International Journal of Luminescence and Applications
Vol 3, No. 1, Jan 2013, Article ID: 015, pages 60 – 63

Luminescence Studies on Eu^{3+} Doped Lead Fluoroborate Glasses

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Abstract:
Two new series of Eu^{3+} ions doped lead fluoroborate glasses B_2O_3+PbO+PbF_2+SrO+BaO+Eu_2O_3 (xEPbFB)/B_2O_3+PbO+PbF_2+Eu_2O_3(ExPbFB) were prepared and their absorption and luminescence analysis have been carried out using JO theory and reported. The FTIR spectral studies explore the vibrational analyses of the prepared glasses and the increase in the formation of NBO with the addition of different modifier oxides. The covalent nature of the Eu–O bond in the prepared glasses is identified through the bonding parameter studies and it increases with the increase in Eu^{3+} ion content. The composition and concentration dependence luminescence intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ transition has been calculated to estimate the local site symmetry around the Eu^{3+} ions. JO parameters Ω_λ, (λ=2,4,6) were obtained from the emission spectra and the same is used to estimate various radiative properties for the excited levels of the Eu^{3+} ions. The decay profiles were found to be single exponential for all the title glasses. The higher lasing action corresponding to the $^5D_0 \rightarrow {}^7F_2$ emission transition at 614 nm confirm the potentially of the prepared glasses as a red laser active medium.

Keywords: AFTIR, Bonding parameter, Luminescence intensity ratio, Stimulated emission cross-section.

1. INTRODUCTION

Recently rare earth (RE) doped heavy metal oxy fluroride glasses gained vital importance due to their low phonon energy, high refractive index, low melting temperature, high polarizability, good rare-earth ion solubility and hence it increases the optical and electronic properties like radiative properties, quantum efficiency and electrical conductivity of these glasses [1]. Among the RE ions, Eu^{3+} ion has been chosen as a probe to explore the optical behavior of the lead fluoroborate glasses due to the fact that Eu^{3+} ($4f^6$) ion possess narrow band emission, almost monochromatic light and longer lifetime of the optically active state. Also the local structure around the Eu^{3+} ions can be obtained from the f-f transition spectra [2,3]. The non-degenerate $^7F_0$ ground state and the $^5D_0$ excited state of the Eu^{3+} ions are highly suitable for studying the symmetry in the host matrix [4,5]. The objective of the present work is to explore the luminescence behavior of the Eu^{3+} ions in a series of lead fluoroborate glasses through absorption and luminescence measurements.

2. EXPERIMENTAL

The Eu^{3+} doped lead fluoroborate glasses were prepared by conventional melt-quenching technique following the procedure reported in literature [5]. The starting materials used in the present work are high purity analytical grade (from Sigma Aldrich 99.99% purity) chemicals such as H_3BO_3, PbO, PbF_2, Sr_2CO_3, $BaCO_3$ and Eu_2O_3. The xEPbFB glass composition is (40-x)B_2O_3+20PbO+20PbF_2+10SrO+0BaO+xEu_2O_3 and the codes are 0.1EPbFB, 0.5EPbFB, 1EPbFB and 3EPbFB corresponding to the Eu^{3+} ion content as 0.1,0.5,1 and 3 in wt% respectively. The ExPbFB series is (99-x) B_2O_3+(x/2)PbO+(x/2)PbF_2+1Eu_2O_3 (where x = 40,50 and 60 in wt%) and the glass codes are E4PbFB, E5PbFB and E6PbFB respectively. FTIR spectra of the title glasses were measured using Perkin Elmer Peragon 500 FTIR spectrophotometer. Optical absorption spectra were recorded using Perkin Elmer Lambda 35 UV-Vis-NIR spectrometer in the wavelength range 350–2300 nm. The luminescence measurements were made using Perkin Elmer LS55 spectrometer in the wavelength range 550–725 nm. All these measurements were carried out at room temperature (RT) only.

