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Spectral and Raman Analysis of Eu^{3+}Doped in Zinc Lithium Cadmium Magnesium Borophosphate Glasses

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Abstract
Glass sample of Zinc Lithium CadmiumMagnesium Borophosphate(40-x) P_2O_5:10ZnO:10Li_2O:10CdO:10MgO:20B_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, fluorescence and ramanspectra of three Eu^{3+} doped zinc lithium cadmium magnesium borophosphateglasses have been recorded at room temperature. The various interaction parameters likeSlater-Condonparameters F_k (k=2,4,6),Lande'parameter (ζ_{4f}),nephelauexetic ratio(β'),bondingparameter ($b^{1/2}$)and Racah parametersE^k(k=1,2 3) have been computed.Judd-Ofelt intensity parameters and laser parameters have also been calculated.

Keywords: *ZLCMBPglasses,Energy interaction parameters,Optical properties,Raman analysis.*

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I. Introduction

Glasses with dopants of rare earth ions have continuously drawn the attention through their potential applications in solid state lasers, optical Amplifiers and sensor fields [1-5].

Recently, phosphate glasses have received a great deal of attention due to their potential applications in laser technologies and optical data transmission, sensors andenergy solar cell [6-10].Phosphate glasses doped with a transition metal or rare-earth ions are considered as valuable materials for both optical and electrical applications[11,12].The addition of CdO improves the physical and chemical properties of the glass [13,14].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[15, 16].Phosphate glasses have a low glass transition temperature, high coefficient of thermal expansion, low melting temperature and high gain density. The high gain density in phosphate glasses is due to high solubility of rare earth ions in phosphate network.These characteristics are known to have some influences on various factors such as the preparation temperature, nature and the composite type.The relatively poor chemical durability of some specific types of phosphate glasses has played the role in limiting their practical applications. This disadvantage can be solved by the addition of some transition metal ions or alkaline earth as well as intermediate oxides to the host glass [17-19].

The aim of the present study is to prepare theEu^{3+}dopedzinc lithium cadmiummagnesium borophosphateglass with different Eu_2O_3concentrations.The absorption, fluorescence and raman 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 borophosphate glass samples (40-x) P_2O_5:10ZnO:10Li_2O:10CdO:10MgO:20B_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 P_2O_5,ZnO, Li_2O,CdO,MgO, $B_2O_3$and Eu_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 1065^0C 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 350^0C 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 %)
ZLCMBP(UD)	$40P_2O_5$:10ZnO:10Li_2O:10CdO:10MgO:20B_2O_3
ZLCMBP(EU1)	$39P_2O_5$:10ZnO:10Li_2O:10CdO:10MgO:20B_2O_3:1Eu_2O_3
ZLCMBP(EU1.5)	$38.5P_2O_5$:10ZnO:10Li_2O:10CdO:10MgO:20B_2O_3:1.5Eu_2O_3
ZLCMBP(EU2)	$38P_2O_5$:10ZnO:10Li_2O:10CdO:10MgO:20B_2O_3:2Eu_2O_3

ZLCMBP(UD) -Represents undopedZinc Lithium CadmiumMagnesium Borophosphateglass specimen.
ZLCMBP(EU) -Represents Eu^{3+}dopedZinc Lithium CadmiumMagnesium Borophosphateglass specimens.

III. Theory

3.1Oscillator Strength

The spectralintensity is expressed in terms of oscillator strengths using the relation [20].

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

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[21], using the modified relation:

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

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

3.2. Judd-Ofelt Intensity Parameters

According to Judd[22] and Ofelt[23] 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:

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

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

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

$\lambda = 2, 4, 6$

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

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

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 $|4f^N (S', L') J'>$ to a final many fold $|4f^N (S,L)J>$ is given by

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

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 [24, 25]. 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 - P_2O_5 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.

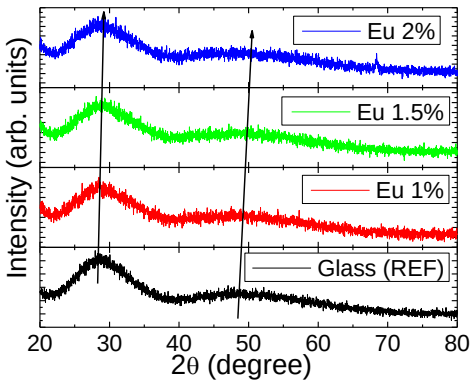

Fig.1:X-ray diffraction pattern of ZLCMBP (EU) glasses.

4.2 Raman spectra

The Raman spectrum of Zinc Lithium Cadmium Magnesium Borophosphate(ZLCMBP) glass specimens is recorded and is shown in Fig. 2. The spectrum peaks located at 397 and 779 cm^{-1}. The band at 397 $cm^{-1}$is is related to the bending motion of phosphate polyhedral PO_4 units with cation like ZnO as the modifier. The broad band at 779cm^{-1} is due to symmetric stretching of (P–O–P) bridging oxygen bonds in $(P_2O_7)_4$ units.

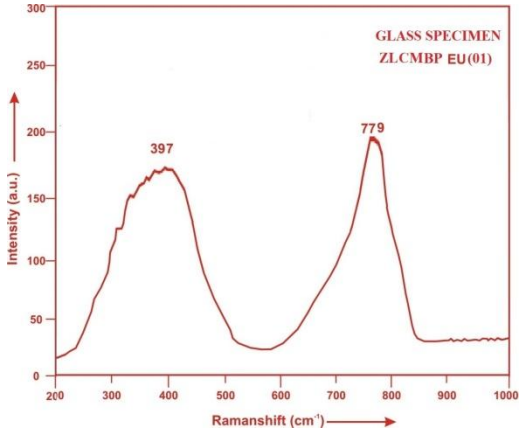

Fig.2: Raman spectrum of ZLCMBP EU (01) glass.

