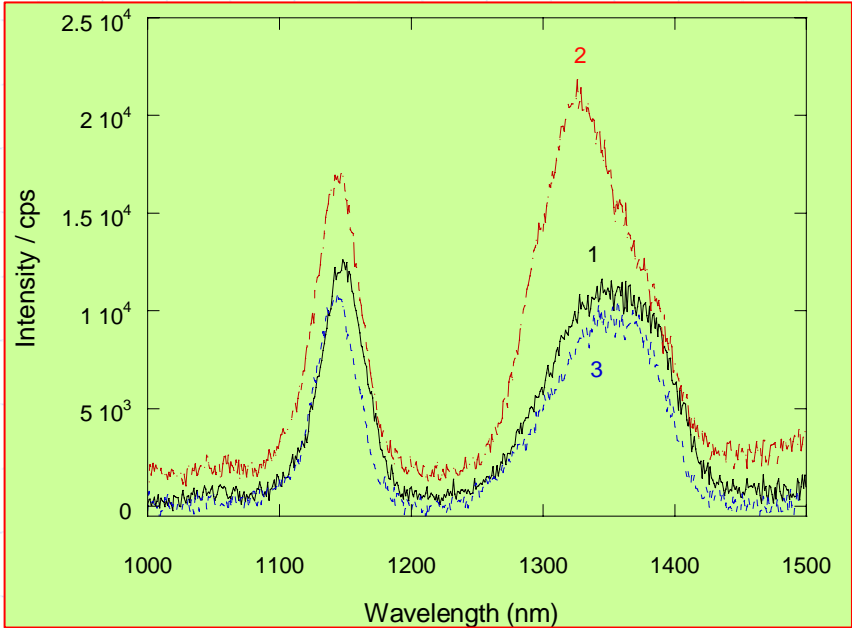
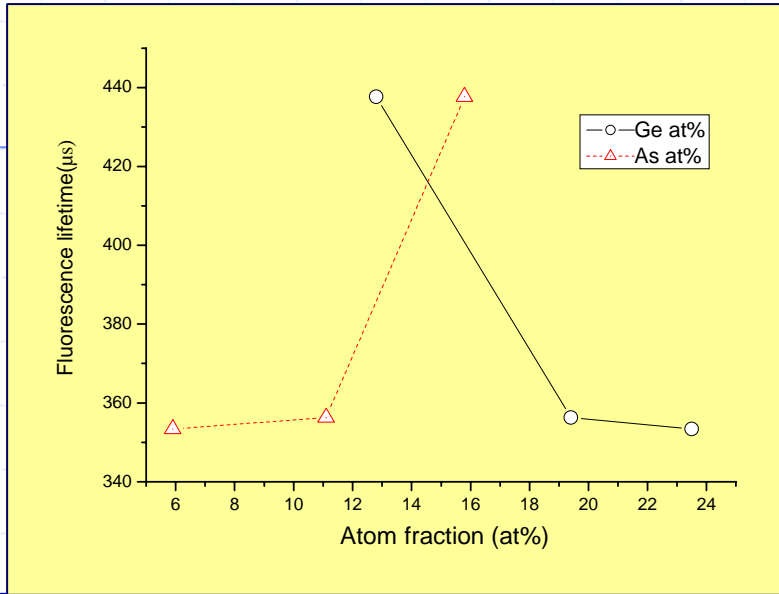
Transmission and emission spectra of Dy^{3+} doped Ge-Ga-Se glasses

