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Spectroscopic Properties of Eu^{3+} Ions Doped Boro-phosphate Glasses for Optoelectronic Applications

P. Jayanthi, R. Nagaraj, K. Marimuthu*

Department of Physics, Gandhigram Rural Institute–Deemed University, Gandhigram – 624 302, India

*Corresponding author: mari_ram2000@yahoo.com

Abstract

A new series of Eu^{3+} ions doped boro-phosphate glasses with the chemical composition $(60\text{–}x)B_2O_3 + 10P_2O_5 + 20Li_2O + 10ZnO + xEu_2O_3$ (where, x = 0.25, 0.5, 1 and 2 in wt %) have been prepared by conventional melt quenching technique and labeled as 0.25EuBP, 0.5EuBP, 1EuBP and 2EuBP glasses respectively. From the absorption spectra, bonding parameters have been calculated to examine the nature of the bond between the Eu^{3+} ions and its surrounding ligands. The Judd-Oflet (JO) intensity parameters were calculated from the emission spectra to explore the symmetry of the ligand environment around the Eu^{3+} ion site. Radiative properties were obtained from the emission spectra to ensure the suitability of studied glasses for solid state laser applications. The decay curves exhibit single exponential behavior for all the title glasses irrespective of the change in Eu^{3+} ion concentration and the observed results were discussed in detail and reported.

Keywords: Glasses, Absorption, Luminescence, JO Parameters, Decay Analysis.

1. Introduction

For the past few decades considerable work on rare earth (RE) doped materials have been carried out for the design and development of efficient optoelectronic devices such as solid state lasers, LED's and color display devices. Of all the RE ions, Eu^{3+} ion possess lots of importance because of its narrow band emission around 612 nm due to its $^5D_0 \rightarrow {}^7F_2$ transition for red laser applications. The f–f transition of Eu^{3+} ions provide information about the local structure around the RE ions in different host matrices and hence they can be used as a probe to analyze the ligand structure around the RE^{3+} ions site [1]. In order to avail the advantages of both borate and phosphate glass formers like high refractive index, high RE ion solubility, low melting temperature, high transparency and high thermal stability it is combined together as boro-phosphate glasses to attain good optical quality glasses.

Spectroscopic properties of Eu^{3+} ions doped boro-phosphate glasses have been studied as a function of Eu^{3+} ion concentration and the results were discussed and reported

2. Experimental

Eu^{3+} doped title glasses have been prepared by conventional melt quenching technique following the procedure reported in literature [2]. The absorption spectral measurements were made employing Perkin Elmer Lambda 35 UV-Vis-NIR spectrophotometer. Luminescence spectra of the prepared glasses were recorded using Perkin Elmer LS55 spectrophotometer. Sciencetech modular spectrometer was employed for lifetime measurements using xenon flash lamp as an excitation source.

3. Optical absorption spectra

The absorption spectra of the Eu^{3+} doped boro-phosphate glasses were recorded in the wavelength region 375–2300 nm and as a representative case absorption spectrum of the 1EuBP glass is shown in figure 1. The spectrum exhibit ten absorption bands at 394, 401, 414, 465, 524, 533, 578, 587,

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2097 and 2205 nm analogous to the $^7F_0 \rightarrow ^5L_6$, $^7F_1 \rightarrow ^5L_6$, $^7F_1 \rightarrow ^5D_3$, $^7F_0 \rightarrow ^5D_2$, $^7F_0 \rightarrow ^5D_1$, $^7F_1 \rightarrow ^5D_1$, $^7F_0 \rightarrow ^5D_0$, $^7F_1 \rightarrow ^5D_0$, $^7F_0 \rightarrow ^7F_6$ and $^7F_1 \rightarrow ^7F_6$ transitions respectively. Among them, $^7F_0 \rightarrow ^5L_6$ transition is found to be higher in intensity.

The bonding parameter (δ) values can be estimated using the relation δ = ((1−)/)×100, where $\overline{\beta}$ is the average value of the Nephelauxetic ratios (β). The calculated δ values of the studied glasses are found to be 0.0052, 0.0050, 0.0046 and 0.0040 corresponding to the 0.25EuBP, 0.5EuBP, 1EuBP and 2EuBP glasses respectively. The positive δ values indicate the covalent nature of the Eu–O bond. The decreasing B_2O_3 content reduces the polarization of oxygen ions upon Eu^{3+} ions which in turn leads to have a fall in the covalency of the Eu–O bonds.

