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XV, Part 1: Optical hole burning studies in europium doped oxide glasses

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Optical hole burning studies in europium doped glasses*

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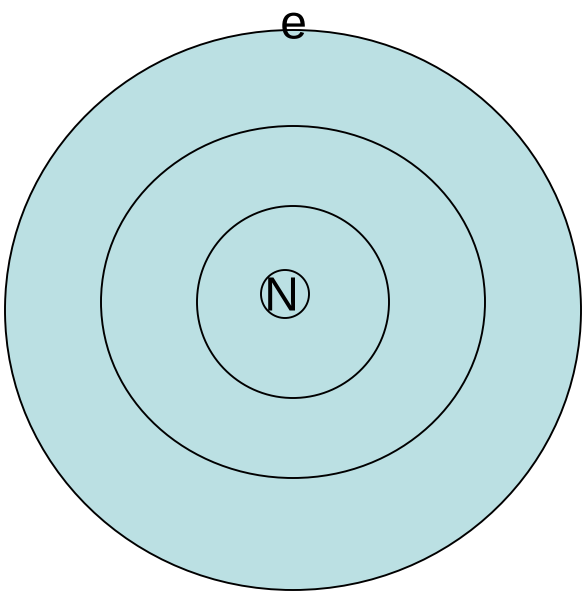
Outline

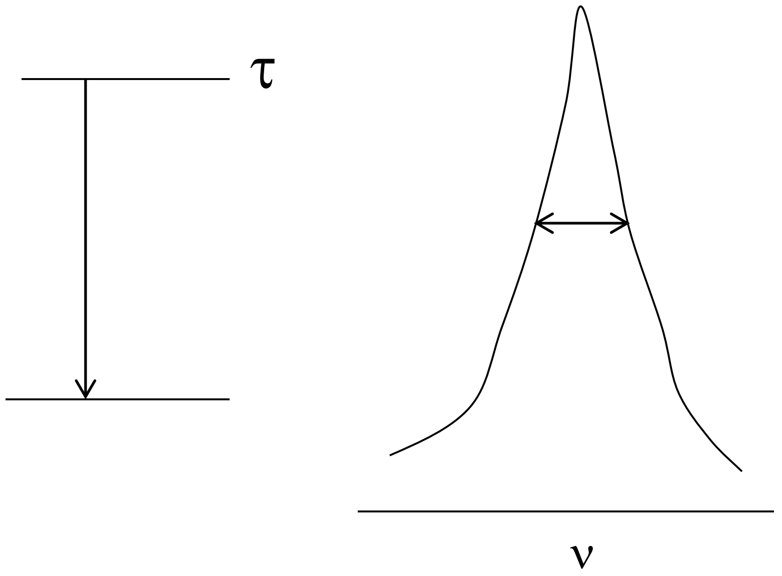
- Introduction
- Spectral Hole Burning
- Application
- Glass preparation
- Experimental Setup
- Optical Characterization and ESR
- Results
- Conclusions

Ionic energy levels

- Electron orbits



- Energy levels

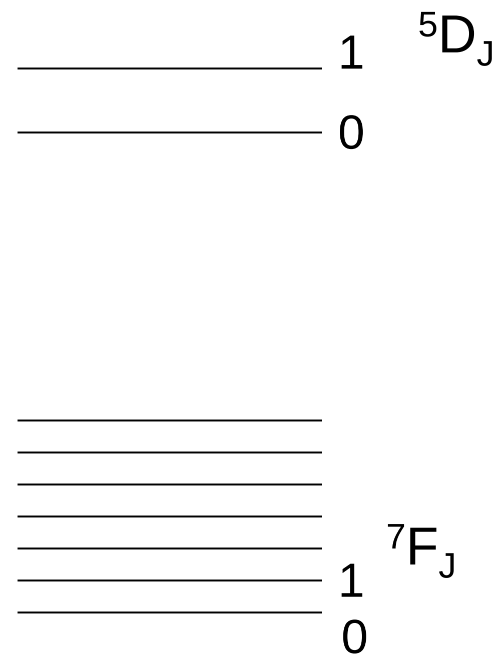


Units: What is the resolution?

- Laser wavelength: 500nm
- Wavenumber: 20,000cm^{-1}
- 1cm^{-1} = 30 GHz
- Typical optical frequencies: 10^{14}Hz
- High resolution spectroscopy:
  - MHz resolution

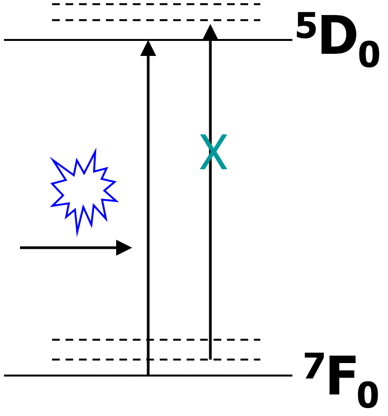
Ionic energy levels

- Rare-earths: in general forms trivalent compounds
- Sm^{2+} and Eu^{2+} also possible (special conditions)
- Example: Europium, at. No.=63
- Electron configuration of Eu^{3+}
- $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^6$
- Eu^{3+} levels (free ion)
- ^5D_J (J=0,1,2,3), ^7F_J(J=0,1,2,3,4,5,6), ----
- Eu^{3+} doped solids: Crystal field splitting
  - Example: J=1; three components (2J+1)
- Hyperfine splitting



Zero Phonon Line (ZPL)

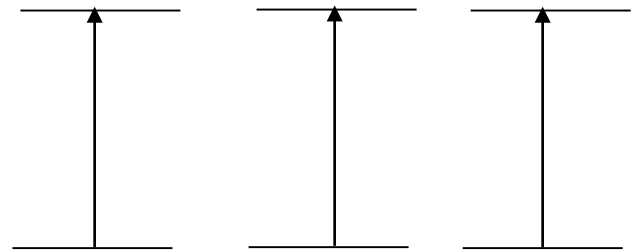
- ZPL: Pure electronic transition

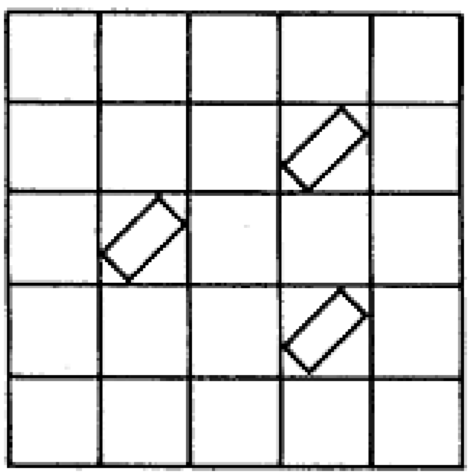


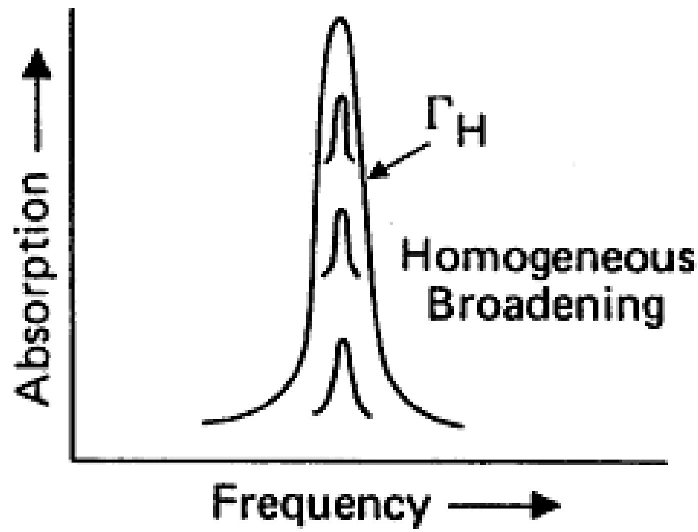
Eu^{3+} ion

Homogenous broadening

Energy levels at different centers





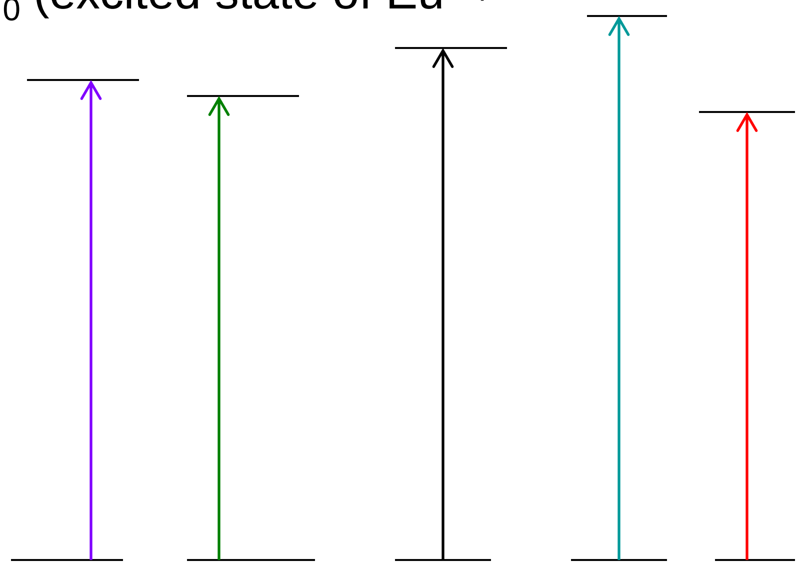


perfect crystal

Inhomogeneous broadening

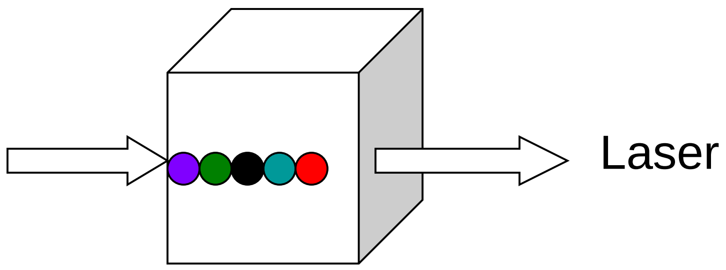
Energy levels at different sites

$^5D_0$ (excited state of Eu^{3+})



$^7F_0$ (ground state of Eu^{3+})

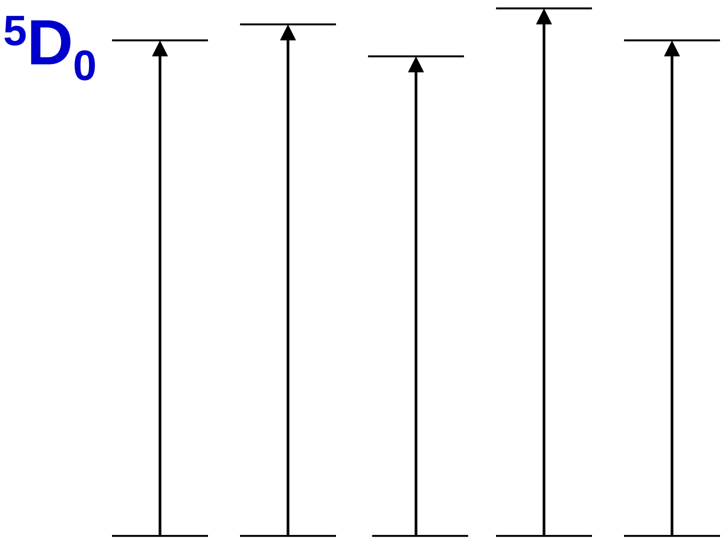
Inhomogeneous crystal field



Crystal field is different at each ion
So energy gap is different at each ion

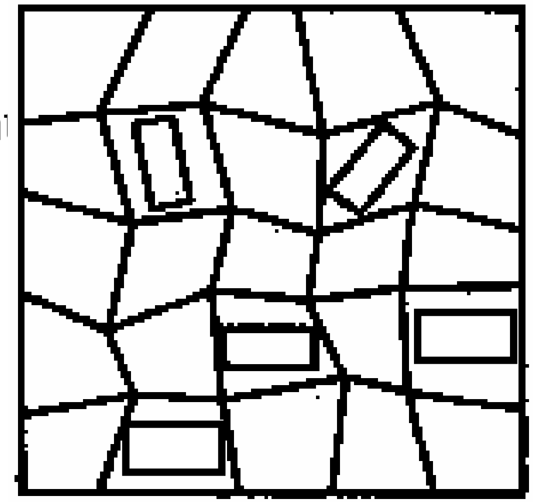
Typical concentration: $10^{17} – 10^{20}$/cc