Background

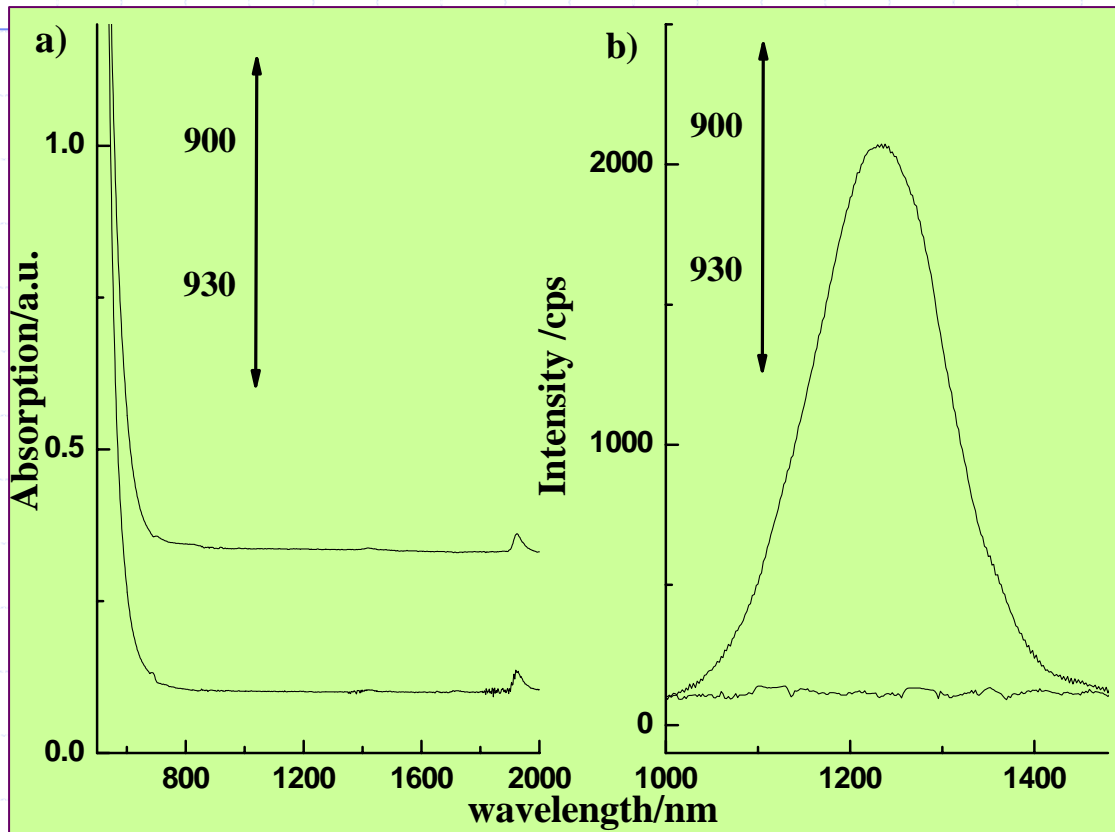


Energy Levels of Dy³⁺