3. RESULTS AND DISCUSSION

3.1. Vibrational studies

Figure 1 shows the FTIR spectrum of the Eu^{3+} doped 1EPbFB lead fluoroborate glass. The IR spectral vibrations are mainly divided into following regions. (i) the bands around 1200–1600 cm^{-1} are attributed to the asymmetric stretching relaxation of B–O bond of trigonal BO_3 units [5] (ii) bands in the range 850–1200 cm^{-1} are due to the B–O bond stretching of tetrahedral BO_4 units [7] (iii) peaks around 700 cm^{-1} is due to the bending of B–O–B linkages in the borate network (iv) absorption at 450 cm^{-1} is ascribed to the vibration of Pb^{2+} ions or Pb–O–B in the network vacancies [4].

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Journal ISSN No: 2277 – 6362

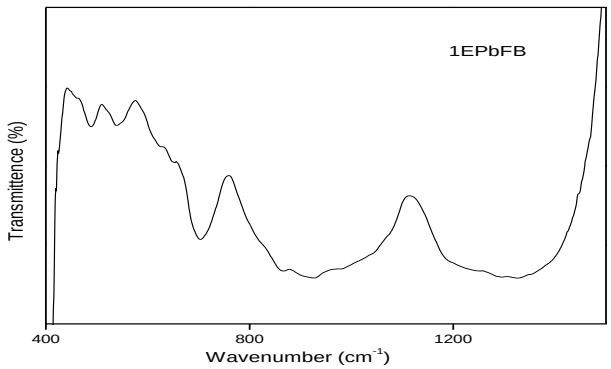

Fig.1: FTIR spectrum of 1EPbFB glass

The absorption band around 1323 cm^{-1} is assigned to the B–O asymmetric stretching vibrations of BO_3 units from various borate groups. The absorption peak appear around 1010 cm^{-1} is due to the asymmetric stretching modes of BO_4 vibrations attached with the non-bridging oxygen in the borate network [5]. Further the observed peak at 443 cm^{-1} is assigned to the existence of vibration of Pb^{2+} ions in the network vacancies [6].

3.2. Absorption and PSB studies

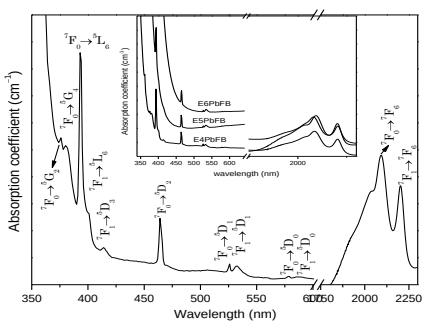

Fig.2: Absorption spectrum of 1EPbFB glass

Figure 2 shows the absorption spectrum of the Eu^{3+} doped lead fluroborate glass and the electronic transition bands originate from the $^7F_0$ and $^7F_1$ ground states of the Eu^{3+} ion and the inset shows the absorption spectra of the ExPbFB glasses. Eleven absorption bands namely $^7F_1 \rightarrow {}^7F_6$, $^7F_0 \rightarrow {}^7F_6$, $^7F_1 \rightarrow {}^5D_0$, $^7F_0 \rightarrow {}^5D_0$, $^7F_1 \rightarrow {}^5D_1$, $^7F_0 \rightarrow {}^5D_1$, $^7F_0 \rightarrow {}^5D_2$, $^7F_1 \rightarrow {}^5D_3$, $^7F_1 \rightarrow {}^5L_6$, $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5G_2$ with energies at 4539, 4775, 16985, 17275, 18781, 19022, 21558, 24086, 24952, 25381, 26256, 26554 and 27625 cm^{-1} respectively have been observed from the absorption spectra. It is observed from the inset figure 2 that, the fundamental absorption edge gradually shift towards higher energy with the increase in PbO ion content which is due to the structural rearrangement in the title glasses. The band gap values for the direct and indirect allowed transitions are found to be 3.41, 3.15 and 2.87 eV and 3.11, 2.83 and 2.64 eV for the E4PbFB, E5PbFB and E6PbFB glasses respectively. It is observed from these results that, the band gap values changes with the increase in PbO content due to structural changes and the formation of greater number of non-bridging oxygens taking place in the glass network [6]. While increasing the PbO content, it changes the oxygen bonding in the glass forming network and any change in oxygen bonding such as the formation of non-bridging oxygen changes the absorption characteristics. The degree of covalency in the bonds between the RE ion and their surrounding ligands is an important feature of the local structure and is reflected by the nephelauxetic parameter [7]. The bonding parameter (δ) can be calculated from $\delta = (1-\bar{\beta} / \bar{\beta}$, where β is the nephelauxetic ratio and the bonding parameter values are presented in table 2. It is observed that the Eu–O bond is of covalent in nature and the covalency deceases with the addition of Eu_2O_3 content in the xEPbFB glasses whereas the covalent nature increases with the increase in PbO content in ExPbFB glasses.