Energy levels at differen

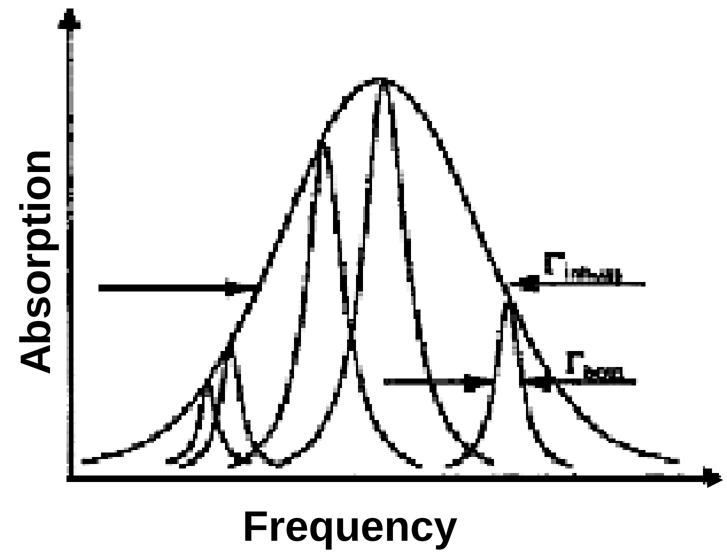


$^7F_0$ (ground state of Eu^{3+})

Different ions are in different crystal fields Energy gap are slightly different at each ion

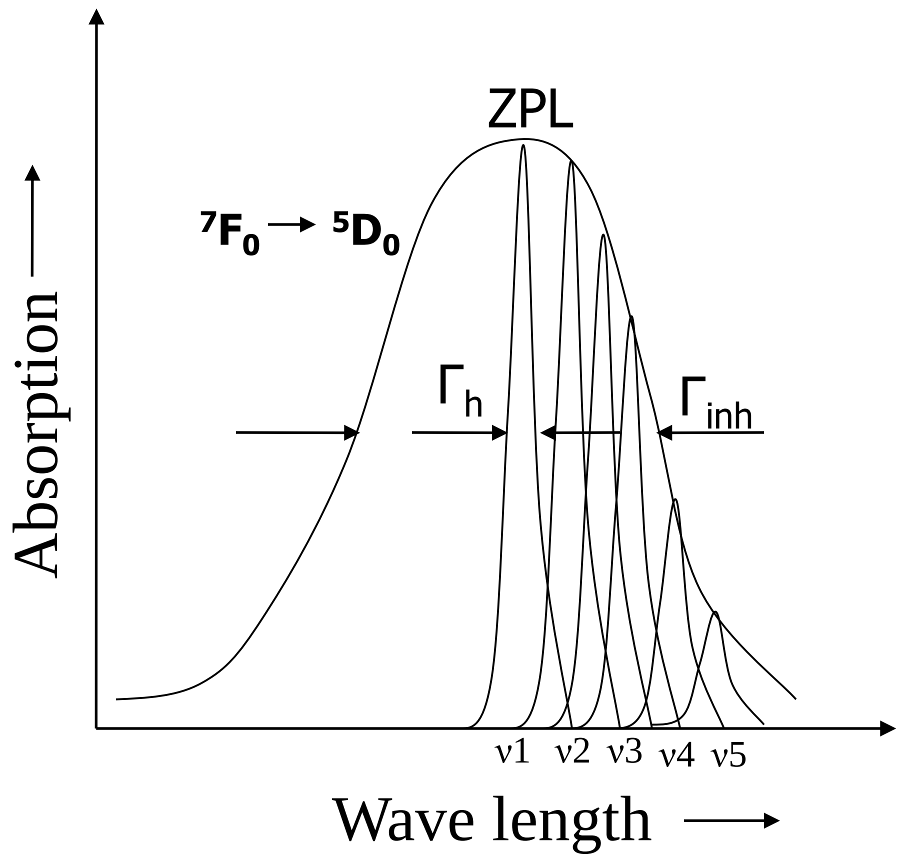


real solid matrix



Inhomogeneous broadening

Optical absorption transitions



Each subset of ions absorb light at a specific frequency - ϑ

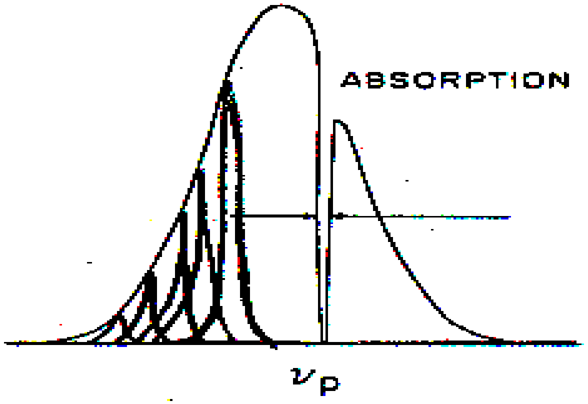
Γ_{inh} :1GHz – 1THz

Γ_h :1KHz – 100MHz

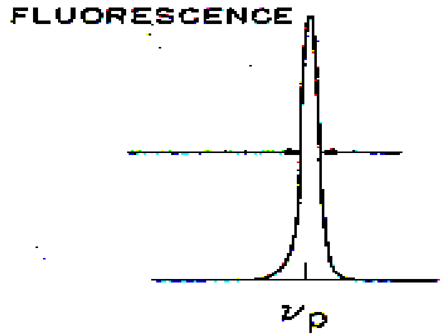
Number of Channels: Γ_{inh}/Γ_h

$$\boldsymbol{\Gamma_h \propto 1/\tau}$$

Fluorescence line narrowing



Inhomogeneous absorption

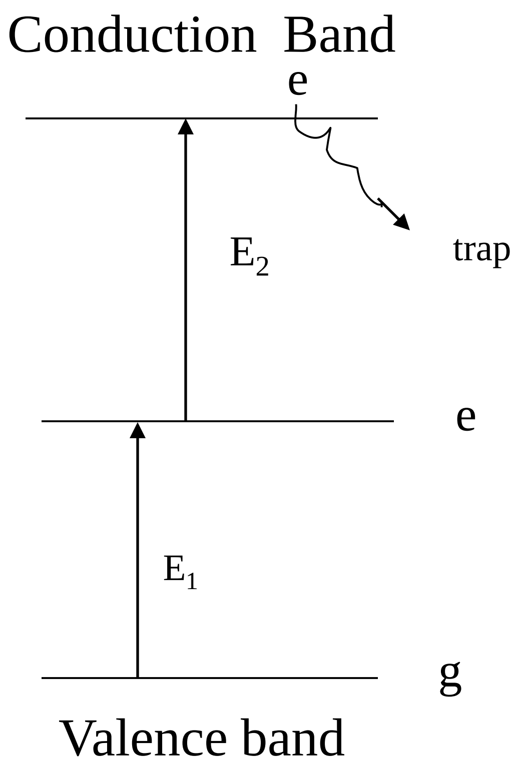


FLN

Optical hole burning

- High resolution spectroscopy technique: investigate ZPL
- Application: high density optical memory
- HB: selective bleaching of a subset of ions within the ZPL (inhomog.)
- Spectral hole burning
  - Transient Hole burning (opt.pump.quadrupole levels)
  - Persistent spectral hole burning
    - » Photophysical (change in environment, TLS interaction)
    - » Photochemical(ex: photoionization, bond breakage)
    - » Gated hole burning (Ex: two-photon ionization)

Photon gated hole burning



Winnacker et al, OL (1985); BaFCl:Sm^{2+}

Kaplyanskii, J.Lumin. (1998); CaS:Eu^{2+}

Required criteria for hole burning

- ZPL: Inhomogeneous broadening
- Homogeneous < Inhomogeneous
  linewidth linewidth
- Narrow laser
- Exhibit FLN: narrow holes
- <u>Material criteria</u>
  - No cross talk between holes
  - Holes have to be permanent
  - Burn holes with low power
  - Potential to burn/retain more holes

Optical hole burning

- HB Materials
  - Inorganic (crystals, glasses, color centers etc.,)
  - Organics (dye doped polymers etc.,)
  - Biological
- Drawback: works at low temp.

- Our effort: make materials for high temp. HB
  - Understand the HB mechanisms
  - Improve the HB efficiency, hole density

Why to investigate glasses?

Large inhomogeneous broadenings
Vary the composition
Easy to prepare samples
PSHB

Glasses investigated:

Sodium borates
Silicates
Borosilicates
Germanates
Tellurites

History of hole burning

- Pioneering HB work
- Ruby- Al_2O_3:Cr^{3+} (A. Szabo) 1972 (patented)
- LaF_3:Pr^{3+}(Erickson)
- Eu^{3+}
- More literature: Pr^{3+}, Eu^{3+}: R6G dye laser
- Organics (K. Rebane group)

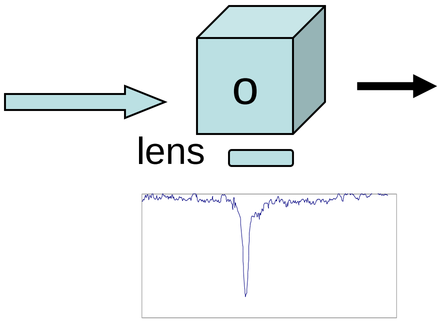
- Sm-doped glasses
  - $Sm^{2+:}$ doped borate glass (1993)
  - Sm^{2+}: fluorohafnate glass (1993)
  - Sm^{2+}: $SrFCl_xBr_{(1-x)}$ (1995)

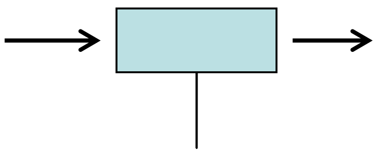
HB in Eu-doped glasses

- Macfarlane et al, silicate (1983); <20K
- Mao et al, aluminosilicate (1996); 77K
- Fujita et al, sod. Alumin. Silicate (1998), RT, phot.red.
- Fujita et al, sodium borate (2001); 77k – RT
- Nogami et al, Sol-gel: Eu photoinduced rearrangement of protons/local structure (1998)--- rearrangement of OH bonds
- Meltzer et al, (1999); Eu^{3+} nanoparticles (sol-gel, Y_2O_3)

How to burn and probe the hole?

