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Spectral and Thermal Properties of Eu^{3+} ions doped Zinc Lithium AluminoAntimony Borogermanate Glasses

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Abstract
Glass of the system: (35-x)GeO_2:10ZnO:10Li_2O:10Al_2O_3:10Sb_2O_3:25B_2O_3: xEu_2O_3(where x=1,1.5,2 mol%) have been prepared by melt-quenching technique. The amorphous nature of the prepared glass samples was confirmed by X-ray diffraction. The absorption spectra of three Eu^{3+} doped zinc lithium alumino antimony borogerminateglasses have been recorded at room temperature. The various interaction parameters likeSlater-Condonparameters F_K (k=2,4,6),Landeparameter (ξ_{4F}),nephelauexetic ratio(β'),bondingparameter ($b^{1/2}$)and Racah parameters E^K(k=1,2 3) have been computed.Judd-Ofelt intensity parameters and laser parameters have also been calculated.

Keywords: *ZLAABG Glasses,Energy interaction parameters,Optical properties,Judd-Ofelt analysis.*

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I. INTRODUCTION

Glasses are receiving considerable attention due to their unique properties like hardness, good strength, transparency and excellent corrosion resistance. Transparent glassceramic as host materials for active optical ions have attracted great interest recently due to their potential application in optical devices such as frequency-conversion materials, lasers and optical fiber amplifiers [1-5]. Among them, Sb_2O_3-based glasses possess easier preparation, large transparency window, better thermal stability, high refractive index and better chemical durability than that of fluoride or tellurite glasses [6,7].Germanate glasses, presumably due to the large mass of Ge, have smaller maximum vibrational frequencies than those shown by silicate, phosphate and borate glasses. The reduced phonon energy increases the quantum efficiency of luminescence from excited states of rare earth ions in these matrices and provides incentive for developing a more efficient medium for optical lasers and fiber optical amplifiers [8, 9].An important characteristic of these materials is the relatively low cutoff phonon energy compared with other oxide glasses such as silicate or phosphate glasses. Eu^{3+} doped glasses are very important because of the possibility of their application in optoelectronic and optic device fields, such as lasers, fiber optic and solar cells [10-13].

The aim of the present study is to prepare theEu^{3+}dopedzinc lithium aluminoantimony borogermanateglass with different Eu_2O_3concentrations.The absorption spectra, fluorescence spectra of $Eu^{3+}$of the glasses were investigated.The Judd-Ofelt theory has been applied to compute the intensity parameters Ω_λ(λ=2, 4,6).These intensity parameter have been used to evaluate optical optical properties such as spontaneous emission probability, branching ratio,radiative life time and stimulated emission cross section.

II. EXPERIMENTAL TECHNIQUES

Preparation of glasses

The following Eu^{3+} doped borogermanate glass samples (35-x) GeO_2:10ZnO: 10Li_2O:10Al_2O_3:10Sb_2O_3:25B_2O_3:xEu_2O_3 (where x=1,1.5, 2) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of GeO_2,ZnO, Li_2O,Al_2O_3,Sb_2O_3,$B_2O_3$and Eu_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 1150^0C by an electrical muffle furnace for 2h., After complete melting, the melts were quickly poured in to a preheated stainless steel mould and annealed at temperature of 450^0C for 2h to remove thermal strains and stresses.Every time fine powder of cerium oxide was used for polishing the samples. The glass samples so prepared were of good optical quality and were transparent.The chemical compositions of the glasses with the name of samples are summarized in Table 1.

Table 1

Chemical composition of the glasses

Sample	Glass composition (mol %)
ZLAABG(UD)	$35GeO_2$:$10ZnO$:$10Li_2O$:$10Al_2O_3$:$10Sb_2O_3$:$25B_2O_3$
ZLAABG(EU1)	$34GeO_2$:$10ZnO$:$10Li_2O$:$10Al_2O_3$:$10Sb_2O_3$:$25B_2O_3$:$1Eu_2O_3$
ZLAABG(EU1.5)	$33.5GeO_2$:$10ZnO$:$10Li_2O$:$10Al_2O_3$:$10Sb_2O_3$:$25B_2O_3$:$1.5Eu_2O_3$
ZLAABG (EU2)	$33GeO_2$:$10ZnO$:$10Li_2O$:$10Al_2O_3$:$10Sb_2O_3$:$25B_2O_3$:$2Eu_2O_3$

ZLAABG(UD) -Represents undopedZinc Lithium AluminoAntimony Borogermanateglass specimen.
ZLAABG(EU) -Represents Eu^{3+}dopedZinc Lithium AluminoAntimonyBorogermanateglass specimens.