4.3 Absorption Spectrum

The absorption spectra of Eu^{3+} doped ZLCMBP(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 $^5D_2$,$^5L_6$,($^5G_2$,$^5G_4$,$^5G_6$)and $^5D_4$ for Eu^{3+}doped ZLCMBP glasses.

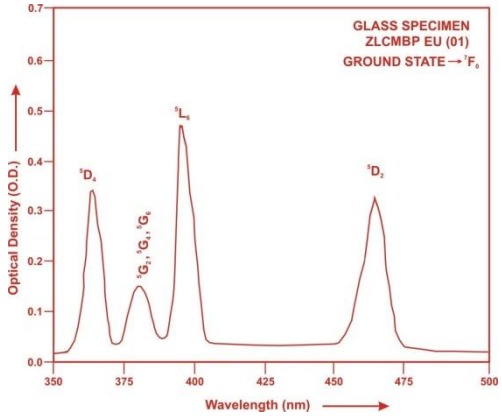

Fig.3: Absorption spectrum of ZLCMBP EU(01)glass.

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

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

Energy level $^7F_0$	**Glass ZLCMBP(EU01)**		**Glass ZLCMBP(EU1.5)**		**Glass ZLCMBP(EU02)**	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^5D_2$	2.26	2.36	2.23	2.35	2.20	2.32
$^5L_6$	3.68	3.80	3.66	3.79	3.62	3.77
$^5G_2$,$^5G_4$,$^5G_6$	0.83	0.95	0.81	0.95	0.79	0.94
$^5D_4$	3.02	3.15	2.99	3.14	2.96	3.12
r.m.s. deviation	0.1156		0.1344		0.1469	

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 ZLCMBP 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 1.069 and 1.072 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 ZLCMBP glass specimens.

Glass Specimen	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4/Ω_6	Trend	References
ZLCMBP(EU01)	4.649	3.509	3.274	1.072	$\Omega_2>\Omega_4>\Omega_6$	P.W.
ZLCMBP(EU1.5)	4.618	3.496	3.271	1.069	$\Omega_2>\Omega_4>\Omega_6$	P.W.
ZLCMBP(EU02)	4.576	3.474	3.244	1.071	$\Omega_2>\Omega_4>\Omega_6$	P.W.
LSBP(DY)	5.24	2.32	1.97	1.178	$\Omega_2>\Omega_4>\Omega_6$	[18]
PKAICAF(EU)	7.49	6.30	0.50	12.60	$\Omega_2>\Omega_4>\Omega_6$	[22]
NSGP(DY)	12.38	6.31	3.20	1.972	$\Omega_2>\Omega_4>\Omega_6$	[23]
NSGP(EU)	15.65	10.00	8.12	1.232	$\Omega_2>\Omega_4>\Omega_6$	[23]

From Table 4 it is observed that Ω_2 parameter is high. The Ω_2 parameter dependsgenerally 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.

4.4. Fluorescence Spectrum

The fluorescence spectrum of Eu^{3+}doped in zinc lithium cadmiummagnesium borophosphateglass is shown in Figure 4. There are three broad bands observed in the Fluorescence spectrum ofEu^{3+}dopedzinc lithium cadmiummagnesium borophosphateglass. The wavelengths of these bands along with their assignments are given in Table 5. Fig. (4).Shows the fluorescence spectrum with seven peaks ($^5D_0\rightarrow{}^7F_0$),($^5D_0\rightarrow{}^7F_1$),($^5D_0\rightarrow{}^7F_2$),($^5D_0\rightarrow{}^7F_3$),($^5D_0\rightarrow{}^7F_4$), ($^5D_0\rightarrow{}^7F_5$) and ($^5D_0\rightarrow{}^7F_6$) for glass specimens.

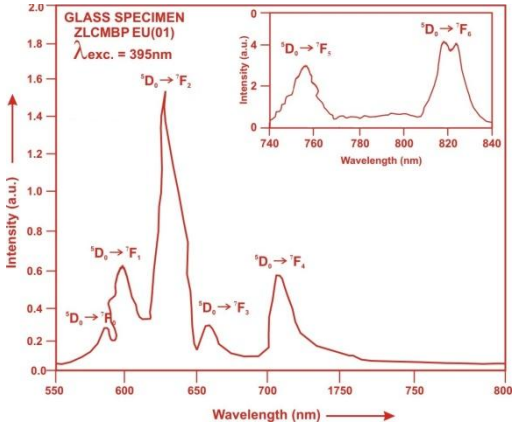

Fig.4: fluorescence spectrum of ZLCMBP EU (01) glass.

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 ZLCMBP glasses.

Transition		ZLCMBPEU 01				ZLCMBPEU 1.5				ZLCMBPEU 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)	$\tau_R(\mu s)$
$^5D_0\rightarrow{}^7F_2$	615	46.626	0.2676	0.0153	5738.79	46.428	0.2671	0.0150	5752.69	46.073	0.2664	0.0147	5782.97
$^5D_0\rightarrow{}^7F_4$	710	127.13	0.7296	0.0675		126.90	0.7300	0.0670		126.35	0.7307	0.0657	
$^5D_0\rightarrow{}^7F_6$	820	0.4997	0.0029	0.000317		0.5001	0.0029	0.000314		0.4971	0.0029	0.000310	

V. Conclusion

In the present study, the glass samples of composition (40-x) P_2O_5:10ZnO:10Li_2O:10CdO:10MgO:20B_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 $\Omega_\lambda(\lambda=2, 4, 6)$. 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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