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Spectral and Upconversion Properties of Eu^{3+} Doped in Zinc Lithium Cadmium Alumino Borogermanate Glasses

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ABSTRACT: Glass sample of Zinc Lithium Cadmium Alumino Borogermanate(35-x) $\text{GeO}_2:10\text{ZnO}:10\text{Li}_2\text{O}:10\text{CdO}:10\text{Al}_2\text{O}_3:25\text{B}_2\text{O}_3:x\text{Eu}_2\text{O}_3$ (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 cadmium alumino borogermanate glasses have been recorded at room temperature. The various interaction parameters like Slater-Condon parameters F_k ($k=2,4,6$), Lande's parameter (ξ_{4f}), nephelauxetic ratio (β'), bonding parameter ($b^{1/2}$) and Racah parameters E^k ($k=1,2,3$) have been computed. Judd-Ofelt intensity parameters and laser parameters have also been calculated.

KEYWORDS: ZLCABG glasses, Energy interaction parameters, Optical properties, Judd-Ofelt analysis.

I. INTRODUCTION

Glasses doped with rare earth ions have drawn much attention due to their potential applications in optical amplifier, solid state lasers, optical sensors, fluorescence labeling, high chemical durability and thermal stability [1-6]. Germinate glasses are both scientifically and technologically important materials because they generally offer some unique physical properties better than other Glasses [7-11]. ZnO is a wide band gap semiconductor and has received increasing research interest. It is an important multifunctional material due to its specific chemical, surface and microstructural properties [12]. B_2O_3 is one of the most common glass former oxides and is present in almost all commercially important glasses. It is often used as a dielectric and insulating material [13]. Eu^{3+} doped ceramic glasses considerable literature has recently emerged concerning the structure, optical, mechanical, thermal, and electrical properties [14-17].

The aim of the present study is to prepare the Eu^{3+} doped zinc lithium cadmium alumino borogermanate glass with different Eu_2O_3 concentrations. 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 ($\lambda=2, 4, 6$). These intensity parameter have been used to evaluate 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 germinate glass samples (35-x) $\text{GeO}_2:10\text{ZnO}:10\text{Li}_2\text{O}:10\text{CdO}:10\text{Al}_2\text{O}_3:25\text{B}_2\text{O}_3:x\text{Eu}_2\text{O}_3$ (where $x=1,1.5, 2$) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of $\text{GeO}_3, \text{ZnO}, \text{Li}_2\text{O}, \text{CdO}, \text{Al}_2\text{O}_2$ and B_2O_3 and Eu_2O_3 . They were thoroughly mixed by using an agate pestle mortar. then melted at 1055°C 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 350°C 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 %)
ZLCABG(UD)	35GeO ₂ :10ZnO:10Li ₂ O:10CdO:10Al ₂ O ₃ :25B ₂ O ₃
ZLCABG(EU1)	34GeO ₂ :10ZnO:10Li ₂ O:10CdO:10Al ₂ O ₃ :25B ₂ O ₃ :1Eu ₂ O ₃
ZLCABG(EU1.5)	33.5GeO ₂ :10ZnO:10Li ₂ O:10CdO:10Al ₂ O ₃ :25B ₂ O ₃ :1.5Eu ₂ O ₃
ZLCABG(EU2)	33GeO ₂ :10ZnO:10Li ₂ O:10CdO:10Al ₂ O ₃ :25B ₂ O ₃ :2Eu ₂ O ₃

ZLCABG(UD) -Represents undoped Zinc Lithium Cadmium Alumino Borogermanate glass specimen.

ZLCABG(EU) -Represents Eu³⁺ doped Zinc Lithium Cadmium Alumino Borogermanate glass specimens.

III. THEORY

3.1 Oscillator Strength

The spectral intensity is expressed in terms of oscillator strengths using the relation [18].

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

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 [19], using the modified relation:

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

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 $\Delta\nu_{1/2}$ is half band width.

3.2. Judd-Ofelt Intensity Parameters

According to Judd [20] and Ofelt [21] theory, independently derived expression for the oscillator strength of the induced forced electric dipole transitions between an initial J manifold $|4f^N(S, L) J\rangle$ level and the terminal J' manifold $|4f^N(S', L') J'\rangle$ is given by:

$$\frac{8\pi^2 m c \bar{\nu}}{3h(2J+1)n} \left[\frac{(n^2+2)^2}{9} \right] \times S(J, J') \quad (3)$$

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

by the equation

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

$\lambda = 2, 4, 6$

In the above equation m is the mass of an electron, c is the velocity of light, $\bar{\nu}$ 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 $|4f^N(S', L') J'\rangle$ to a final manifold $|4f^N(S, L) J\rangle$ is given by:

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



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 $|4f^N(S', L')J\rangle$ to a final manifold $|4f^N(S, L)J\rangle$ is given by

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

Where, the sum is over all terminal manifolds.