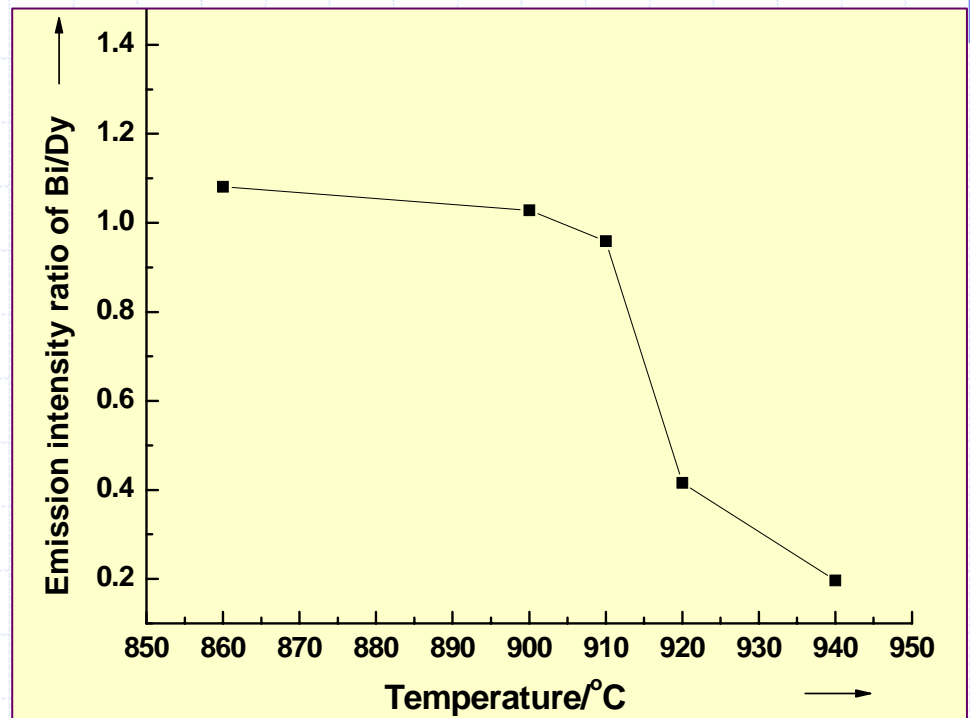
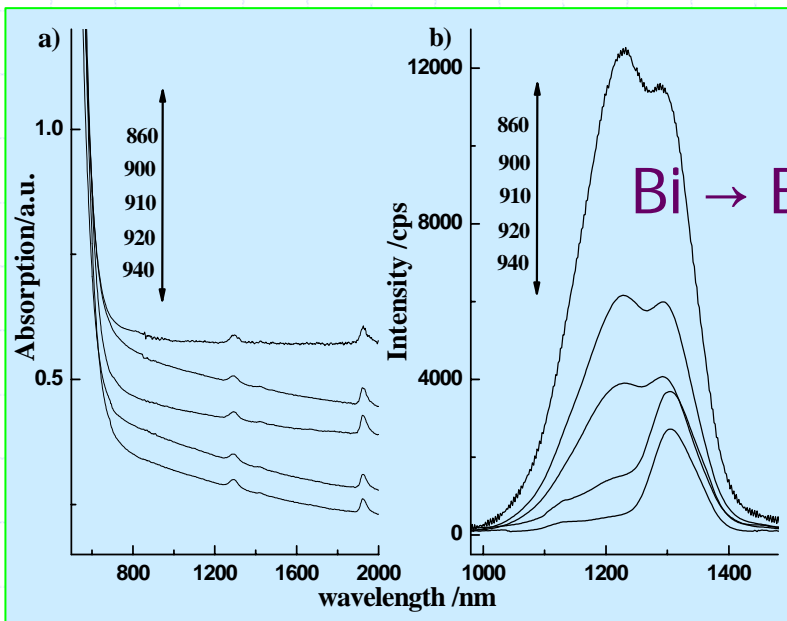