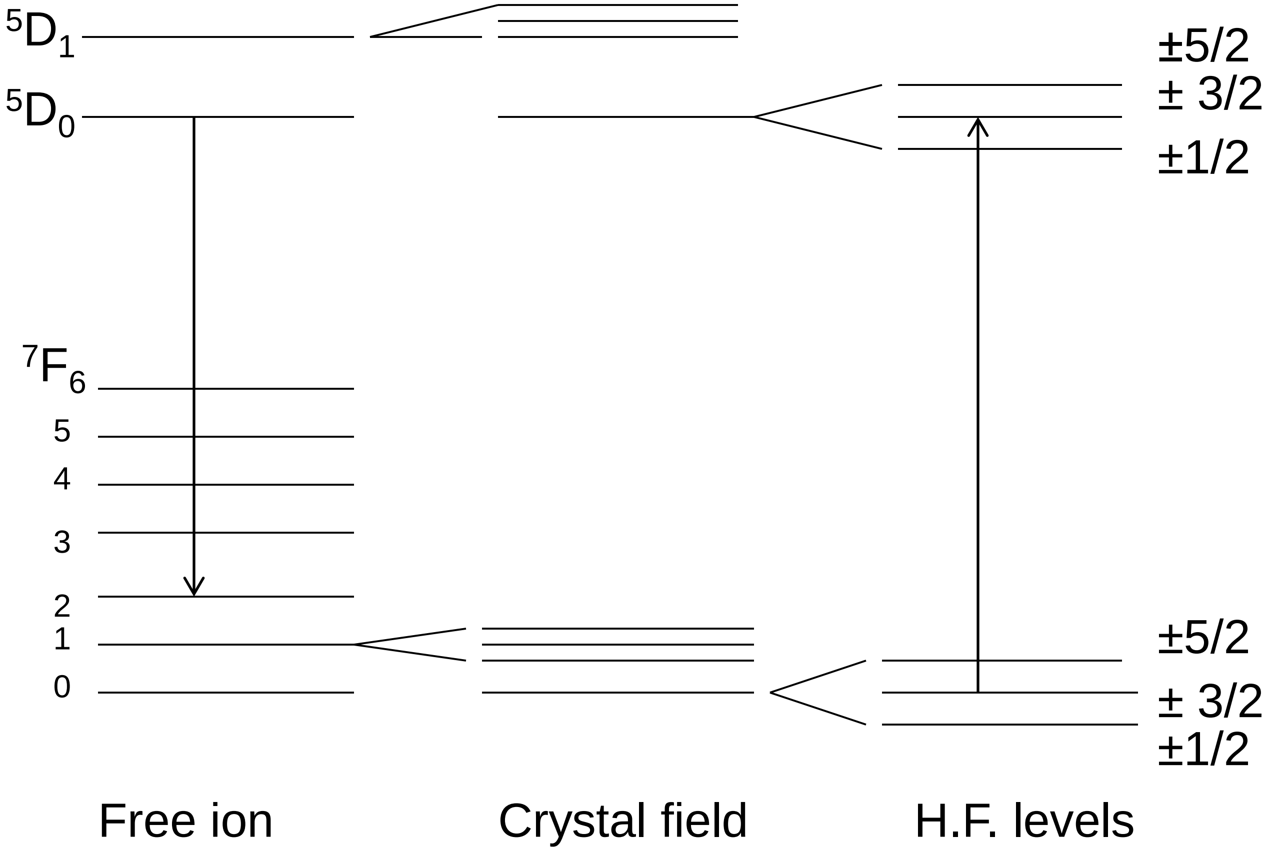
- Saturate absorption
- Excitation spectrum
  - Single laser to burn and probe
- Sideband spectroscopy
  - Use carrier frequency to burn the hole
  - Sideband frequency to probe the hole
- rf-optical double resonance



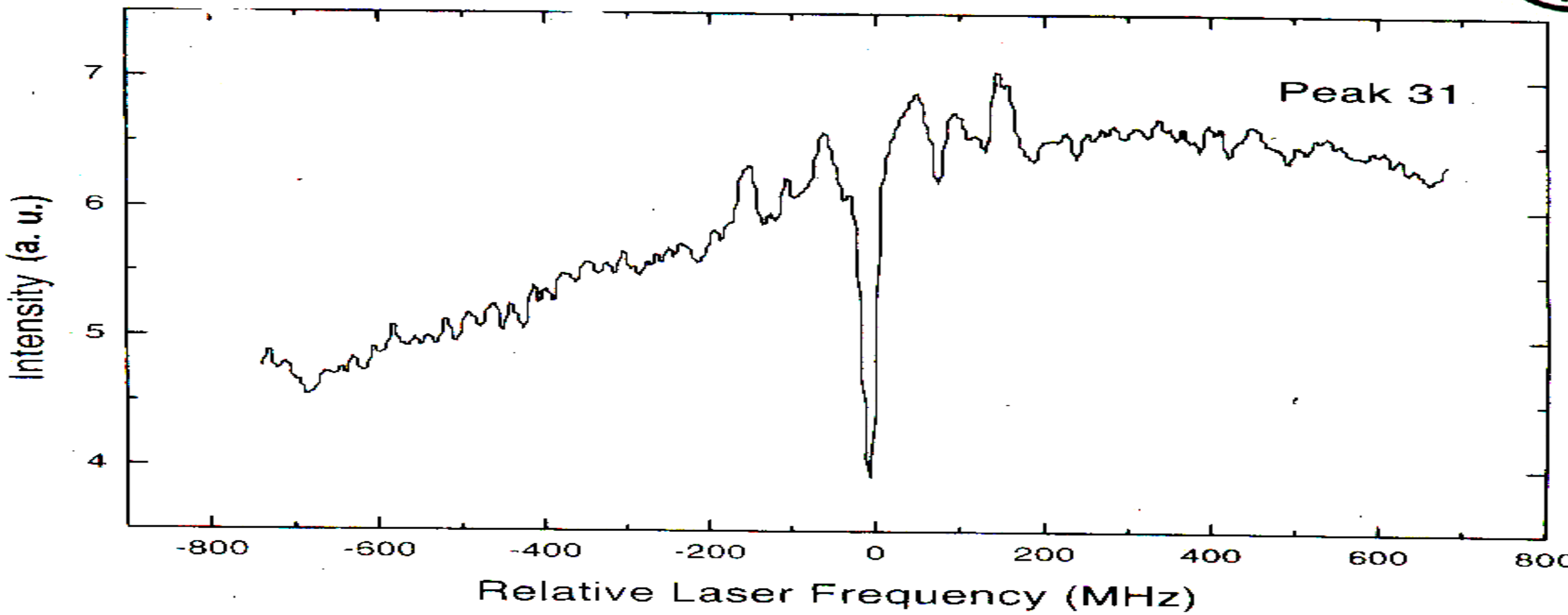


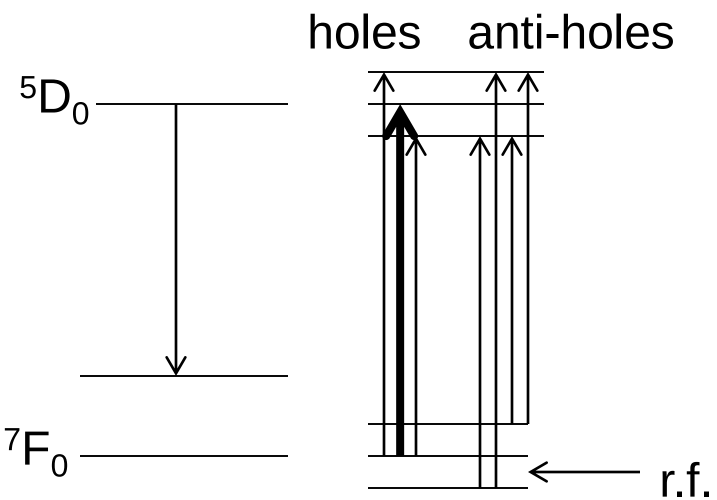
Transient hole burning in Eu^{3+}

- Partial energy level diagram



Transient HB: Population rearrangement among hf levels

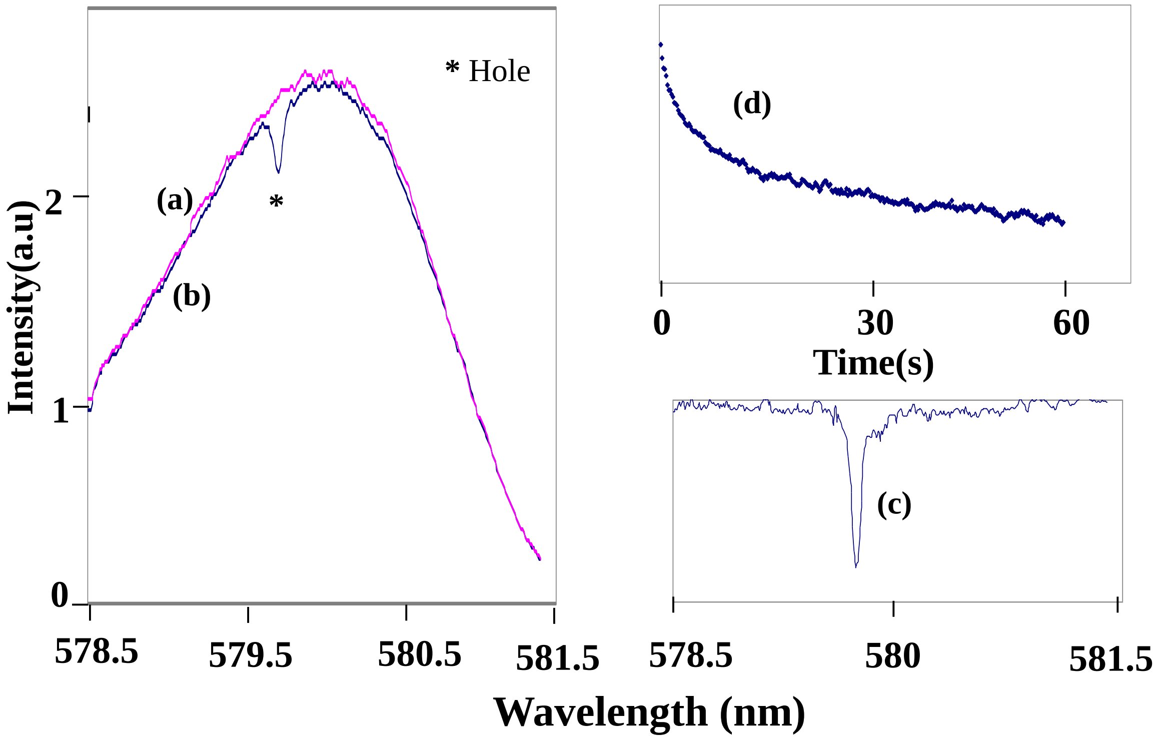


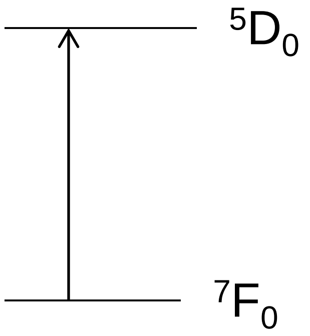


Eu^{3+}-doped crystal

Appl. Opt. (1999)

Hole burning spectra(10K)





Excitation spectra of 612nm Eu^{3+} emission

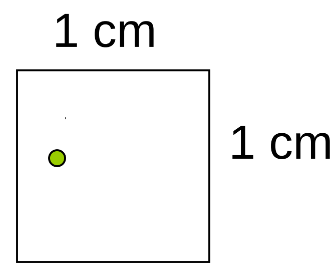
(a) before and (b) after hole burning in Sodium Silicate glass

(c) Spectral hole

(d) Intensity vs Time plot obtained during hole burning

Application: optical memory concept

Number of holes $= \dfrac{\text{inhomog.width}}{\text{hole width}} = \dfrac{5\times10^{9}}{10^{4}} = 5\text{x}10^{5}$



Spot size = 1μm

Spot Area = 10^{-8}cm^{2}

Total spots $= \dfrac{\text{sample area}}{\text{spot area}} = \dfrac{1\ \text{cm}^{2}}{10^{-8}\text{cm}^{2}} = 10^{8}$

