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Spectral and Up conversion Properties of Eu^{3+} Doped in Zinc Lithium Potassiumniobate Borosilicate Glasses

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Abstract: Glass sample of zinc lithium potassiumniobate borosilicate (35-x) SiO_2:10ZnO:10Li_2O:10K_2O:10Nb_2O_5:25B_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 and fluorescence spectra of three Eu^{3+} doped zinc lithium potessiumniobate glasses have been recorded at room temperature. The various interaction parameters like Slater-Condon parameter F_2, Lande parameter (ξ_{4f}), nephelauexetic ratio (β') and bonding parameter ($b^{1/2}$) have been computed. Judd-Ofelt intensity parameters and laser parameters have also been calculated.
Keywords: ZLPNBS glasses, Energy interaction parameters, Optical properties, Upconversion properties

I. INTRODUCTION

Rare-earth ions-doped luminescent materials have wide range of applications in solid state lasers, display devices, optical detectors, optical fibers and optical amplifiers [1-5].Oxide glasses are the most stable host matrices for practical applications due to their high chemical durability and thermal stability. The importance of glasses doped with rare earth elements lies in their distinctive emission properties in several electromagnetic spectral regions [6-8]. Among these hosts, the borosilicate system is attractive due to its superior physical, structural and optical properties [9-13]. 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 micro structural properties [14]. Among different rare –earth ions, the Er^{3+} ion has been identified as the most efficient ion for obtaining the lasing action, frequency up-conversion and optical fiber amplification[15-20].

The aim of the present study is to prepare the Eu^{3+} doped zinc lithium potassiumniobate borosilicate glass with different Eu_2O_3 concentrations. The absorption spectra and 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

A. *Preparation of glasses*

The following Eu^{3+} doped borosilicate glass samples (35-x) SiO_2:10ZnO:10Li_2O:10K_2O:10Nb_2O_5:25B_2O_3: x Eu_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 SiO_2, ZnO, Li_2O, K_2O, Nb_2O_5, B_2O_3 and Eu_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 1070^0C 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 %)
ZLPNBS (UD)	35SiO_2:10ZnO:10Li_2O:10K_2O:10Nb_2O_5:25B_2O_3
ZLPNBS (EU1)	34SiO_2:10ZnO:10Li_2O:10K_2O:10Nb_2O_5:25B_2O_3: 1 Eu_2O_3
ZLPNBS (EU 1.5)	33.5SiO_2:10ZnO:10Li_2O:10K_2O:10Nb_2O_5:25B_2O_3: 1.5 Eu_2O_3
ZLPNBS (EU2)	33SiO_2:10ZnO:10Li_2O:10K_2O:10Nb_2O_5:25B_2O_3: 2 Eu_2O_3

ZLPNBS (UD) -Represents undoped Zinc Lithium Potassiumniobate Borosilicate glass specimen.
ZLPNBS (EU) -Represents Eu^{3+} Zinc Lithium Potassiumniobate Borosilicate glass specimens.

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III. THEORY

A. Oscillator Strength

The spectral intensity is expressed in terms of oscillator strengths using the relation [21].

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

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 [22], 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.

B. Judd-Ofelt Intensity Parameters

According to Judd [23] and Ofelt [24] 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:

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

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

$$S(J, J') = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \langle 4f^N (S, L) J \| U^{(\lambda)} \| 4f^N (S', L') J'\rangle^2$$

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 (λ = 2, 4, 6) are known as Judd-Ofelt intensity parameters.

C. 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:

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

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

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

Where, the sum is over all terminal manifolds.

The radiative life time is given by

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

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

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

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

D. 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 [25, 26]. The Nephelauxetic Ratio is given by

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

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

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

IV. RESULT AND DISCUSSION

A. XRD Measurement

Figure 1 presents the XRD pattern of the sample contain – SiO_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.

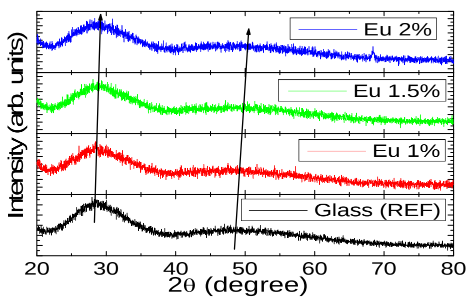

Fig. 1: X-ray diffraction pattern of SiO_2:ZnO:Li_2O:K_2O:Nb_2O_5:B_2O_3: Eu_2O_3

B. Absorption Spectrum

The absorption spectra of ZLPNBS (EU 01) glass specimen have been presented in Figure 2 in terms of optical density versus wavelength (nm). Four absorption bands have been observed from the ground state $^7F_0$ to excited states $^5D_2$,$^5L_6$,$^5G_2$ and ($^5G_6$,$^5G_4$) for ZLPNBS (EU 01) glass.