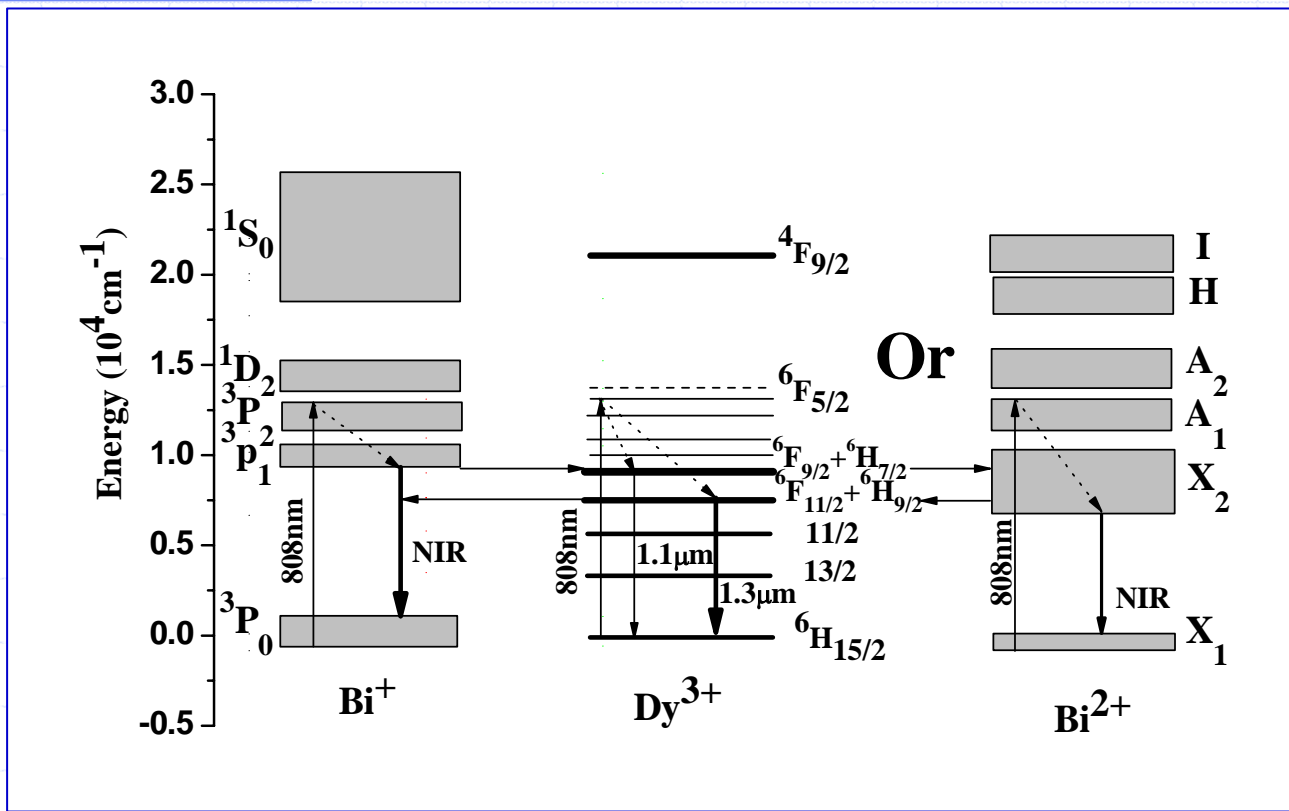
Transmission and emission spectra of Dy^{3+} doped Ge-Ga-As-Se chalcogenide glasses



Absorption (a) and luminescence (b) spectra of Bi doped $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-KBr}$ chalc halide glasses at 900°C and 930 °C