III. THEORY

3.1Oscillator Strength

The spectralintensity is expressed in terms of oscillator strengths using the relation [14].

$$f_{expt.} = 4.318 \times 10^{-9} \int \varepsilon(\nu)\, d\nu \qquad (1)$$

Where, $\varepsilon(\nu)$ is molar absorption coefficient at a given energy ν (cm^{-1}), to be evaluated from Beer–Lambert law. Under Gaussian Approximation, using Beer–Lambert law, the observed oscillator strengths of the absorption bands have been experimentally calculated[15], using the modified relation:

$$P_m = 4.6 \times 10^{-9} \times \frac{1}{cl} \log \frac{I_0}{I} \times \Delta\upsilon_{1/2} \qquad (2)$$

Where c is the molar concentration of the absorbing ion per unit volume, l is the optical path length, $\log I_0/I$ is optical density and $\Delta\upsilon_{1/2}$is half band width.

3.2. Judd-Ofelt Intensity Parameters

According to Judd[16] and Ofelt[17] theory, independently derived expression for the oscillator strength of the induced forced electric dipole transitions between an initial J manifold $|4f^N (S, L) J>$ level and the terminal J' manifold $|4f^N (S',L') J'>$ is given by:

$$\frac{8\Pi^2 mc\bar{\upsilon}}{3h(2J+1)} \frac{1}{n}\left[\frac{(n^2+2)^2}{9}\right] \times S(J, J') \qquad (3)$$

Where, the line strength S (J, J') is given by the equation

$$S(J, J') = e^2 \sum \Omega_\lambda \langle 4f^N(S, L)\, J \| U^{(\lambda)} \| 4f^N(S', L')J' \rangle^2$$

$\lambda = 2, 4, 6$

In the above equation m is the mass of an electron, c is the velocity of light, ν is the wave number of the transition, h is Planck's constant, n is the refractive index, J and J' are the total angular momentum of the initial and final level respectively, Ω_λ ($\lambda = 2, 4, 6$) are known as Judd-Ofelt intensity parameters.

3.3 Radiative Properties

The Ω_λ parameters obtained using the absorption spectral results have been used to predict radiative properties such as spontaneous emission probability (A) and radiative life time (τ_R), and laser parameters like fluorescence branching ratio(β_R) and stimulated emission cross section (σ_p).

The spontaneous emission probability from initial manifold $|4f^N (S', L') J'>$ to a final manifold $|4f^N (S,L) J>|$ is given by:

$$A[(S', L') J'; (S,L)J] = \frac{64\pi^2\nu^3}{3h(2J'+1)}\left[\frac{n(n^2+2)^2}{9}\right] \times S(J', \bar{J}) \qquad (4)$$

Where, $S(J', J) = e^2 [\Omega_2 \| U^{(2)} \|^2 + \Omega_4 \| U^{(4)} \|^2 + \Omega_6 \| U^{(6)} \|^2]$

The fluorescence branching ratio for the transitions originating from a specific initial manifold $|4f^N$ (S', L') J'> to a final many fold $|4f^N$(S,L)J > is given by

$$\beta [(S', L') J'; (S, L)J] = \sum_{S\,L\,J} \frac{A[(S' L)]}{A[(S' L')J' (S L)]} \quad (5)$$

Where, the sum is over all terminal manifolds.

The radiative life time is given by

$$\tau_{rad} = \sum_{S\,L\,J} A[(S', L') J'; (S,L)] = A_{Total}^{-1} \quad (6)$$

Where, the sum is over all possible terminal manifolds.The stimulated emission cross -section for a transition from an initial manifold $|4f^N$ (S', L') J'> to a final manifold $|4f^N$ (S,L)J>| is expressed as

$$\sigma_p(\lambda_p) = \left[\frac{\lambda_p^4}{8\pi c\, n^2 \Delta\lambda_{eff}}\right] \times A[(S', L')J'; (\bar{S}, \bar{L})\bar{J}] \quad (7)$$

Where,λ_p the peak fluorescence wavelength of the emission band and $\Delta\lambda_{eff}$ is the effective fluorescence line width.