Total holes = total spots $\times$ holes at each spot

Each hole = one bit

Total bits $= 10^{8}\times5\text{x}10^{5} = 5\times10^{13}\ \text{cm}^{-2}$

Sample preparation: glass compositions

Eu ion doped sodium borates

$34Na_2O + 65\ B_2O_3 + 1\ Eu_2O_3$

(2) $33Na_2O + 65\ B_2O_3 + 2\ Eu_2O_3$

(3) $27Na_2O + 66\ B_2O_3 + 5\ Y_2O_3 + 2\ Eu_2O_3$

(4) $33.6Na_2O + 66.4\ B_2O_3 + 3\ Eu_2O_3$

(5) $27.5\ Na_2O + 67.4\ B_2O_3 + 5.1\ Y_2O_3$

Eu ion doped sodium germanates

(10) & (11) $21Na_2O + 78\ GeO_2 + 1\ Eu_2O_3$

(12)$21Na_2O + 73\ GeO_2 + 5\ Y_2O_3 + 1\ Eu_2O_3$

(13)$21Na_2O + 75\ GeO_2 + 3\ Y_2O_3 + 1\ Eu_2O_3$

Eu ion doped sodium silicates

(6) & (7) $34Na_2O + 64\ SiO_2 + 2\ Eu_2O_3$

(8) $34Na_2O + 64\ SiO_2$

(9) $27Na_2O + 66\ B_2O_3 + 5\ Y_2O_3 + 2\ Eu_2O_3$

Samples1, 6,8,10,12 were made in ambient air and

Samples 2, 3,4,5, 7,9,11,13 were made in reduced(N_2+H_2) atmosphere

Material Preparation

High temperature box and tubular furnaces

Germanate Glass-Composition

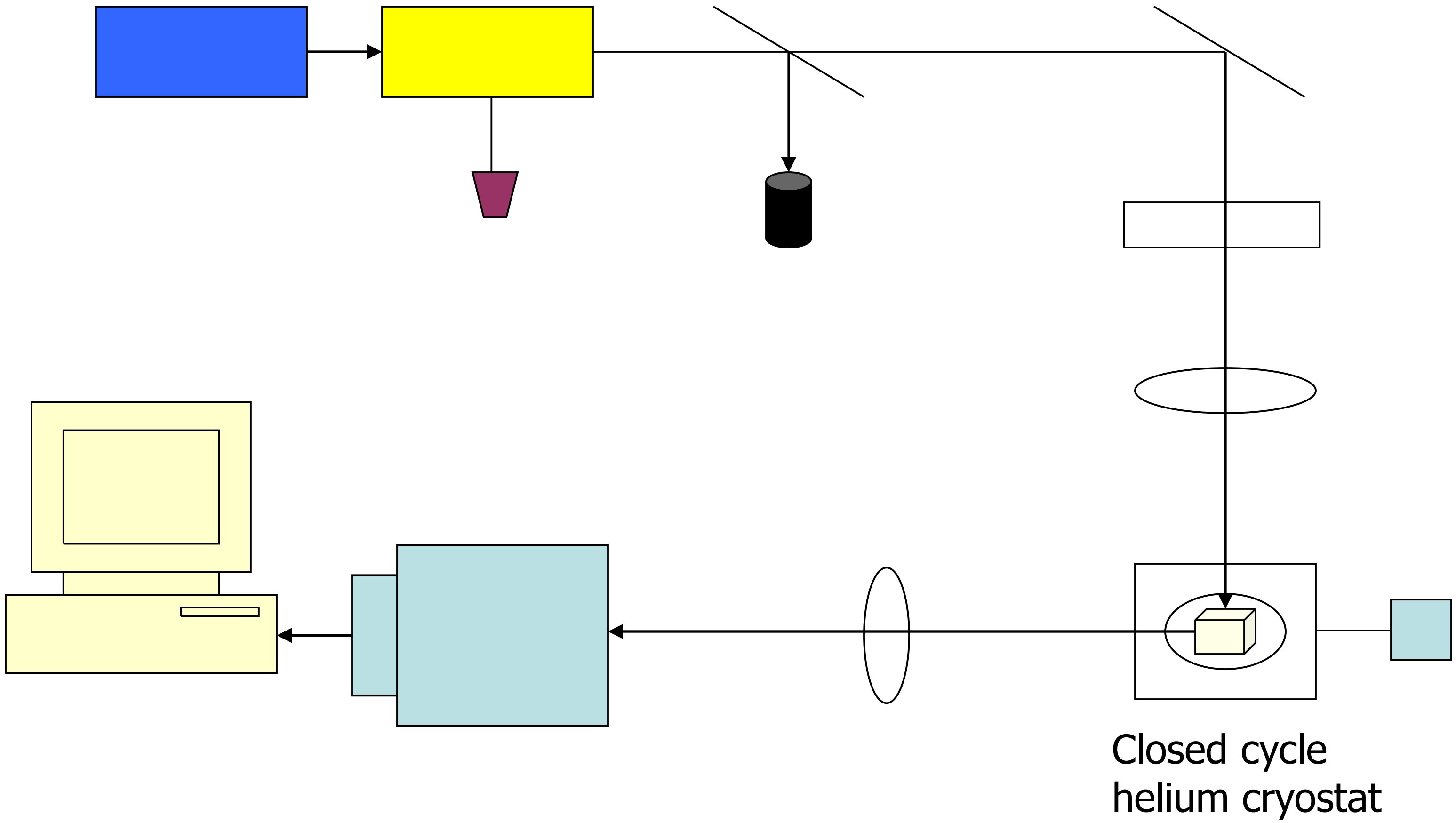
	S#	GeO_2 (mol%)	Na_2CO_3 (mol%)	Y_2O_3 (mol%)	Eu_2O_3 (mol%)
	1	78	21	0	1
	2	73	21	5	1
	3	78	21	0	1
	4	75	21	3	1

Samples 1 and 2 are melted in air

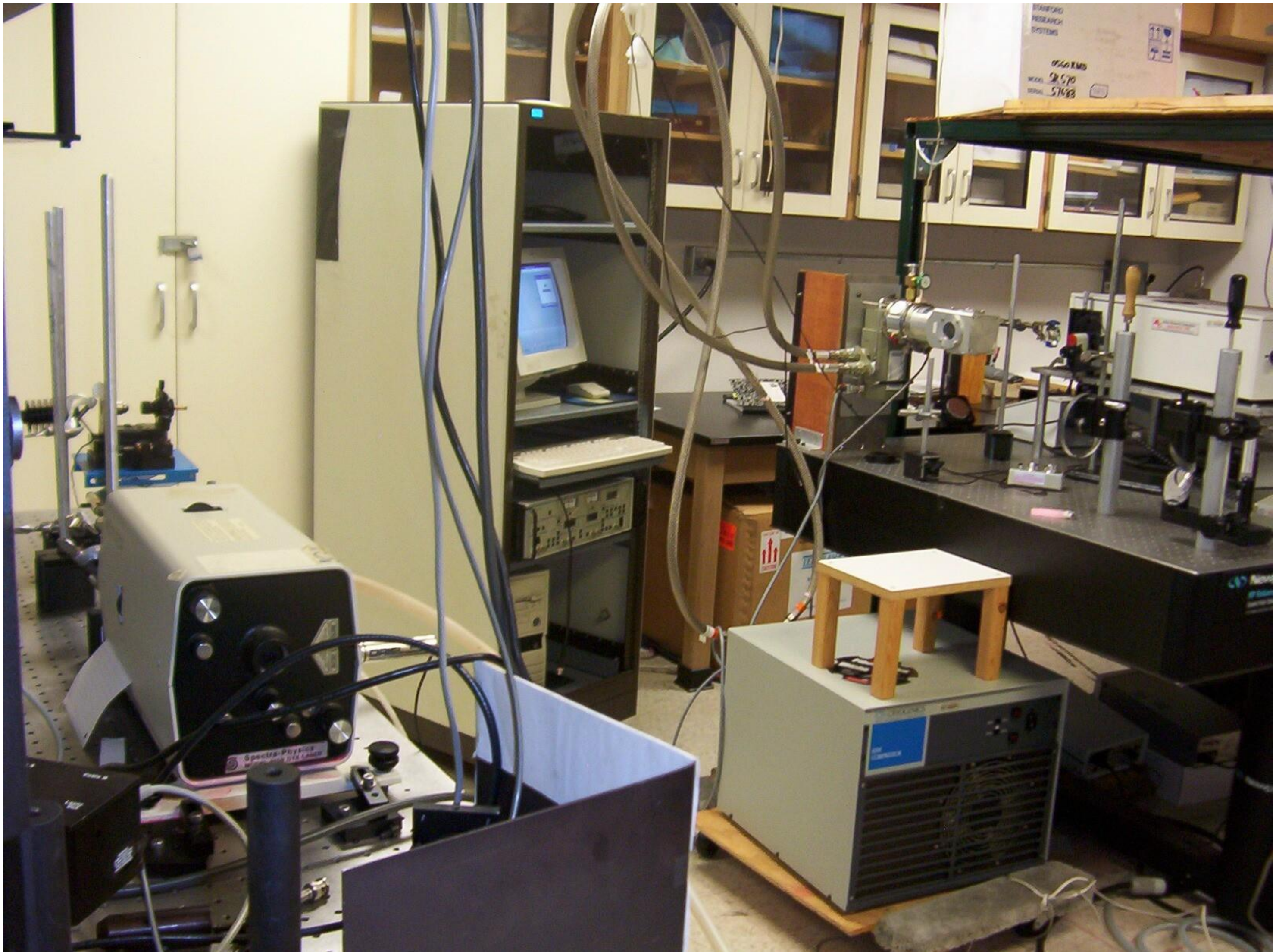
Samples 3 and 4 are prepared in reduced atmosphere

1 2 3 4

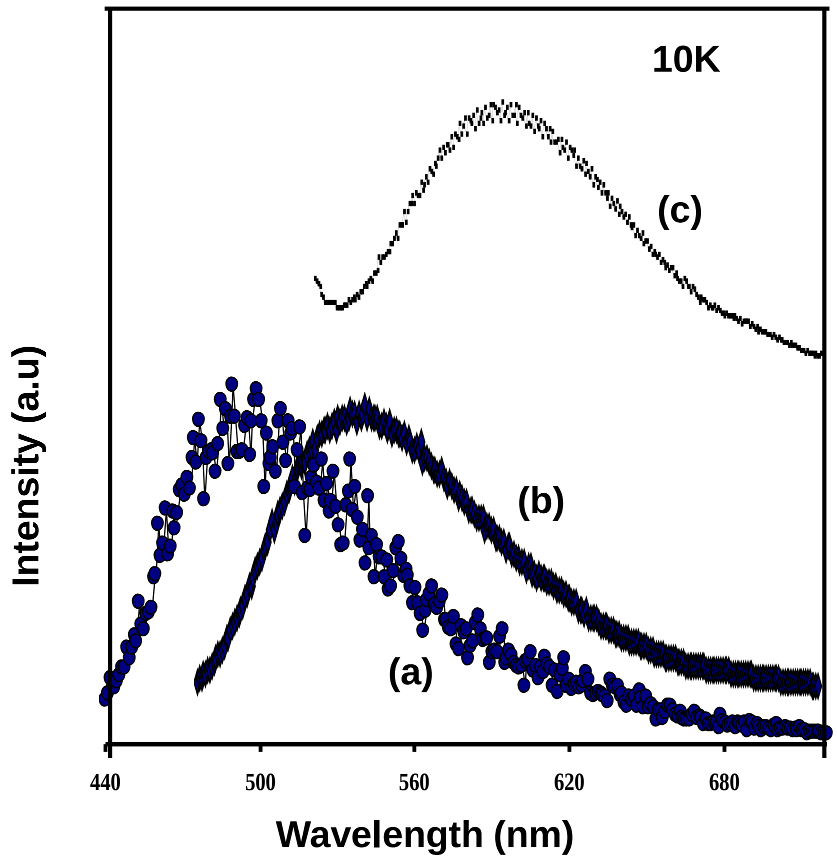
Experimental Setup



Lab Set-Up



Eu^{2+} Fluorescence ($4f^6 5d^1 \rightarrow 4f^7$) in borosilicate Glass



Eu-Doped

Fluorescence Spectra of Eu^{3+}-doped sodium borosilicate glass prepared in reduced atmosphere.