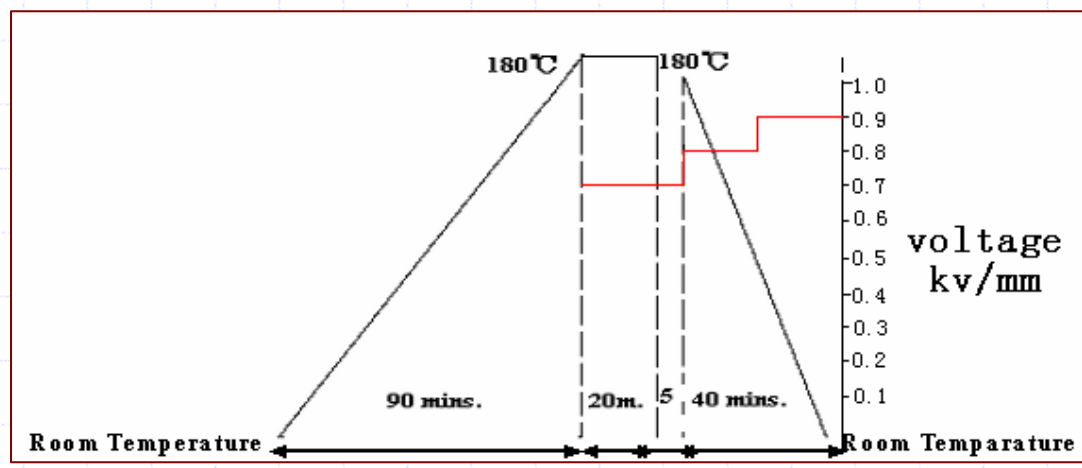
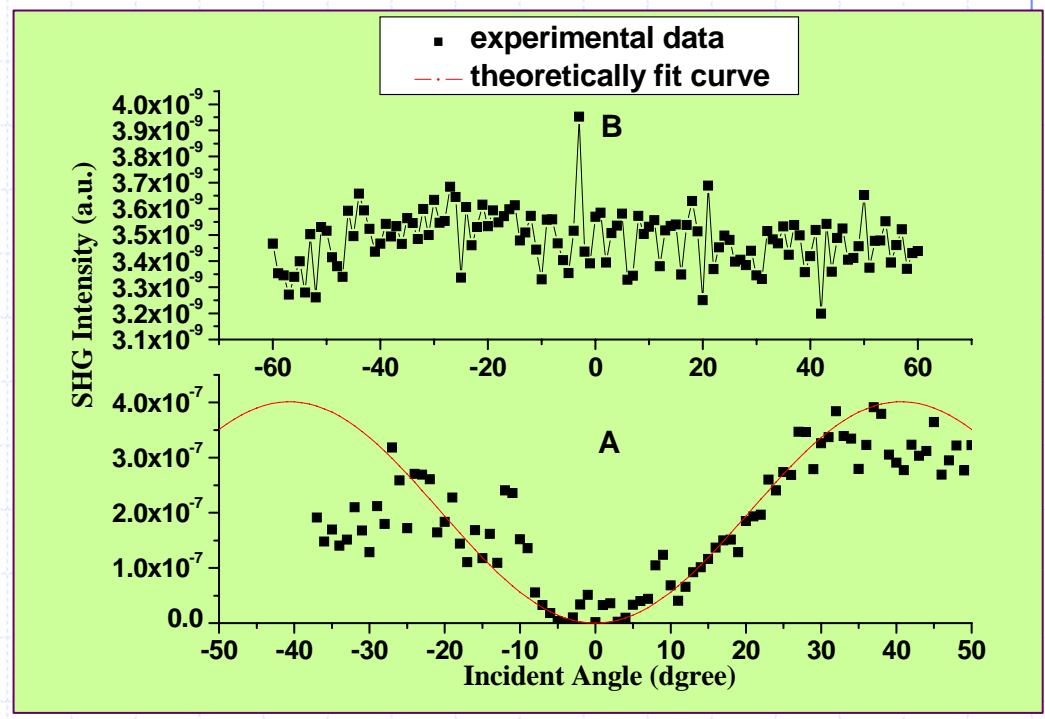
Absorption (a) and luminescence (b) spectra of Bi/Dy co-doped GeS₂-Ga₂S₃-KBr chalcogenide glasses at different temperatures



Absorption (a) and luminescence (b) spectra of Bi/Dy co-doped $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-KBr}$ chalcogenide glasses at different temperatures