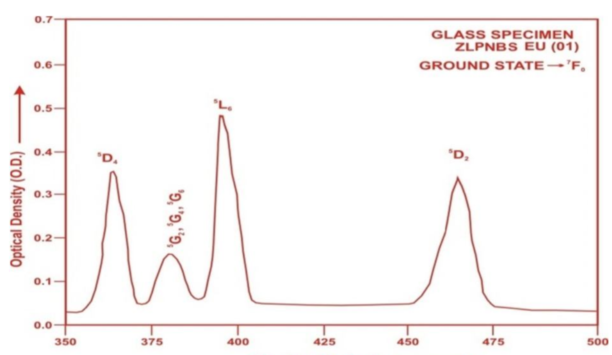

Fig.2: Absorption spectrum of Eu^{3+}doped ZLPNBS (01) glass

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

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

Energy level $^7F_0$	Glass ZLPNBS (EU01)		Glass ZLPNBS (EU1.5)		Glass ZLPNBS (EU02)	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^5D_2$	2.25	2.38	2.22	2.36	2.18	2.34
$^5L_6$	3.68	3.83	3.65	3.82	3.61	3.80
$^5G_2$	0.80	0.96	0.78	0.96	0.75	0.95
$^5G_6$,$^5G_4$	2.99	3.16	2.96	3.14	2.93	3.14
r.m.s. deviation	0.1532		0.1689		0.1938	

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}), Nephlauxetic ratio (β') and bonding parameter($b^{1/2}$) for Eu^{3+}doped ZLPNBS glass specimen are given in Table 3.

Table 3. F_2, $\xi_{4f,}$ 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 1.064 and 1.068 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 ZLPNBS glass specimens.

Glass Specimen	Ω_2(pm^2)	Ω_4(pm^2)	Ω_6(pm^2)	Ω_4 /Ω_6	Trend	References
ZLPNBS (EU01)	4.977	3.735	3.507	1.065	$\Omega_2 > \Omega_4 > \Omega_6$	P.W.
ZLPNBS (EU1.5)	4.938	3.716	3.491	1.064	$\Omega_2 > \Omega_4 > \Omega_6$	P.W.
ZLPNBS (EU02)	4.894	3.710	3.475	1.068	$\Omega_2 > \Omega_4 > \Omega_6$	P.W.
LFB(SM)	3.41	2.92	2.17	1.346	$\Omega_2 > \Omega_4 > \Omega_6$	[27]
ZLSLPNM(SM)	5.016	4.758	4.213	1.129	$\Omega_2 > \Omega_4 > \Omega_6$	[28]

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C. Fluorescence Spectrum

The fluorescence spectrum of Eu^{3+}doped in zinc lithium potassiumniobate borosilicate glass is shown in Figure 3. There are seven bands observed in the Fluorescence spectrum of Eu^{3+}doped zinc lithium potassiumniobate borosilicate glass. Fig. (3).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 ($^5D_0\rightarrow{}^7F$) for glass specimens.

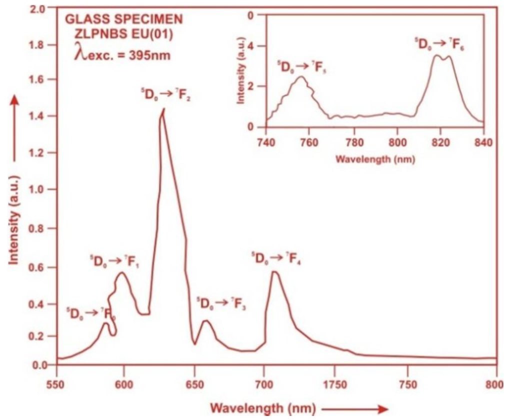

Fig.3: fluorescence spectrum of ZLPNBS EU(01) glass.

D. Up Conversion Mechanism

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

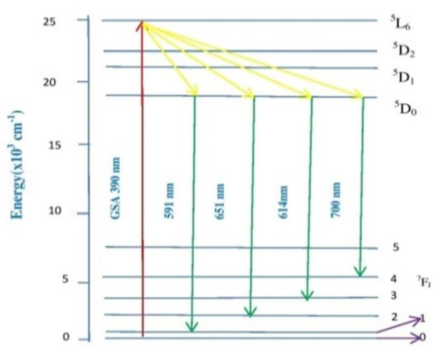

Fig. 4: Energy level diagram and up conversion mechanism of doped ZLCABG (EU) glasses.

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 ZLPNBS glasses

Transition		ZLPNBS EU 01				ZLPNBS EU 1.5				ZLPNBS EU 02			
	λ_{max} (nm)	A_{rad}(s^{-1})	β	σ_p (10^{-20} cm^2)	τ_R(μs)	A_{rad}(s^{-1})	β	σ (10^{-20} cm^2)	τ_R(μs)	A_{rad}(s^{-1})	β	σ_p (10^{-20} cm^2)	τ_R(μs)
$^5D_0\rightarrow{}^7F_2$	619	43.230	0.2688	0.0154	6217.48	42.998	0.2683	0.0151	6240.67	42.679	0.2667	0.0147	6249.55
$^5D_0\rightarrow{}^7F_5$	700	117.14	0.7283	0.0688		116.78	0.7288	0.0675		116.87	0.7304	0.0665	
$^5D_0\rightarrow{}^7F_6$	820	0.4636	0.0029	0.000320		0.4624	0.0029	0.000315		0.4612	0.0029	0.000310	

V. CONCLUSION

In the present study, the glass samples of composition (35-x) SiO_2:10ZnO:10Li_2O:10K_2O:10Nb_2O_5:25B_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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