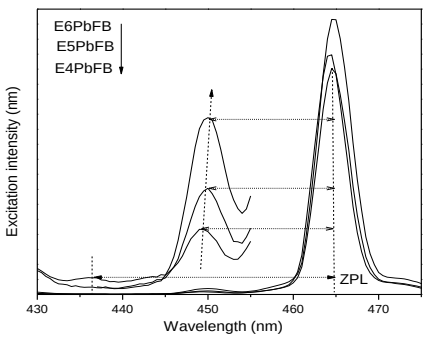

Fig .3: PSB associated with the $^7F_0 \rightarrow {}^5D_2$ transition of the Eu^{3+} doped glasses

Table 1. Bonding parameters and JO intensity parameters of the Eu^{3+} doped glasses

The local structure of the Eu^{3+} ions in the prepared glasses can be explored using phonon sideband (PSB)

Glass	$\bar{\beta}$	δ	R	Ω_2	Ω_4
0.1EPbFB	0.997	0.302	2.34	3.162	0.196
0.5EPbFB	0.9973	0.268	2.87	3.478	0.239
1EPbFB	0.9973	0.267	3.46	3.893	0.274
3EPbFB	0.9974	0.263	3.69	4.451	0.296
E4PbFB	0.9967	0.330	3.92	4.925	0.308
E5PbFB	0.996	0.355	4.29	5.264	0.286
E6PbFB	0.9968	0.317	3.86	4.293	0.207

spectra of the Eu^{3+} ions at the high energy side of the $^7F_0 \rightarrow {}^5D_2$ transition of the excitation spectra [2]. Phonon side band (PSB) associated with the $^7F_0 \rightarrow {}^5D_2$ transition deals with the local structure coordinating Eu^{3+} ions and the nature of the vibrations around the Eu^{3+} ion sites which affect the non-radiative decay of the Eu^{3+} ions [7]. The PSB associated with the excitation spectra of the prepared ExPbFB glasses are shown in figure 3. The PSB observed around 430–460 nm is amplified by 20 times of the excitation spectra of the Eu^{3+} doped lead fluoroborate glasses. The bands correspond to the absorption process is due to the transfer of excess energy from the incident photon to the lattice in the form of phonons [7]. These bands reflects the local vibrational environment due to the fact that the phonons are generated around the environment of the RE ions. The coupling of *f* electrons with the ligands gives rise to simultaneous transition between electronic states of the Eu^{3+} ions and the vibrational states of the host matrix, namely Zero phonon line (ZPL) or pure electronic transitions (PET). There are two phonon energies found to occur at around 765 and 1267 cm^{-1}. It is clearly seen from figure 3 that, the phonon energy decreases with increase in PbO content. The similar trend also observed in the case of xEPbFB glasses and the phonon energy decreases with the increase in Eu^{3+} ion concentration. The electron-phonon coupling quantity, g, can be determined from the ratio of the intensity of the PSBs and the intensity of PET using the relation $g = \int I_{PSBs}\, d\lambda \,/ \int I_{PET}\, d\lambda$. The g values are found to increase in the both xEPbFB and ExPbFB glasses which suggested that the covalency of Eu–O bond increases.