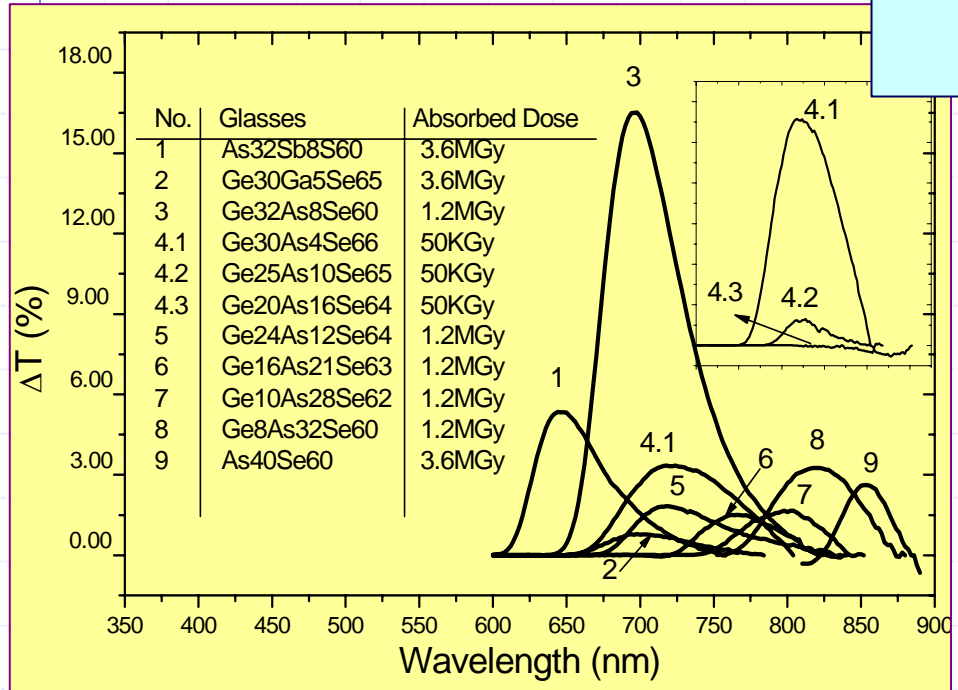
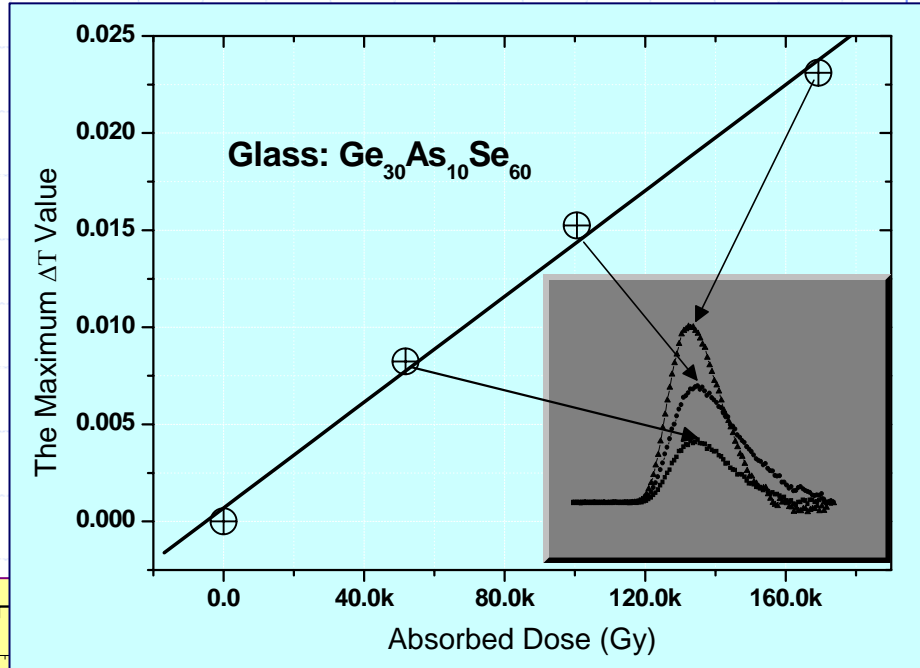
Second Harmonic Generation

Diagram of modified thermal poling technique (below) for SHG measurement (Maker fringe pattern) of chalcogenide glasses with the higher content of alkali ions