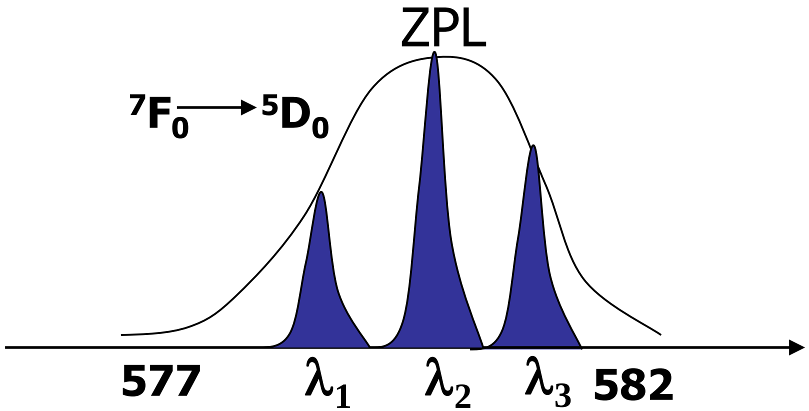
Curve (a) 337nm Laser Excitation

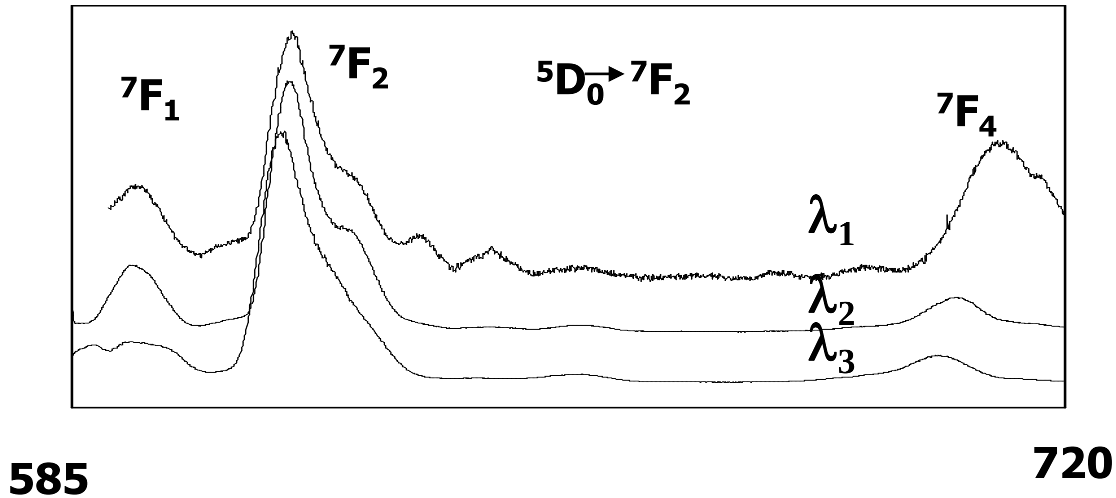
Curve (b) 458nm Laser Excitation

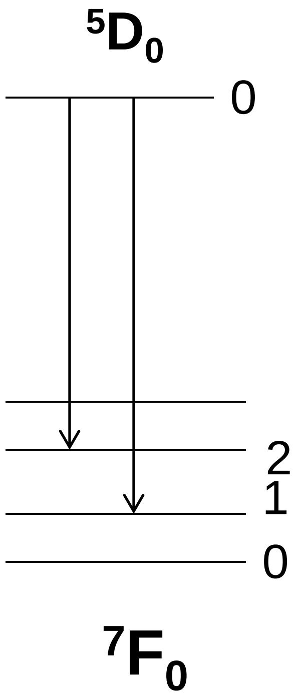
Curve (c) 488nm Laser Excitation

The broad absorption is due to the presence for Eu^{2+}.

Eu^{3+} fluorescence ($4f^6$: $^5D_0 \rightarrow {}^7F_J$)

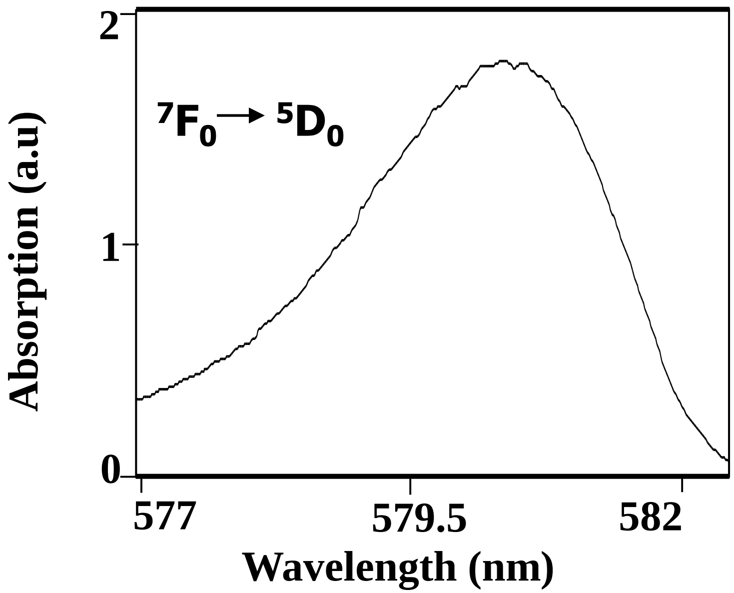


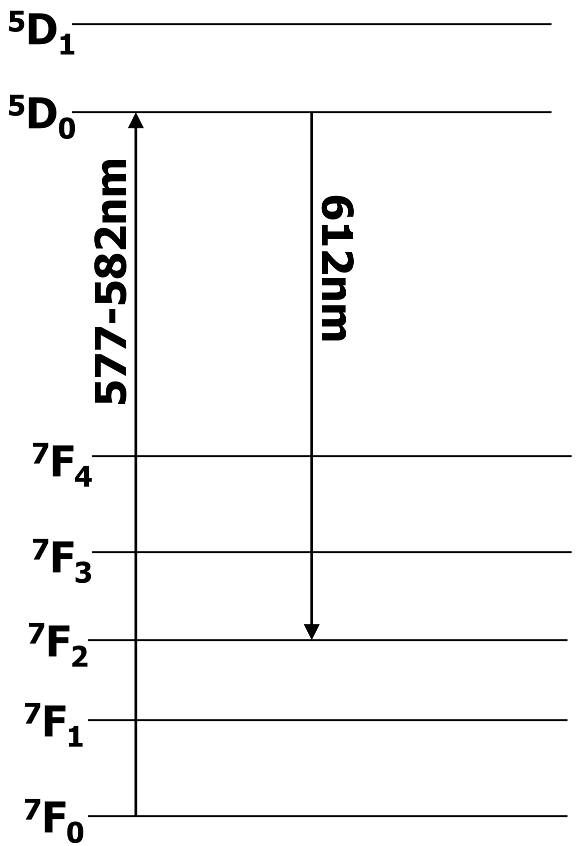




Exhibits site to site variations in the crystal field

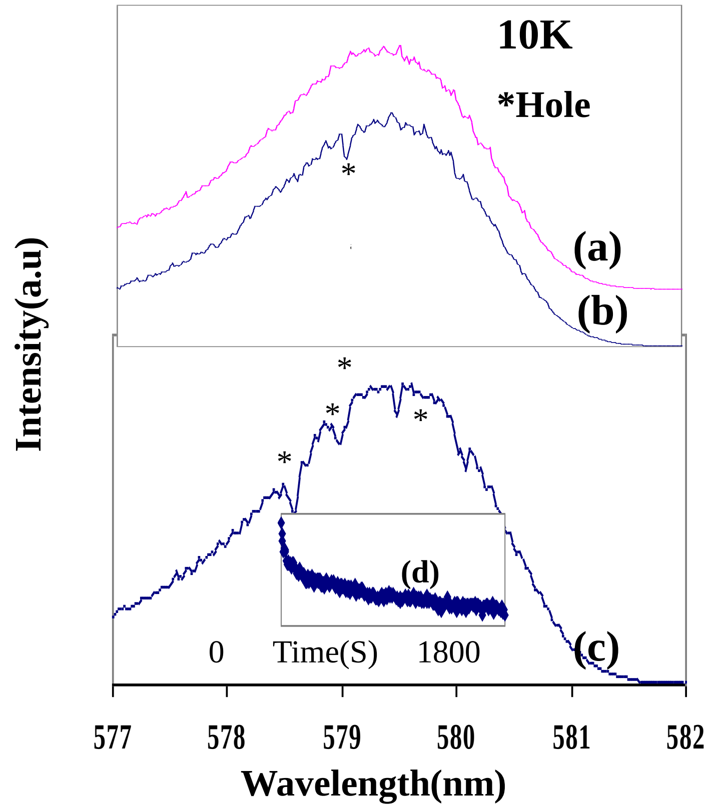
Excitation Spectrum





Spectrum: Recording a ZPL with a low laser power.

HB in Eu- doped sodium borate glass (reduced)



(a) & (b) Eu

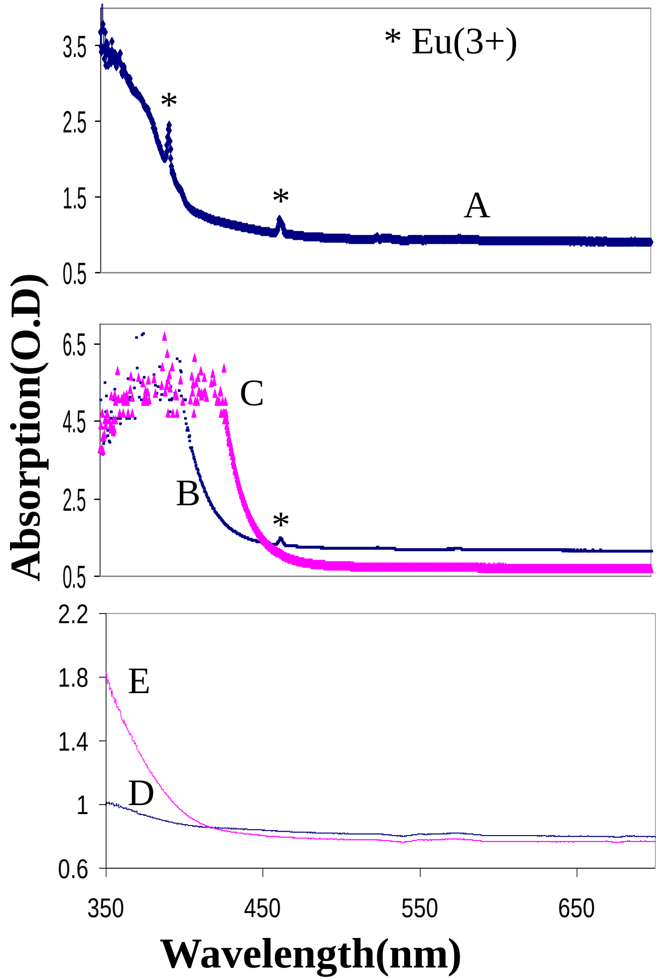
(c) Eu,Y-co-doped

Glass composition

(a) Na_2O(33%), B_2O_3 (65%), Eu_2O_3 (2%)

(b) Na_2O(27%), B_2O_3(66%), Y_2O_3(5%),Eu_2O_3(2%)

RT absorption spectra



(a) $34Na_2O + 65\ B_2O_3 + 1\ Eu_2O_3$

(b) $33Na_2O + 65\ B_2O_3 + 2\ Eu_2O_3$

(c) $27Na_2O + 66\ B_2O_3 + 5\ Y_2O_3 + 2\ Eu_2O_3$

(d) $33.6Na_2O + 66.4\ B_2O_3$

(e) $27.5\ Na_2O + 67.4\ B_2O_3 + 5.1\ Y_2O_3$

Sample (a) was made in air atmosphere and others (b, c, d, e) were made in reduced atmosphere

J. Appl. Phys. 94, 2139 (2003)

Hole burning efficiency

$$\eta = \frac{dT/dt}{(I/h\upsilon)\sigma T_0(1-T_0-R_0)}$$

$\eta_2 / \eta_1 > 10$

η_1 Eu doped glass

η_2 Eu, Y co-doped glass

Reason:

Eu^{2+} and defect concentrations: higher in the co-doped glass

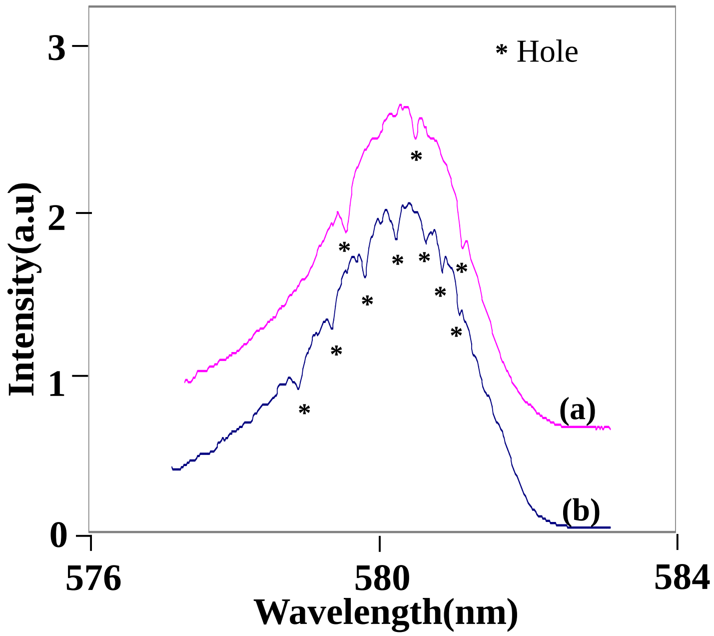
HB mechanism: charge transfer

- Eu^{3+*} + defect (e^-)→Eu^{2+*} + defect
  - Eu^{2+} increases and Eu^{3+} decreases
  - Emission intensities are different before and after hole burning
- $Eu^{3+*} + Eu^{2+} \rightarrow Eu^{2+*} + Eu^{3+}$
  - No change in concentration
  - Emission intensity remains the same before and after hole burning
  - Agrees with the experiment

Glass composition

(a) Na2O(34%), SiO2(64%), Eu2O3(2%)

(b) Na2O3(33%), SiO2 (61%),Y2O3(4%), Eu2O3(2%)

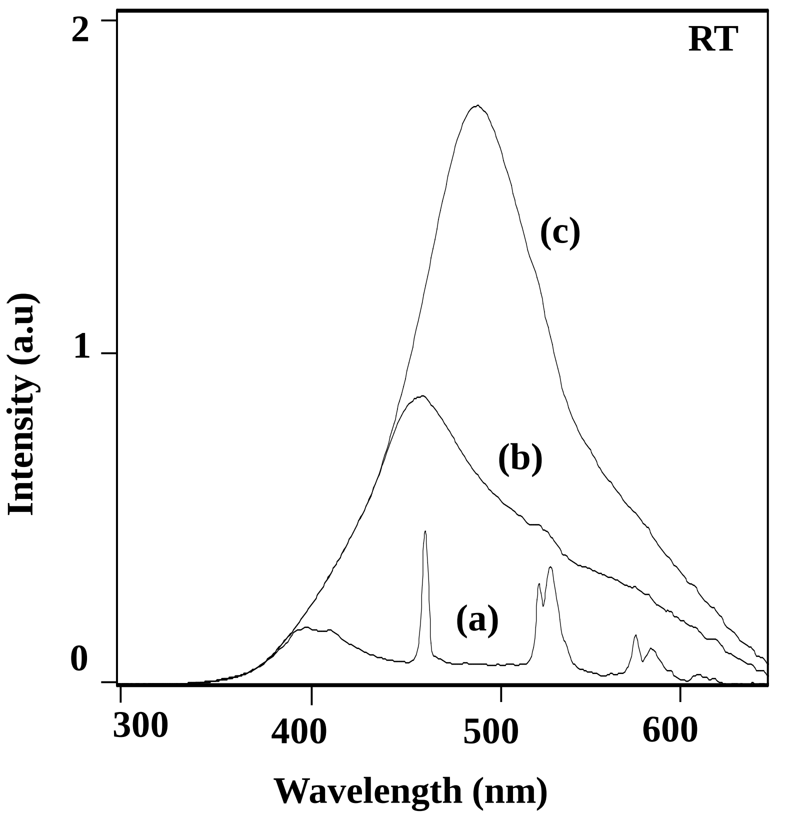


HB in sodium silicate glass

(a) Eu (b) Eu,Y co-doped glasses

Note: HB is possible in a reduced sample

Absorption Spectra-Borosilicate Glass



Room-temperature absorption spectra of Eu-doped glasses. Curve (a) Eu, air

Curve (b) Eu, reduced

Curve (c) Eu, Y, reduced

Sharp peaks are those of Eu^{3+} and the broad absorption is due to the presence for Eu^{2+}.

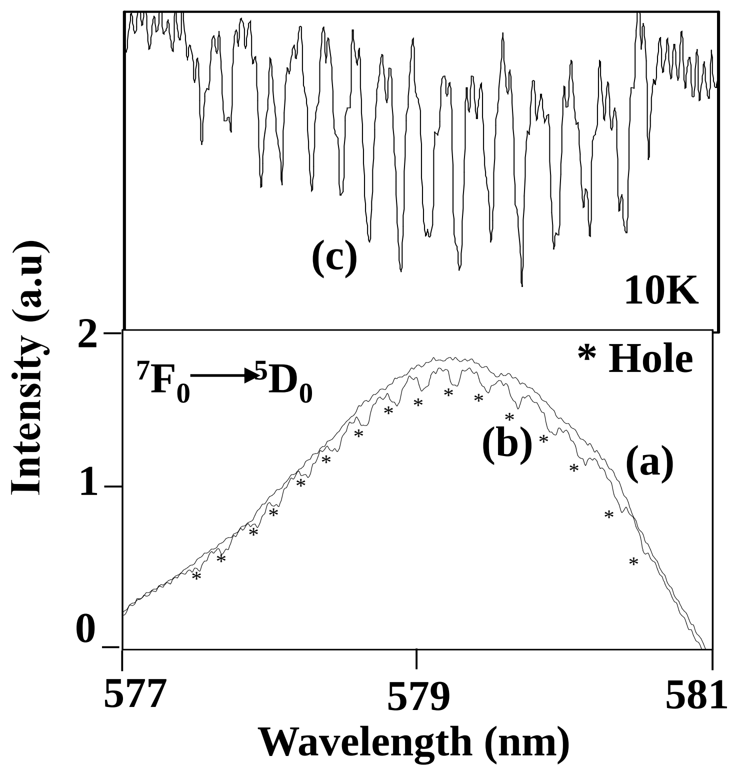
Addition of yttrium – uniform distribution of europium in the glass

(Poster)

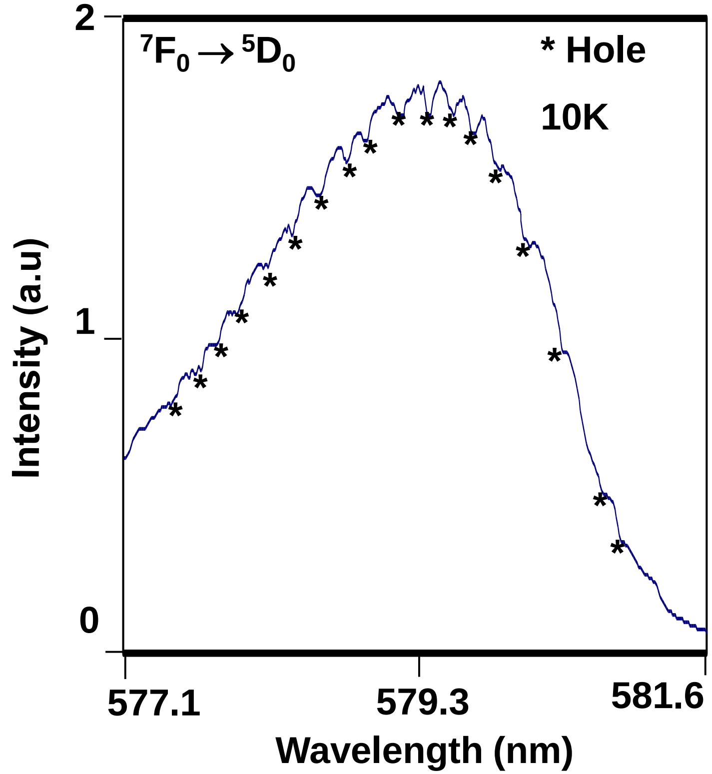
Multiple Hole Burning in Borosilicate Glass

Glass composition

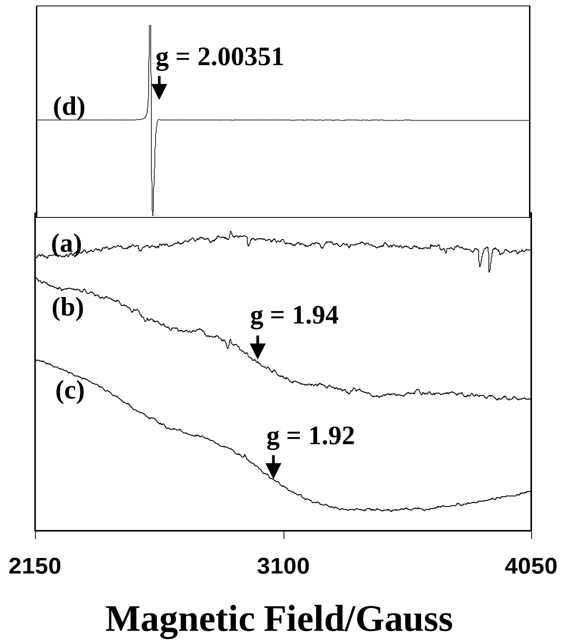
$Na2O(30\%),B2O3(34\%),SiO2(34\%),Eu2O3(2\%)$



Eu^{3+}-Doped



Eu^{3+}, Y^{3+} Co-doped



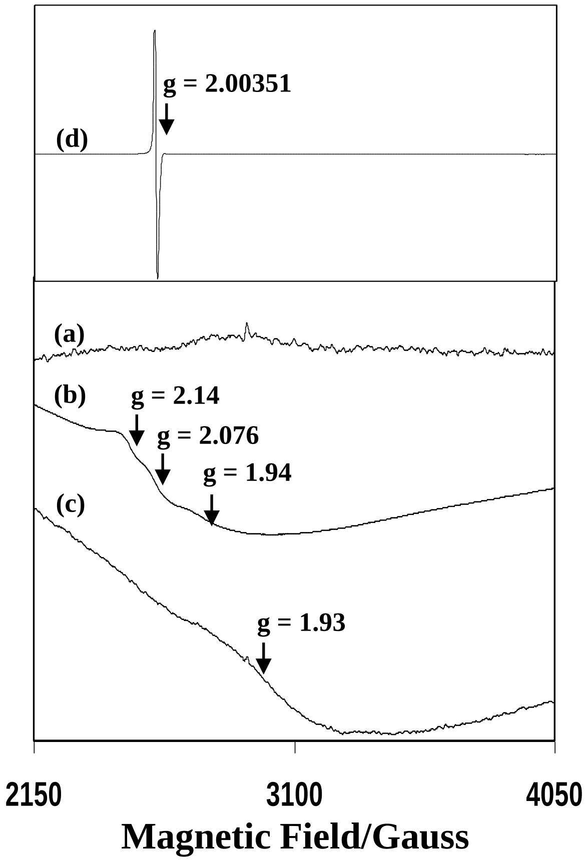
ESR Spectra - Sodium silicate

(a) Eu-doped , air

(b) Eu-doped , N_2+H_2

(c) Eu, Y co-doped, N_2+H_2

(d) DPPH



ESR—Borosilicate at 77K

(a) Eu-doped(air)

(b) Eu-doped(reduced)