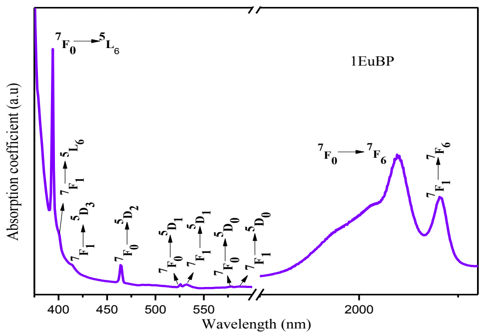

Figure 1. Absorption spectrum of the 1EuBP glass

4. Phonon sideband and luminescence spectral analysis

Figure 2 shows the excitation spectrum of the 1EuBP glass recorded in the wavelength region 350–550 nm by monitoring the emission at 612 nm. The spectrum exhibit six excitation bands at around 363, 380, 395, 412, 463 and 532 nm corresponding to the $^7F_0 \rightarrow ^5D_4$, $^7F_1 \rightarrow ^5L_7$, $^7F_0 \rightarrow ^5L_6$, $^7F_1 \rightarrow ^5D_3$, $^7F_0 \rightarrow ^5D_2$ and $^7F_1 \rightarrow ^5D_1$ transitions respectively. The $^7F_0 \rightarrow ^5L_6$ transition observed at 405 nm is found to be higher in intensity compared to all other transitions and is used as an excitation wavelength to record the emission spectra.

Table 1. The JO parameters (×10^{-20} cm^2), (x,y) color coordinates, peak position of PET and PSB (in cm^{-1}), Phonon energy (cm^{-1}) and g of the xEuBP glasses

Parameters	0.25Eu BP	0.5Eu BP	1Eu BP	2Eu BP
Ω_2	3.82	3.76	3.54	2.74
Ω_4	0.692	0.759	0.620	0.629
Ω_6	0	0	0	0
X	0.603	0.624	0.629	0.644
Y	0.345	0.346	0.348	0.35
PET	21515	21518	21523	21531
PSB	22617	22621	22624	22618
Phonon energy	1172	1166	1160	1153
G	0.0032	0.0029	0.0025	0.0021

The occurrence of phonon sideband in the excitation spectra of the Eu^{3+} ions corresponds to the phonon assisted absorption transition. The phonon sideband (PSB) coupled with the excitation spectrum of the 1EuBP glass and the PSB of all the studied glasses are shown in the insert of figure 2. The electron-phonon coupling constant have been obtained using the expression,

$$(\int I_{PSB}\, d\lambda)/(\int I_{PET}\, d\lambda)$$

where, is the intensity of the phonon sideband and is the intensity of pure electronic transition respectively. Further, phonon energy involved in the non-radiative decay process which leads to luminescence quenching can also be obtained by finding the difference between the energy of the

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pure electronic transition and that of the phonon side band. Table 1 shows the calculated g values and the phonon energies of the title glasses. It is observed from table 1 that the phonon energy of the xEuBP glasses are found to be in the range 1153–1172 cm^{-1} and the same may be due to the vibrations of different borate groups. The lower g values indicate the less covalency of the Eu–O bonds in the studied glasses which is already confirmed through the bonding parameter values.

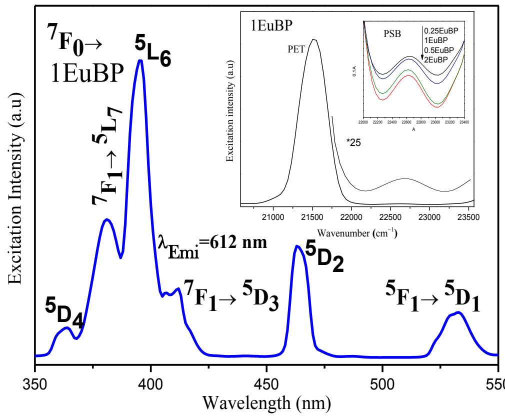

Figure 2. Excitation spectrum of the 1EuBP glass [Inset shows the phonon side bands of the xEuBP glasses]

The luminescence spectra recorded in the wavelength region 550–720 nm is shown in figure 3. The spectra exhibit emission bands at around 574, 595, 612, 653 and 702 nm corresponding to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions respectively. The intensity of the emission bands are found to increase upto 1wt% Eu^{3+} ion concentration and after that luminescence quenching is observed due to the energy transfer process takes place between the Eu^{3+} ions through cross-relaxation mechanism [2]. The CIE chromaticity coordinates have been determined to estimate the emission color of the prepared glasses. The calculated chromaticity coordinates (x,y) of the studied glasses are presented in table 1 and the (x,y) values are found to lie in the red region of the CIE 1931 diagram and the same is shown in the inset of figure 3.