The radiative life time is given by

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

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

3.4 Nephelauxetic 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 [22, 23]. 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

4.1 XRD Measurement

Figure 1 presents the XRD pattern of the sample contain $-\text{GeO}_2$ 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.

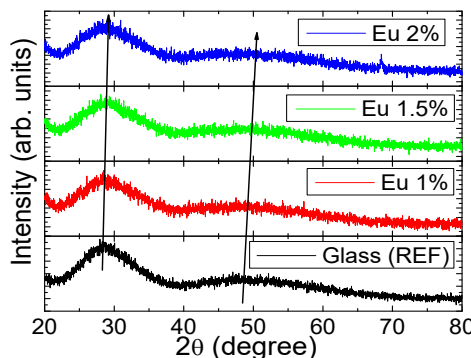


Fig. 1: X-ray diffraction pattern of $\text{GeO}_2:\text{ZnO}:\text{Li}_2\text{O}:\text{CdO}:\text{Al}_2\text{O}_3:\text{B}_2\text{O}_3$

4.2 Absorption Spectrum

The absorption spectra of Eu^{3+} doped ZLCABG(EU 01) glass specimen has been presented in Figure 2 in terms of optical density versus wavelength (nm). Four absorption bands have been observed from the ground state ${}^7\text{F}_0$ to excited states ${}^5\text{D}_2$, ${}^5\text{L}_6$, ${}^5\text{G}_2$ and (${}^5\text{G}_6$, ${}^5\text{G}_4$) for Eu^{3+} doped ZLCABG glasses.

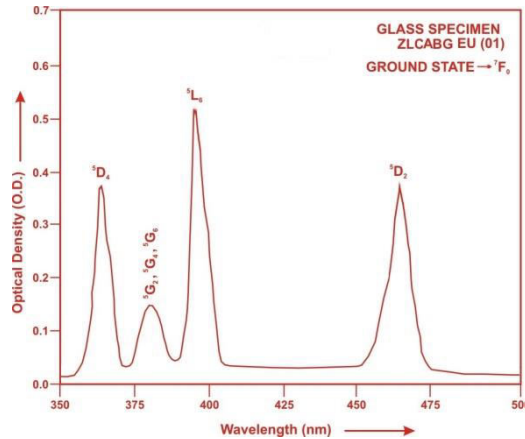


Fig.2: Absorption spectrum of Eu^{3+} doped ZLCABG(01) glass

The experimental and calculated oscillator strengths for Eu^{3+} ions in zinc lithium cadmium aluminum borogermanate glasses are given in Table 2.

Table 2: Measured and calculated oscillator strength ($P_m \times 10^6$) of Eu^{3+} ions in ZLCABG glasses.

Energy level ${}^7\text{F}_0$	Glass ZLCABG(EU01)		Glass ZLCABG(EU1.5)		Glass ZLCABG(EU02)	
	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}
${}^5\text{D}_2$	2.30	2.14	2.30	2.13	2.29	2.11
${}^5\text{L}_6$	3.71	3.52	3.70	3.50	3.67	3.46
${}^5\text{G}_2$	0.93	0.73	0.93	0.72	0.92	0.70
${}^5\text{G}_6, {}^5\text{G}_4$	3.11	2.90	3.10	2.89	3.09	2.86
r.m.s. deviation	0.1907		0.1969		0.2094	

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}), Nephelauxetic ratio (β') and bonding parameter ($b^{1/2}$) for Eu^{3+} doped ZLCABG 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 Ω_λ 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 1.083 and 1.088 in the present glasses.

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

Table 4: Judd-Ofelt intensity parameters for Eu³⁺ doped ZLCABG glass specimens.

Glass Specimen	$\Omega_2(\text{pm}^2)$	$\Omega_4(\text{pm}^2)$	$\Omega_6(\text{pm}^2)$	Ω_4/Ω_6	Trend	References
ZLCABG (EU01)	4.890	3.735	3.450	1.083	$\Omega_2 > \Omega_4 > \Omega_6$	[P.W.]
ZLCABG(EU1.5)	4.876	3.729	3.434	1.086	$\Omega_2 > \Omega_4 > \Omega_6$	[P.W.]
ZLCABG(EU02)	4.853	3.706	3.406	1.088	$\Omega_2 > \Omega_4 > \Omega_6$	[P.W.]
PKBA(EU)	13.272	8.092	1.794	4.511	$\Omega_2 > \Omega_4 > \Omega_6$	[24]
PKBFA(EU)	11.524	5.238	2.222	2.357	$\Omega_2 > \Omega_4 > \Omega_6$	[24]

From Table 4 it is observed that Ω_2 parameter is high. The Ω_2 parameter depends generally on the asymmetry of the sites in the neighborhood of rare earth ion. The higher the Ω_2 parameter the higher is the degree of asymmetry around the rare earth ion and stronger the covalency of rare earth ion-oxygen bond.