(c) Eu-doped and

Y-co-doped (reduced)

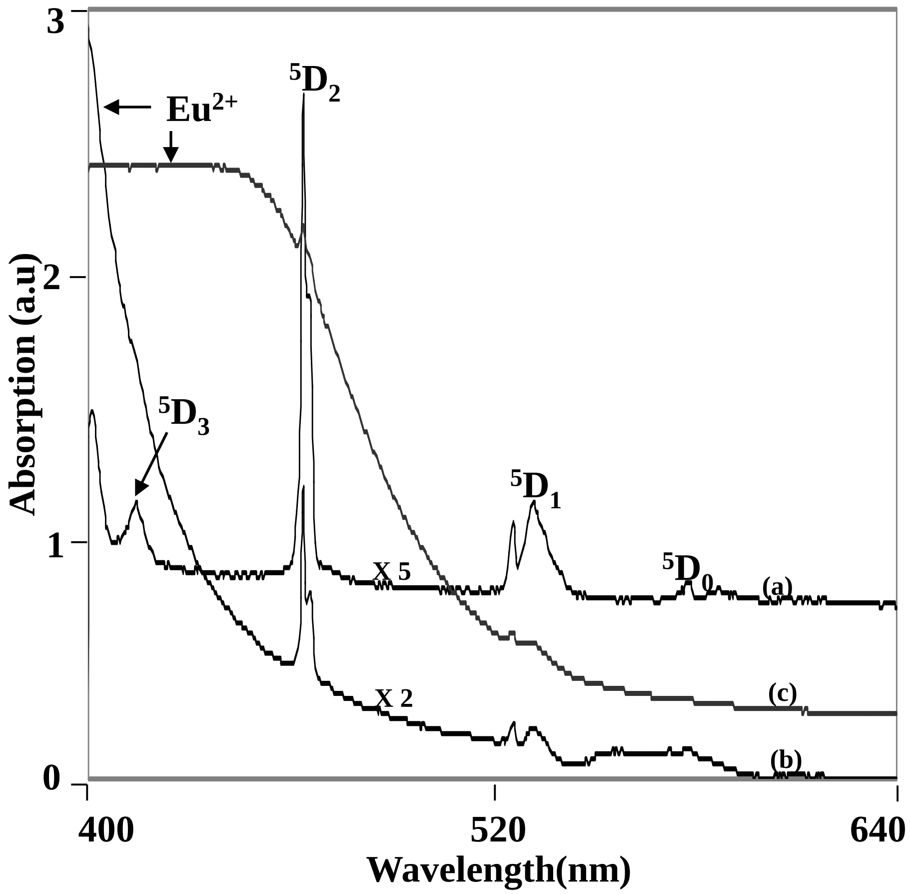
(d) DPPH

There are three types of defect centers in the borosilicate glass

It retains all the holes (higher hole retention capability)

Defects play a role in the hole burning

Absorption Spectra-Germanate Glass



Room-temperature absorption spectra of Eu-doped glasses. Curve (a) Eu, air

Curve (b) Eu, reduced

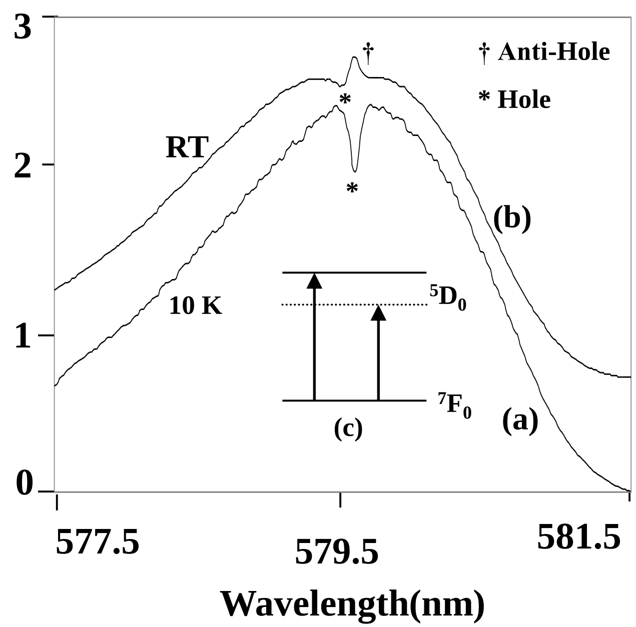
Curve (c) Eu, Y, reduced

Sharp peaks are those of Eu^{3+} and the broad absorption at 400nm is due to the presence for Eu^{2+}.

Addition of yttrium – uniform distribution of europium in the glass

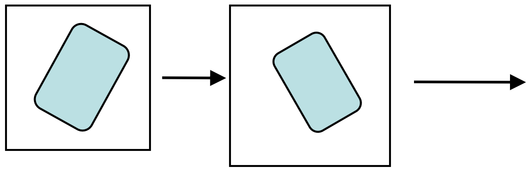
Hole Burning at 10K and 295K

Glass composition: Na2O(xx%), GeO2(xx%), Eu2O3(x%)



J. Appl. Phys. 96, 4012 (2004)

Sample	Temperature
1- Eu,air	77K
2- Eu,Y, air	77K
3- Eu, reduced	250K
4- Eu, Y, reduced	RT



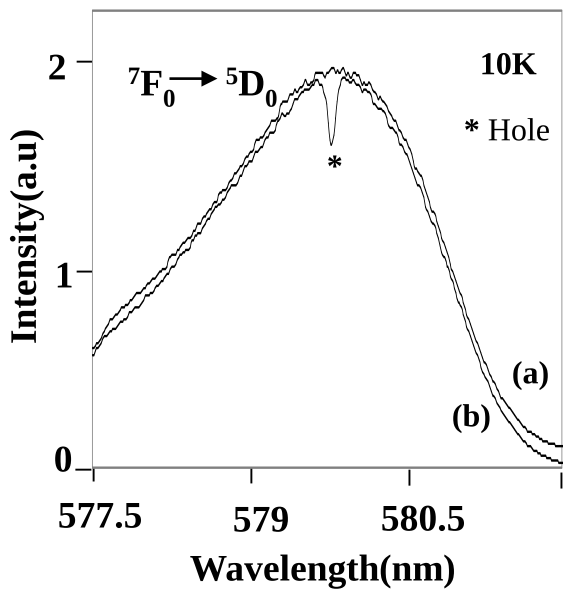
Photophysical Hole burning

Anti-hole formation :

(1) anti-hole is formed only when the number of ions undergoing photophysical process exceeds a certain threshold value

(2) The photophysical process was assisted by the thermal energy

Hole burning in Germanate Glass at 10K



Curve (a) excitation spectrum recorded before hole burning.Curve (b) excitation spectrum recorded after hole burning.

Sample	Dosage:	Hole depth:
1- Eu,air	50	7%
2- Eu,Y, air	1350	5%
3- Eu, reduced	25	13%
4- Eu, Y, reduced	1	18%

Dosage = Laser power X Time of exposure

Mechanism : Photochemical hole burning due to a charge transfer between Eu^{3+} and Eu^{2+} ions

sample#1: charged defects also play a role in HB

Hole Burning Mechanism-Germanate Glass

- Photophysical mechanism – Due to change in crystal field (environmental change/or reorientation)

- Photochemical hole burning due to either a charge transfer between Eu^{3+} and Eu^{2+} or a defect center

$$Eu^{3+*} + e\text{-(defects)} \rightarrow Eu^{2+}$$

$$Eu^{3+*} + Eu^{2+} \rightarrow Eu^{2+*} + Eu^{3+}$$

(where * photoexcited ion)

Comparison of the results-Germanate Glass

Sample3#(Eu,Reduced)

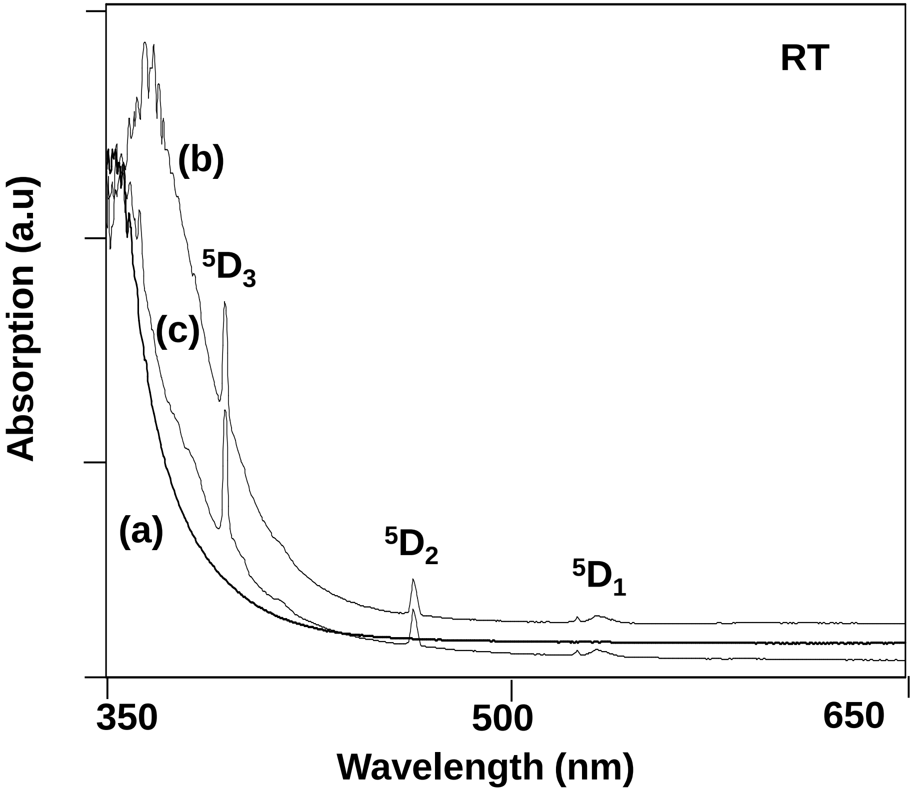
- Min intensity : 1200 W/cm^2
- Min time : 5min
- Hole width : 2.4 cm^{-1}
- Inhomogeneous width : 64.8 cm^{-1}
- No of holes : 10
- Hole depth : 13%
- Excitation spectrum : 250K
- I vs. T : RT

Sample4#(Eu,Y,Reduced)

- Min intensity : 240 W/cm^2
- Min time : 1min
- Hole width : 2.5 cm^{-1}
- Inhomogeneous width : 81.6 cm^{-1}
- No of holes : 16
- Hole depth : 18%
- Excitation spectrum : RT
- I vs. T : RT

Absorption Spectra-Tellurite Glass

Glass composition: Na_2O(20%), TeO_2(79%), Eu_2O_3(1%)



Room-temperature absorption spectra of Undoped and Eu-doped glasses.

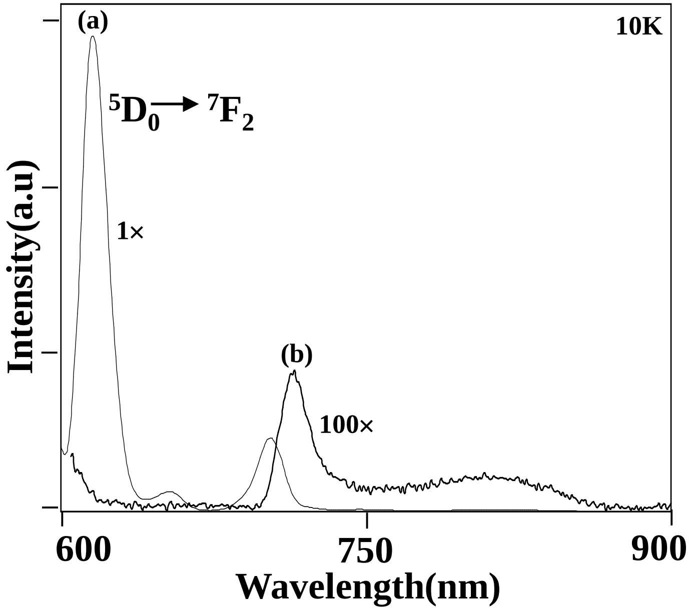
Curve (a) No Dopant, air – Broad absorption up to 450nm and maximum at 370nm (O.D = 4.0). This is due to defects in the host glass.