3.4Nephelauxetic Ratio (β) and Bonding Parameter ($b^{1/2}$)

The nature of the R-O bond is known by the Nephelauxetic Ratio (β') and Bonding Parameter ($b^{1/2}$), which are computed by using following formulae [18, 19]. The Nephelauxetic Ratio is given by

$$\beta' = \frac{\nu_g}{\nu_a} \quad (8)$$

where, ν_g and ν_a refer to the energies of the corresponding transition in the glass and free ion, respectively. The values of bonding parameter ($b^{1/2}$)is given by

$$b^{1/2} = \left[\frac{1-\beta'}{2}\right]^{1/2} \quad (9)$$

IV. RESULT AND DISCUSSION

4.1XRD Measurement

Figure 1 presents the XRD pattern of the sample contain –GeO_2 which is show no sharp Bragg's peak, but only a broad diffuse hump around low angle region. This is the clear indication of amorphous nature within the resolution limit of XRD instrument.

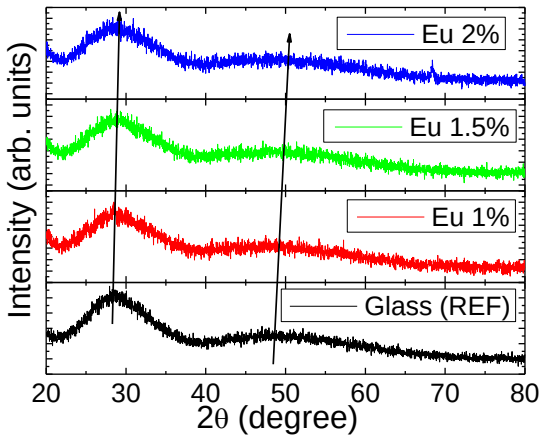

Fig. 1: X-ray diffraction pattern of GeO_2:ZnO:Li_2O:Al_2O_3:Sb_2O_3:B_2O_3:Eu_2O_3.

4.2 Thermal Property

Figure 2, shows the thermal properties of ZLAABGglass from 300^0C to 1000^0C. From the DSC curve of present glasses system, we can find out that no crystallization peak is apparent and the glass transition temperature T_g are 352,456 and 586 respectively. The T_g increase with the contents of Eu_2O_3 increase. We could conclude that thermal properties of the ZLAABG glass are good for fiber drawing from the analysis of DSC curve.

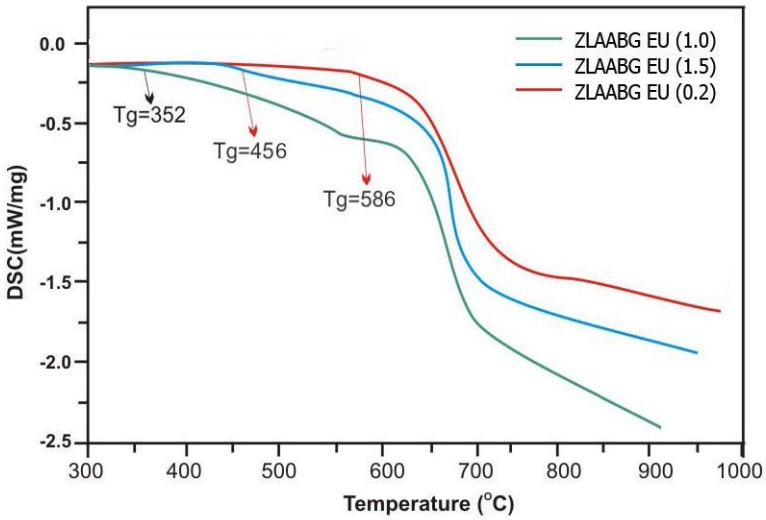

Fig.2: DSC curve ofZLAABG(EU) glasses.

4.3 Absorption Spectrum

The absorption spectra of Eu^{3+} doped ZLAABG (EU 01) glass specimen has been presented in Figure 3 in terms of optical density versus wavelength (nm).Four absorption bands have been observed from the ground state $^7F_0$ to excited states $^5D_2$,$^5L_6$,($^5G_2$,$^5G_6$,$^5G_4$) and $^5D_4$for Eu^{3+}doped ZLAABG glasses.

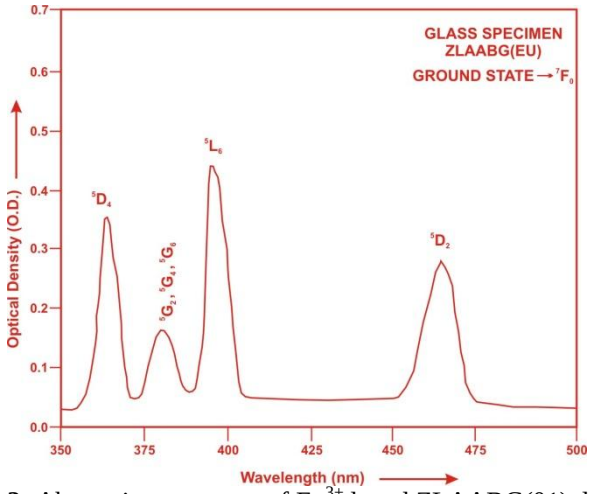

Fig.3: Absorption spectrum of Eu^{3+}doped ZLAABG(01)glass.