4.3. Fluorescence Spectrum

The fluorescence spectrum of Eu³⁺ doped in zinc lithium cadmiumaluminumborogerminateglass is shown in Figure 3. There are two broad bands observed in the Fluorescence spectrum of Eu³⁺ doped zinc lithium cadmiumaluminumborogerminateglass. The wavelengths of these bands along with their assignments are given in Table 5. Fig. (3). Shows the fluorescence spectrum with two peaks (${}^5D_0 \rightarrow {}^7F_2$) and (${}^5D_0 \rightarrow {}^7F_5$), for glass specimens.

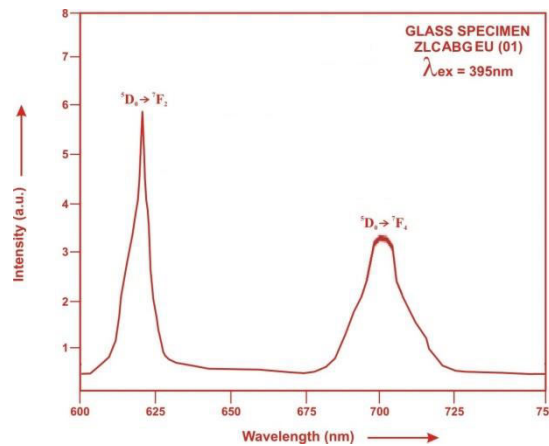


Fig.3: fluorescence spectrum of Eu³⁺ doped ZLCABG(01) glass

4.4 Up conversion mechanism

The up-conversion mechanism is given in Fig. 4.

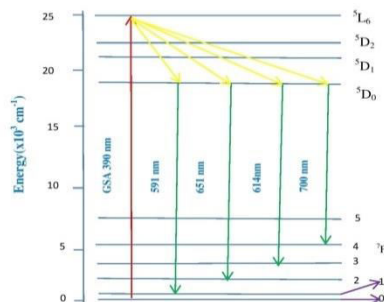


Fig. 4: Energy level diagram and up conversion mechanism of doped ZLCABG (EU) glass



Table 5. 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 ZLCABG glasses

Transition	ZLCABGEU 01					ZLCABGEU 1.5				ZLCABGEU 02			
	λ_{max} (nm)	$A_{rad}(s^{-1})$	β	$\sigma_p(10^{-20} \text{ cm}^2)$	$\tau_R(\mu s)$	$A_{rad}(s^{-1})$	β	$\sigma(10^{-20} \text{ cm}^2)$	$\tau_R(\mu s)$	$A_{rad}(s^{-1})$	β	$\sigma_p(10^{-20} \text{ cm}^2)$	$\tau_R(\mu s)$
$^5D_0 \rightarrow ^7F_2$	619	40.029	0.2541	0.0168	6347.65	40.014	0.2539	0.0164	6346.43	39.885	0.2542	0.0160	6373.54
$^5D_0 \rightarrow ^7F_4$	700	117.509	0.7459	0.0658		117.56	0.7461	0.0648		117.014	0.7458	0.0632	

V. CONCLUSION

In the present study, the glass samples of composition $(35-x) \text{ GeO}_2:10\text{ZnO}:10\text{Li}_2\text{O}:10\text{CdO}:10\text{Al}_2\text{O}_3:25\text{B}_2\text{O}_3: x \text{ Eu}_2\text{O}_3$ (where $x=1, 1.5, 2 \text{ mol } \%$) have been prepared by melt-quenching method. The Judd-Ofelt theory has been applied to calculate the oscillator strength and intensity parameters $\Omega_\lambda (\lambda=2, 4, 6)$. The radiative transition rate and the branching ratio are highest for ($^5D_0 \rightarrow ^7F_4$) transition and hence it is useful for laser action. The stimulated emission cross section (σ_p) value is also very high for the transition ($^5D_0 \rightarrow ^7F_4$). This shows that ($^5D_0 \rightarrow ^7F_4$) transition is most probable transition.

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