Curve (b) Eu, Y, air

Curve (c) Eu, Helium

Both reveal Eu^{3+} sharp peaks at 395, 466, 526, 535 & 580nm.

Emission Spectra-Tellurite Glass



Fluorescence Spectra of (a) Eu3+-doped and (b) undoped glasses observed under 580nm dye laser excitation.

(a) Eu3+ peaks at 612, 653 and 704nm.

(b) defect emission (weak) at 715, and 800nm under dye laser excitation and also at 505nm under Ar^+ laser excitations

Hole Burning in Tellurite Glass at Low and High Temperatures

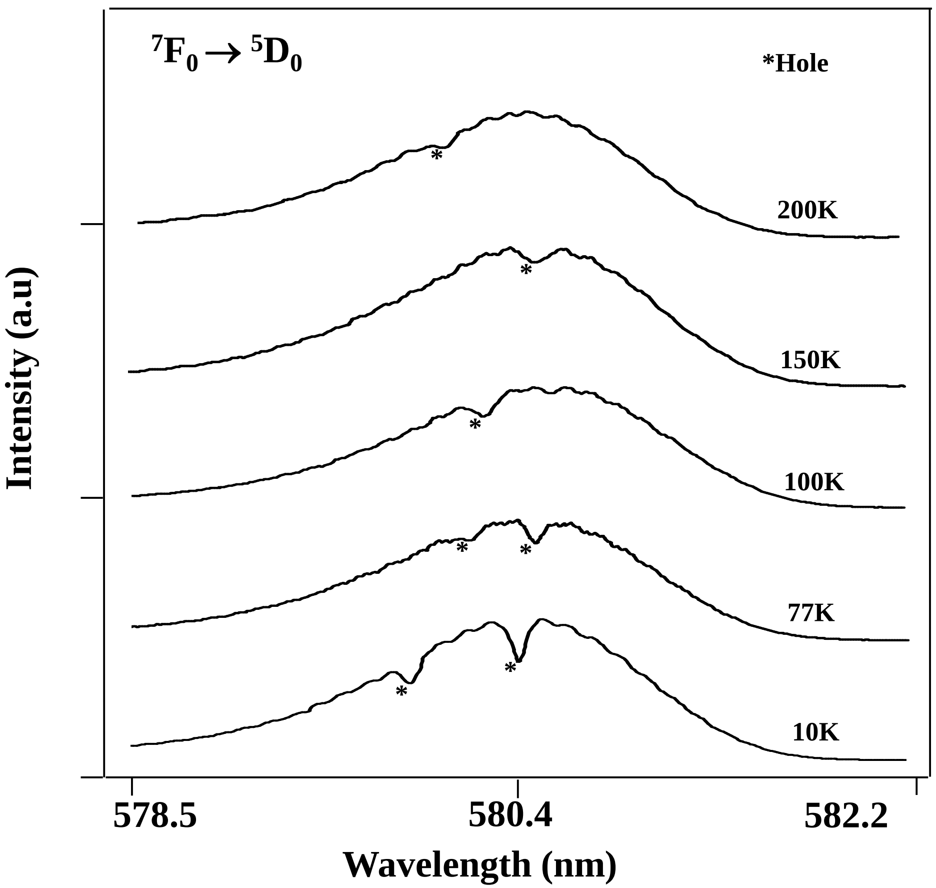


Figure shows hole burning excitation spectra recorded at various temperatures in the Eu^{3+}, Y^{3+} co-doped sample that was melted in ambient air.

Eu^{3+}-doped samples melted in air and helium atmosphere exhibited hole burning up to 100K. (Not shown here).

Multiple Hole Burning-Tellurite Glass

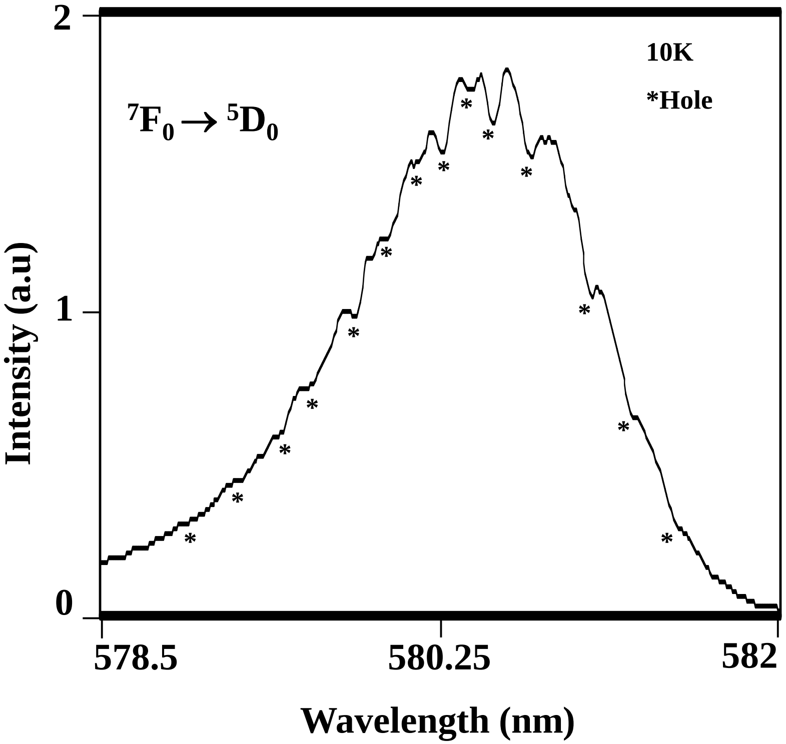
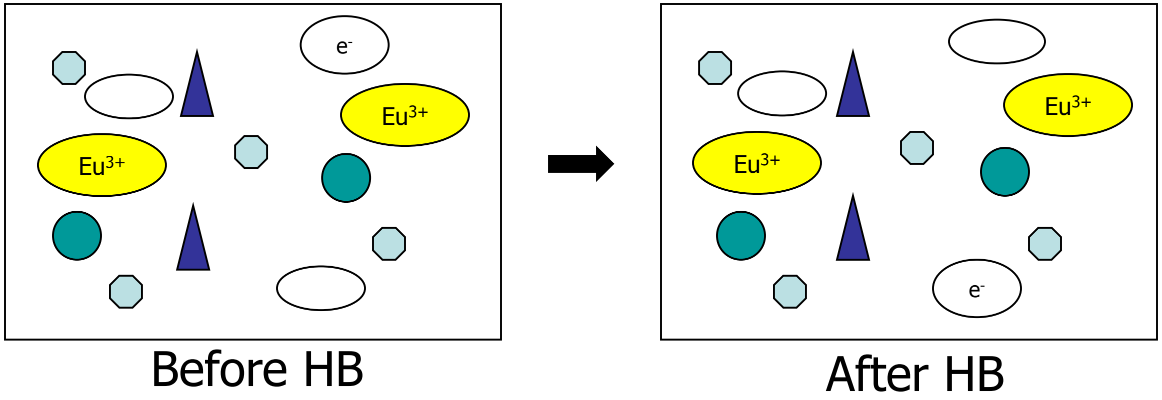


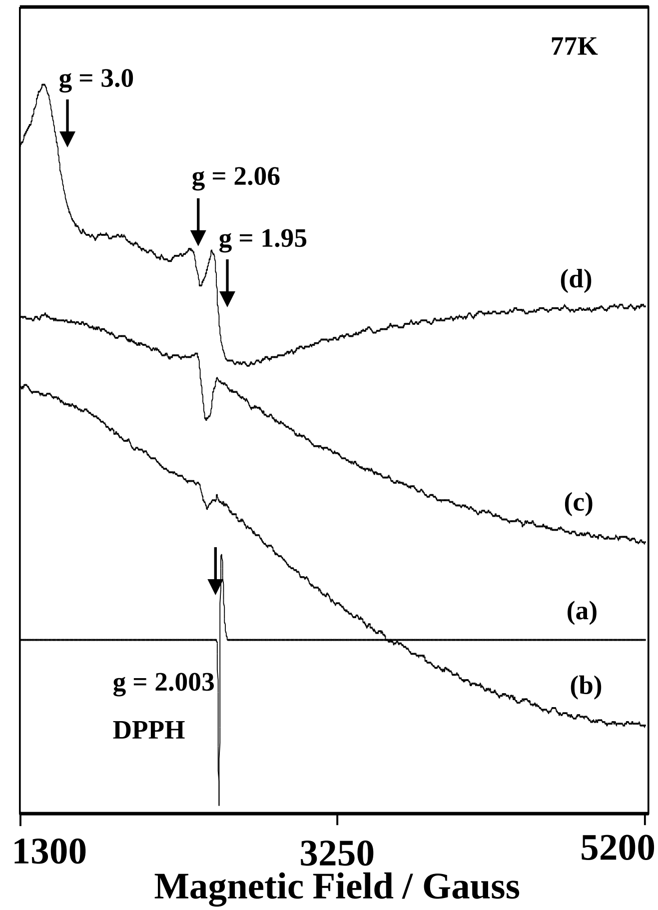
Figure shows multiple hole burning excitation spectrum recorded in the Eu^{3+}, Y^{3+} co-doped sample that was melted in ambient air (14 holes).

Eu^{3+}-doped samples melted in air and helium atmosphere also exhibited multiple hole burning at 10K. (Not shown here).

Hole Burning Mechanism-Tellurite Glass

- PCHB: not probable because Eu^{2+} concentration is not abundant.
- No anti-hole: no evidence for a photophysical mechanism
- HB Mechanism: The motion of photoexcited defect electrons. The glass has high density of charged defects and the defect electrons migrate.





ESR spectra of tellurite glasses

(a) Standard (b) undoped (c) Eu doped (d) Eu,Y co-doped glasses

Comparison of the salient features of different glasses

	Sample Composition							T_{max}[a)]	Γ_{inh}[b)]	Γ_h[c)]	HD[d)]	HN[e)]	P_{min}[f)]	Atmos[g)]
	B_2O_3	**SiO_2**	**GeO_2**	**TeO_2**	**Na_2O**	**Y_2O_3**	**Eu_2O_3**	(K)	(cm^{-1})	(cm^{-1})	(%)		(mw)	
1	65	-	-	-	33	0	2	100	62.6	1.8	11	-	100	N_2+H_2
2	66	-	-	-	27	5	2	300	72.0	1.8	24	-	40	N_2+H_2
3	-	64	-	-	34	0	2	250	62.4	2.2	27	3	1	N_2+H_2
4	-	61	-	-	33	4	2	295	74.6	1.9	29	7	<1	N_2+H_2
5	34	34	-	-	30	0	2	250	91.4	3.5	17	16	1	N_2+H_2
6	34	31.5	-	-	27.5	5	2	295	86.5	3.0	18	18	<1	N_2+H_2
7	-	-	78	-	21	0	1	295	65.4	2.3	13	10	10	N_2+H_2
8	-	-	75	-	21	3	1	295	80.1	2.8	18	16	5	N_2+H_2
9	-	-	78	-	21	0	1	77	81.1	2.9	7	11	10	Air
10	-	-	-	79	20	0	1	100	47.4	2.6	8	6	>200	Air
11	-	-	-	69	27	3	1	200	48.0	2.2	31	14	100	Air
12	-	-	-	81	18	0	1	100	47.3	2.6	9	4	>200	He

General conclusions: Hole burning mechanisms

Sodium borate, silicate and borosilicate Glasses-

Charge transfer between Eu^{3+} and Eu^{2+} or defect

Sodium germanate Glass-

Both photophysical and photochemical processes

Sodium tellurite Glass-

Migration of photoexcited defect electrons