The experimental and calculated oscillator strengths for Eu^{3+}ions inzinc lithium aluminoantimony borogermanateglasses are given in Table 2.

Table2: Measured and calculated oscillator strength ($P_m \times 10^{+6}$) of Eu^{3+}ions in ZLAABG glasses.

Energy level from $^7F_0$	**Glass ZLAABG (EU01)**		**Glass ZLAABG (EU1.5)**		**Glass ZLAABG (EU02)**	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^5D_2$	2.18	2.32	2.16	2.31	2.13	2.30
$^5L_6$	3.59	3.75	3.56	3.74	3.52	3.72
$^5G_2$,$^5G_6$,$^5G_4$	0.77	0.94	0.75	0.94	0.72	0.93

$^5D_4$	2.97	3.15	2.93	3.12	2.89	3.11
r.m.s. deviation	±0.1626		±0.1781		±0.2032	

The small value of r.m.s. deviation indicates fairness of fitting between experimental and calculated oscillator strengths.

Computed values of F_2, Lande' parameter (ξ_{4f}), Nephlauxeticratio (β') and bonding parameter($b^{1/2}$) for Eu^{3+}doped ZLAABG glass specimen are given in Table 3.

Table 3. F_2,ξ_{4f}, β' and$b^{1/2}$parameters for Europium doped glass specimen.

Glass Specimen	F_2	ξ_{4f}	β'	$b^{1/2}$
Eu^{3+}	372.63	1445.73	0.9645	0.1332

In the present case the three $\Omega_\lambda$parameters follow the trend $\Omega_2>\Omega_4>\Omega_6$. The spectroscopic quality factor (Ω_4/Ω_6) related with the rigidity of the glass system has been found to lie between 1.080 and 1.084 in the present glasses.

The value of Judd-Ofelt intensity parameters are given in **Table 4**

Table4: Judd-Ofelt intensity parameters for Eu^{3+} doped ZLAABG glass specimens

Glass Specimen	**Ω_2(pm^2)**	**Ω_4(pm^2)**	**Ω_6(pm^2)**	**Ω_4/Ω_6**	**Trend**	**References**
ZLAABG (EU01)	5.325	4.090	3.772	1.084	**$\Omega_2>\Omega_4>\Omega_6$**	P.W.
ZLAABG (EU1.5)	5.305	4.057	3.754	1.081	**$\Omega_2>\Omega_4>\Omega_6$**	P.W.
ZLAABG (EU02)	5.281	4.037	3.737	1.080	**$\Omega_2>\Omega_4>\Omega_6$**	P.W.
YZnLiBiB(EU)	2.478	2.221	1.726	1.287	**$\Omega_2>\Omega_4>\Omega_6$**	[20]

From Table 4 it is observed that Ω_2 parameter is high. The Ω_2 parameter is indicative of the amount of covalent bonding while $\Omega_6$parameter is the rigidity of the host.

4.4Excitation Spectrum

The Excitation spectra of Eu^{3+}doped ZLAABG glass specimens have been presented in Figure 4 in terms of Excitation Intensity versus wavelength.The excitation spectrum was recorded in the spectral region 300–650 nm fluorescence at 612nm having different excitation band centered at 322,353, 372, 395, 410, 454 , 464 nm,530 and 572are attributed to the($^7F_0\rightarrow{}^5H_3$),($^7F_0\rightarrow{}^5D_4$),($^7F_0\rightarrow{}^5G_2$),($^7F_0\rightarrow{}^5L_6$),($^7F_0\rightarrow{}^5D_3$),($^7F_0\rightarrow{}^5D_2$),($^7F_0\rightarrow{}^5D_1$) and ($^7F_0\rightarrow{}^5D_0$)transitions, respectively.From all these bands, the transition ($^7F_0\rightarrow{}^5L_6$) at 395 nm shows the prominent excitation intensity than the other bands.So this is to be chosen for excitation wavelength.