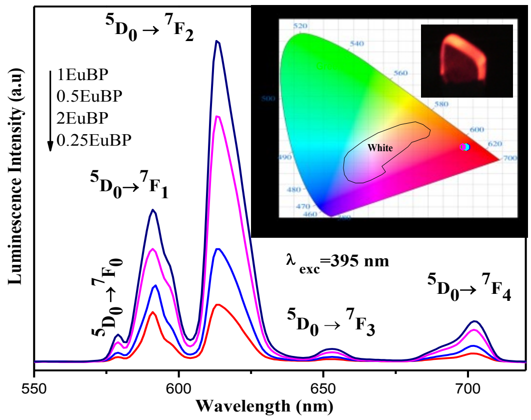

Figure 3. Luminescence spectra of the xEuBP glasses [Inset shows the CIE 1931 diagram of the xEuBP glasses]

1. Judd-ofelt analysis and decay curves

The JO parameters give valuable information about the metal-ligand bonding nature and the symmetry of the ligand field around the RE ion site. The JO parameters of the studied glasses were calculated from the emission spectra following the procedure reported in literature [3,4] and they mainly depend upon the emission intensities of the $^5D_0 \rightarrow {}^7F_{2,4,6}$ transitions. Table 1 shows the calculated JO parameters of the title glasses and the Ω_2 values are found to decrease with the increase in Eu^{3+} content which indicates that Eu^{3+} ions are located in the lower asymmetrical ligand environment and the Eu–O bond possess less covalency. The Ω_6 values of all the prepared were taken as zero because the $^5D_0 \rightarrow {}^7F_6$ transition usually occurs in the near infrared region which could not be observed due to experimental limitations.

Using the JO parameters, radiative properties such as radiative transition probability (A_R), stimulated emission cross-section (σ_p^E), branching ratios (β_R) and radiative lifetime of the $^5D_0 \rightarrow {}^7F_J$

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(J=1,2,4) transitions were obtained from the emission spectra and the same is shown in table 2. The stimulated emission cross-section and the branching ratio values should be on higher side to avail good lasing action [5]. Among the studied glasses, 1EuBP glass possess higher A_R, β_R and σ_P^E values pertaining to the $^5D_0 \rightarrow ^7F_2$ transition and the same can be suggested as an active medium for red laser applications. The decay profile of the $^5D_0 \rightarrow ^7F_2$ transition have been recorded by fixing the excitation at 395 nm and emission at 612 nm and the same is shown in figure 4. The decay curves exhibit single exponential behavior for all the studied glasses and the obtained τ_{exp} values are presented in table 2 along with the quantum efficiency values (η).

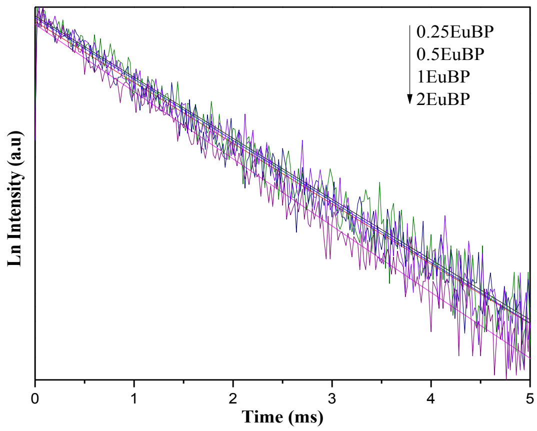

Figure 4. Decay curves of the xEuBP glasses

It is observed that the τ_{exp} values are found to be lower than the τ_{cal} values and is due to the non-radiative relaxation caused by the interaction of Eu^{3+} ions with the vibrations of the host matrix.

Table 2. The A (s^{-1}), β and (10^{-22} cm^2), τ_{cal}, τ_{exp} and η values of the xEuBP glasses

Transitions	Factors	0.25Eu BP	0.5Eu BP	1Eu BP	2Eu BP
$^5D_0 \rightarrow ^7F_1$	A	61.8	61.6	61.4	61.1
	σ_P^E	3.63	5.01	5.88	4.07
	β_R	0.313	0.303	0.253	0.263
$^5D_0 \rightarrow ^7F_2$	A	114.4	109.6	148.8	149.0
	σ_P^E	7.83	9.14	12.24	10.05
	β_R	0.597	0.609	0.683	0.658
$^5D_0 \rightarrow ^7F_4$	A	13.16	13.3	10.2	13.1
	σ_P^E	1.96	2.47	1.65	2.14
	β_R	0.068	0.067	0.044	0.057
τ_{cal} (ms)		3.774	3.610	3.247	3.450
τ_{exp} (ms)		1.857	1.844	1.832	1.817
η (%)		49	51	56	53

5. Conclusion

Eu^{3+} doped boro-phosphate glasses have been synthesized following the melt quenching technique. The decreasing δ and Ω_2 values indicate the fact that colvalency of the metal-ligand bond decreases with the increase in Eu^{3+} ion concentration in the title glasses. It is observed from all these studies that among the prepared glasses, 1EuBP glass exhibit higher A_R, β_R, σ_P^E and η values pertaining to the $^5D_0 \rightarrow ^7F_2$ transition and the same is suggested as a suitable candidate for red light emitting sources and for the fabrication of solid state lasers.

6. References

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