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

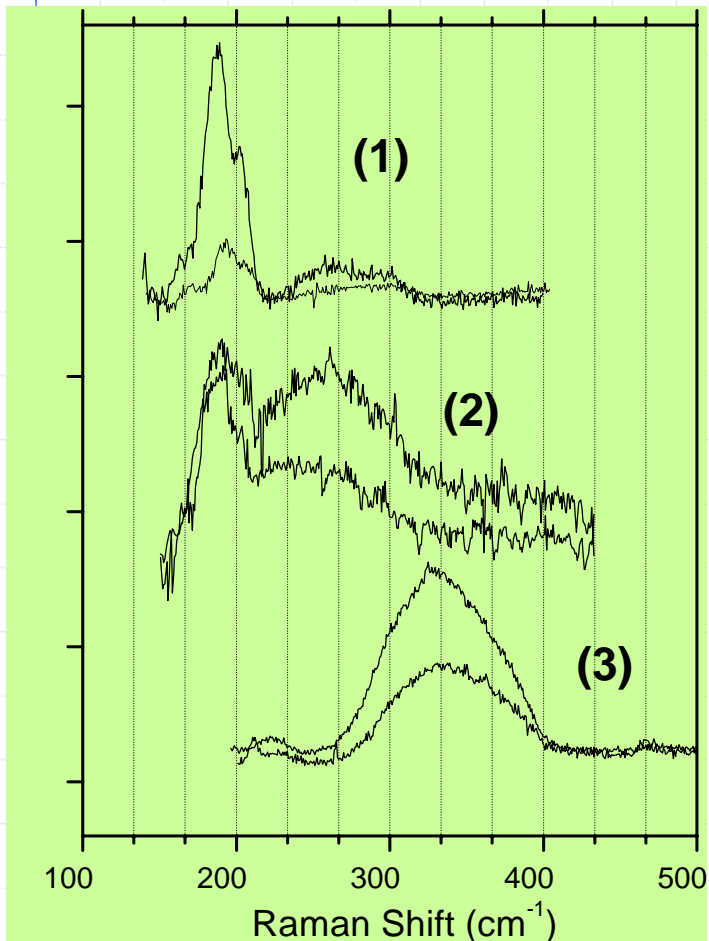
Optical transmission changes (ΔT)(below) and maximum ΔT versus the absorbed dose for glass sample 30Ge10As60Se



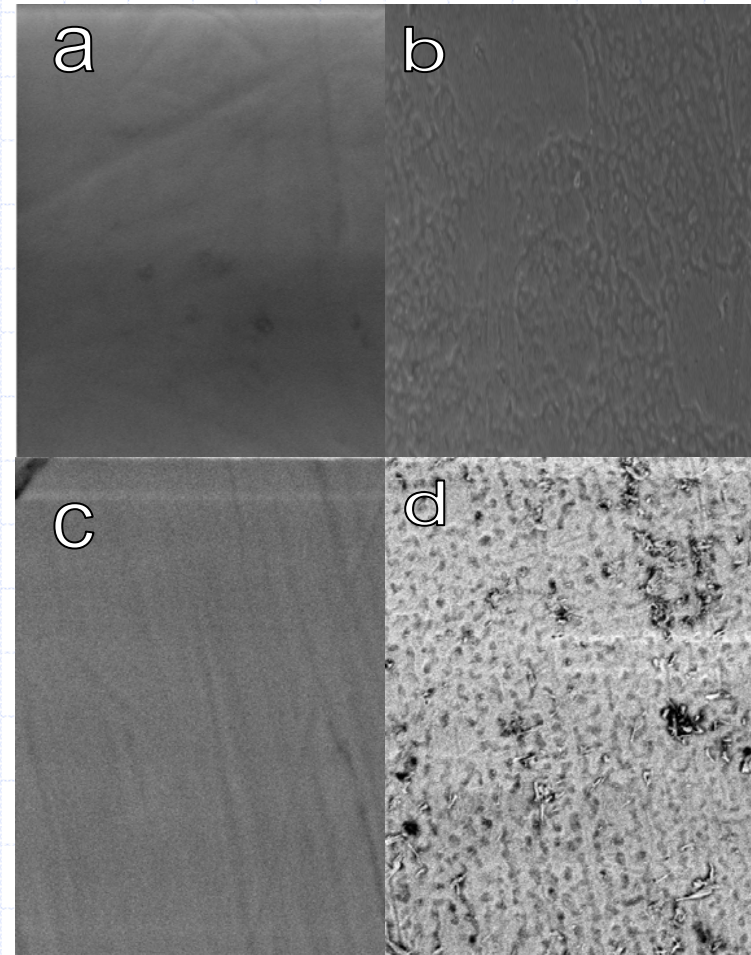
NIMB, 234(2005) 523-530

J. Am. Ceram. Soc., 89(2006)3582-3584

**Raman spectra for glasses (1)
30Ge5Ga65Se (3.6MGy), (2)
35Ge5As60Se (14KGy), (3)
40As60S (3.6MGy).**



SEM observations of glass samples
42As58S (a, b) and 24Ge12As64Se(c, d)
before and after irradiation (3.6MGy)



Thank You