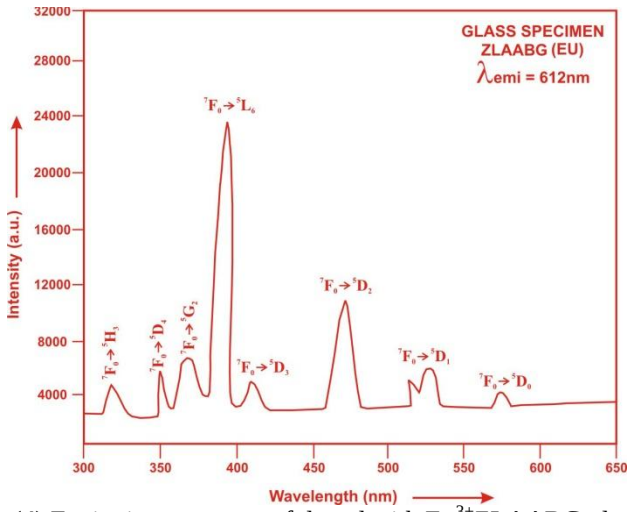

Fig. (4) Excitation spectrum of doped with Eu^{3+}ZLAABG glasses.

4.5. Fluorescence Spectrum

The fluorescence spectrum of Eu^{3+}doped in zinc lithium aluminoantimony borogermanateglass is shown in Figure 5. There are two broad bands observed in the Fluorescence spectrum ofEu^{3+}dopedzinc lithium alumino antimony borogermanate glass. The wavelengths of these bands along with their assignments are given

in Table 5. Fig. (5).Shows the fluorescence spectrum with two peaks ($^5D_0 \rightarrow {}^7F_2$) and ($^5D_0 \rightarrow {}^7F_5$), for glass specimens.

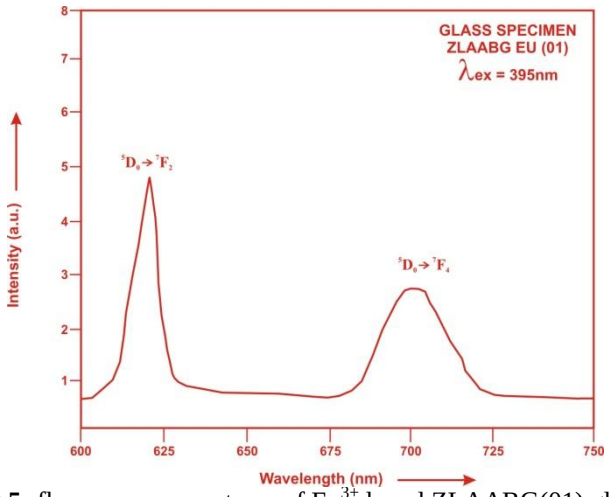

Fig.5: fluorescence spectrum of Eu^{3+}doped ZLAABG(01) glass

Table5. Emission peak wave lengths (λ_{max}),radiative transition probability (A_{rad}),branching ratio (β),stimulated emission cross-section(σ_p) and radiative life time(τ_R) for various transitions in Eu^{3+}doped ZLAABG glasses

Transition		ZLAABG EU 01				ZLAABG EU 1.5				ZLAABG EU 02			
	λ_{max} (nm)	$A_{rad}(s^{-1})$	β	σ_p (10^{-20} cm^2)	$\tau_R(\mu s)$	$A_{rad}(s^{-1})$	β	σ (10^{-20} cm^2)	$\tau_R(\mu s)$	$A_{rad}(s^{-1})$	β	$\sigma_p(10^{-20}$ $cm^2)$	$\tau_R(\mu s)$
$^5D_0 \rightarrow {}^7F_2$	619	35.608	0.2532	0.0169	7110.67	35.564	0.2541	0.0167	7145.10	35.441	0.2539	0.0163	7164.55
$^5D_0 \rightarrow {}^7F_5$	700	105.026	0.7468	0.0666		104.392	0.7459	0.0652		104.14	0.7461	0.0640	

V. CONCLUSION

In the present study, the glass samples of composition (35-x) GeO_2:10ZnO:10Li_2O:10Al_2O_3:10Sb_2O_3:25B_2O_3: x Eu_2O_3 (where x=1, 1.5, 2mol %) have been prepared by melt-quenching method. The Judd-Ofelt theory has been applied to calculate the oscillator strength and intensity parameters Ω_λ(λ=2, 4, 6). The radiative transition rate and the branching ratio are highest for ($^5D_0 \rightarrow {}^7F_5$) transition and hence it is useful for laser action. The stimulated emission cross section (σ_p) value is also very high for the transition ($^5D_0 \rightarrow {}^7F_5$). This shows that ($^5D_0 \rightarrow {}^7F_5$) transition is most probable transition.

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