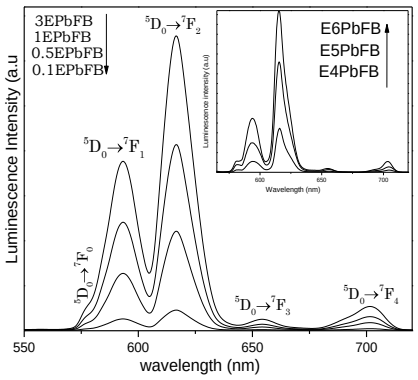

Fig.4: Luminescence spectra of Eu^{3+} doped glasses

Figure 4 shows the luminescence spectra of the Eu^{3+} doped lead fluoroborate glasses recorded monitoring an excitation at 396 nm. All the spectra exhibit emission bands at 536, 556, 581, 593, 614, 654 and 702 nm corresponding to the $^5D_1 \rightarrow {}^7F_1$, $^5D_1 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions. It is observed from the emission spectra that, the $^5D_0 \rightarrow {}^7F_2$ transition possess higher intensity than that of all other emission transitions which occurs through electric dipole transition. The $^5D_0 \rightarrow {}^7F_1$ emission originate due to the magnetic-dipole transition indicating that the Eu^{3+} ions occupy a site with inversion symmetry [3,4]. The $^5D_0 \rightarrow {}^7F_2$ emission transition originate due to an electric-dipole transition resulting large transition probability in the crystal field with inversion anti symmetry. The luminescence intensity of the $^5D_0 \rightarrow {}^7F_2$ transition of the Eu^{3+} ions in the prepared glasses is stronger than that of $^5D_0 \rightarrow {}^7F_1$ transition and further it suggest that the Eu^{3+} ions take a site with inversion anti symmetry [6].The ratio of the integrated emission intensity of the $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ transition is defined as luminescence intensity ratio (R) and is related to the strength of covalent/ionic bonding between the Eu^{3+} ion and their surrounding ligand fields and the R value decreases while the Eu–O ionicity increases [5,7]. The calculated luminescence intensity ratio values of the prepared glasses are presented in table 1. The asymmetric ratio is found to increase with an increase in Eu^{3+} ion content in the xEPbFB glass series whereas in case of ExPbFb glasses asymmetric ratio increases with an increase in PbO content.

3.3. JO intensity parameters and Radiative properties

Judd–Ofelt (JO) intensity [8,9] parameter values are measured from the luminescence spectra and are used to estimate the radiative parameters and the results are presented in table 2. The Ω_2 intensity parameter is structure sensitive and depends on the covalency of the rare earth ion site with its surrounding ligands [3−5]. The higher values of Ω_2 indicate the presence of covalent bonding between the Eu^{3+} ions and their surrounding ligands. The Ω_2 values are found to be 2.484, 2.507, 2.645 and 2.959 for the prepared Eu^{3+} doped 0.1EPbFB, 0.5EPbFB, 1EPbFB and 3EPbFB glasses respectively. It is observed from the tabulated results that, the calculated Ω_2 values are found to increase with an increase in Eu^{3+} ion concentration and it indicates the increase in covalency between rare earth ions and their surrounding ligands. The Ω_4 and Ω_6 parameters mainly depend on 'long range effects' and are related to the bulk properties and rigidity of the RE^{3+} doped materials. The trends of the JO intensity parameter values are found to follow the order as $\Omega_2 > \Omega_4 > \Omega_6$ for all the prepared glasses. The stimulated emission cross-section and branching ratio are the important laser parameters while designing new luminescent devices and hence higher values of

these parameters predict the higher luminescence efficiency of the title glasses. For all the prepared glasses, σ_P^E values are found to be higher for the $^5D_0 \rightarrow {}^7F_2$ transition and the values are found to be 13.04, 13.36, 14.28 and 15.40 corresponding to the 0.1EPbFB, 0.5EPbFB, 1EPbFB and 3EPbFB glasses respectively. The σ_P^E is found to increase in the order $^5D_0 \rightarrow {}^7F_4 < {}^5D_0 \rightarrow {}^7F_1 < {}^5D_0 \rightarrow {}^7F_2$ for all the prepared glasses. The experimental and calculated branching ratio values ($\beta_{R(cal)}$) are found to be higher for the $^5D_0 \rightarrow {}^7F_2$ transition for all the prepared glasses. The experimental and calculated branching ratio values are found to decrease in the order $^7F_2 > {}^7F_1 > {}^7F_4 > {}^7F_3 > {}^7F_0$ for the emission transitions of the Eu^{3+} ions [5]. The luminescence decay curves of the excited $^5D_0$ level for the prepared Eu^{3+} doped glasses are shown in figure 5. It is clearly observed from the figure that, the decay profiles are found to be single exponential for all the prepared glasses and the lifetime values are found to be increase with the increase in both Eu^{3+} ion and PbO content in the prepared glasses [6]. The excited state lifetime values are found to be 2.67, 2.88, 2.60 ms for the prepared E4PbFB, E5PbFB and E6PbFB glasses. The quantum efficiency (η) of the emission transition depends on the σ_P, A, τ values of the excited state, RE ion concentration and the ligand field effect. All the prepared glasses exhibit more than 50% quantum efficiency and the same can be used for suitable laser applications in the visible region.

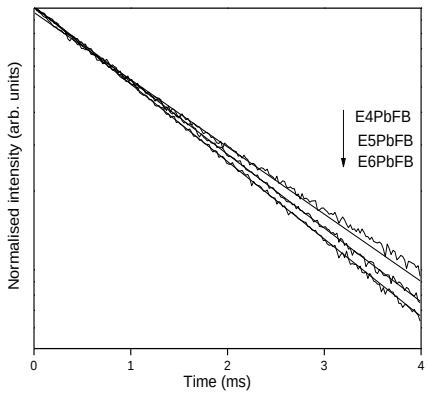

Fig. 5: Decay curves of the $^5D_0$ level of the Eu^{3+} ions in the ExPbFB glasses

4. CONCLUSION

The structural and luminescence behavior of the Eu^{3+} ions in the prepared glasses have been studied and reported. The presence of B−O bonds in the BO_3 and BO_4 units are confirmed through the FTIR spectral analysis. The covalent nature of the Eu−O bond is identified through the bonding parameter studies, higher electron coupling strength and higher R values. The higher Ω_2 values of the Judd–Ofelt parameter confirms the hypersensitive nature of the $^5D_0 \rightarrow {}^7F_2$ transition and further it indicates the covalent character of the Eu–O bond and higher asymmetry/lower symmetry in the title glasses. The measured lifetime values of the $^5D_0$ energy level of the Eu^{3+} ion in the prepared glasses are found to decrease with an increase in Eu^{3+} ion content and the observed lifetime values are almost equal due to the negligible non-radiative energy transfer between the Eu^{3+}–Eu^{3+} ions. Among the emission transitions $^5D_0 \rightarrow {}^7F_2$ level exhibit higher R, σ_P^E and β_R and higher radiative lifetime values which indicates its suitability for red laser applications.

Table2. Radiative properties (λ_p, A, $\sigma_P^E \times 10^{-22} cm^2$, β_R, τ_{cal} ms), of the $^5D_0 \rightarrow {}^7F_2$ emission level of Eu^{3+} ions

Glass	λ_p	$\Delta\lambda$	A	σ_P	β_R	τ_{cal}
0.1EPbFB	615	6.35	98.44	13.04	0.647	2.86
0.5EPbFB	615	6.86	110.3	13.36	0.665	2.81
1EPbFB	615	7.24	125.5	14.28	0.687	2.73
3EPbFB	615	7.71	145.9	15.40	0.711	2.52
E4PbFB	615	7.23	107.2	12.09	0.711	3.01
E5PbFB	616	6.66	187.2	21.77	0.727	3.58
E6PbFB	616	7.28	168.7	18.34	0.711	3.99

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