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Structural and luminescence behavior of lead fluoroborate glasses containing Eu^{3+} ions

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ABSTRACT

Structural and luminescence behavior of lead fluoroborate glasses prepared with the chemical composition $(50-x)B_2O_3+20PbO+20PbF_2+10ZnO+xEu_2O_3$ (where $x=0.05$, 0.1, 0.5, 1, 2 and 3 in wt%) have been studied by varying the trivalent europium ion content. Structural behavior of the prepared glasses has been explored through XRD, FTIR and Raman spectral analysis. Optical characterization has been made using UV–vis–NIR absorption, excitation, luminescence and decay curves of the present glasses. Through the absorption spectra, bonding parameters ($\overline{\beta}$ and δ) have been determined and the positive value of δ indicates the covalent nature. The band gap values are found to decrease with increasing Eu^{3+} ion concentration whereas Urbach's energy values are found to increase. The PSB associated with the $^7F_0 \rightarrow {}^5D_2$ excitation transition is used to determine the electron–phonon coupling constant and the local structure of the Eu^{3+} ions with its surrounding ligands. The 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. Judd–Ofelt (J–O) intensity parameters Ω_λ ($\lambda=2,4,6$) were obtained from the emission spectra and the same is used to estimate the transition probability (A), stimulated emission cross-section (σ_P^E) and branching ratios (β_R) 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 values of A, σ_P^E and β_R corresponding to the $^5D_0 \rightarrow {}^7F_2$ emission level at 614 nm confirm the potential of the present glasses as a red laser active medium.

1. Introduction

Over the past few decades, research on structural and optical properties of rare earth (RE) doped oxyfluoride glasses gained lot of interest due to their technological applications in the field of photonics and optoelectronics, as display devices, optical amplifiers, laser materials, sensors, high density optical memory devices, solid state lasers and amplifiers for fiber-optic communication [1,2]. In addition to that, glasses containing heavy metal oxides (HMO) such as Pb, Cd and Bi have also become of vital importance due to their low phonon energies, high refractive indices, low transition temperature, high polarizability and good rare-earth ions solubility and hence it significantly increases the optical and electronic properties such as radiative properties, quantum efficiencies and electrical conductivity of these glasses [3,4]. Further, fluoride glasses offer lower phonon energy than oxide matrices, whereas the oxide matrices possess advantages like higher mechanical strength, chemical durability and thermal stability [5]. In general, host glasses with low phonon energy provide less non-radiative relaxation rates and high quantum efficiencies. Transparent oxyfluoride glasses combine the advantages of both the fluoride and oxide matrices and are considered to be a good choice as hosts for RE ions and thus turned to be one of the most promising optical materials.

Among the lanthanides, trivalent europium ion Eu^{3+} 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 Eu^{3+} ions can be obtained from the f–f transition spectra. 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 and in-homogeneity in the host matrix [6,7]. The Eu^{3+} ions doped into several glasses and crystals have been investigated in order to obtain the strong red luminescent materials because of its hypersensitive radiative emission transition at 616 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition and non-radiative emission transition at 593 nm corresponding to the $^5D_0 \rightarrow {}^7F_1$ transition [8]. Thus the radiative to the non-radiative luminescence intensity ratio is widely used to investigate the chemical bond of anions

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coordinating the Eu^{3+} ions and it can be modulated by varying the glass composition as well as the RE ion concentration [9,10]. The trivalent Eu^{3+} ion is also observed as a phonon sideband (PSB) on the high energy side of the $^7F_0 \rightarrow {}^5D_2$ transition in the excitation spectra which is due to the local structure coordinating Eu^{3+} ions [11,12]. The changes in the local environment of the Eu^{3+} ions in glasses have been widely investigated and reported by many researchers [13–15]. Though a large amount of literature is available on Eu^{3+} doped borate glasses [7–9], studies on optimization of optical properties by varying the Eu^{3+} ion concentration in fluoroborate based glasses is meager.

The aim of the present study is (i) to synthesis Eu^{3+} doped lead fluoroborate glasses, (ii) to explore the presence of various functional groups through FTIR and Raman spectral analysis, (iii) to examine the energy levels and bonding parameters ($\overline{\beta}$ and δ) to claim covalent/ionic nature of the prepared glasses, (iv) to determine the optical band gap energy, band tailing parameter and Urbach's energy at the fundamental absorption edge, (v) to determine the electron–phonon coupling constant through the phonon side band spectrum (PSB) associated with the $^7F_0 \rightarrow {}^5D_2$ excitation transition, (vi) to evaluate the J–O parameters (Ω_λ, λ=2,4,6) using Judd–Ofelt (J–O) theory [16,17] and to compare the trends of Ω_λ, with respect to other Eu^{3+} doped glasses, (vii) to determine radiative properties for significant energy levels and to compare the results with similar Eu^{3+} systems and finally (viii) to study the excited state dynamics of the Eu^{3+} ions through the lifetime of the $^5D_0$ energy level in the title glasses and to compare the results with similar studies.

2. Experimental

The Eu^{3+} doped lead fluoroborate glasses were prepared by following melt-quenching technique following the procedure reported in literature [6,12]. 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, ZnO and Eu_2O_3.

Density of the present glasses was measured using xylene as an immersion liquid following Archimedes's principle. The refractive index of the glasses was measured by using Abbe Refractometer with monobromonapthalene as the contact liquid at sodium wavelength (589.3 nm). The sample codes, refractive index and density of the Eu^{3+} doped lead fluoroborate glasses are presented in Table 1. The amorphous nature of the title glasses were confirmed through the X-ray diffraction pattern recorded using JEOL 8030C X-ray Diffractometer with CuK_α radiation. Fourier transform infrared (FTIR) spectra of the glasses were measured using Perkin Elmer Peragon 500 FTIR spectrophotometer with a spectral resolution of $\pm 4.0\ cm^{-1}$. Optical absorption spectra were recorded using Perkin Elmer Lambda 35 UV–vis spectrometer in the wavelength range 350–650 nm with a spectral resolution of ± 0.1 nm. The luminescence measurements were made using Perkin Elmer LS55 spectrometer in the wavelength range 500–725 nm with a resolution of ± 0.1 nm. The lifetime measurements were made using Scientech modular spectrophotometer using xenon flash lamp as an excitation source. All these measurements were carried out at room temperature (RT) only.

3. Results and discussion

3.1. Fourier transform infra-red spectral analysis

The XRD pattern of the Eu^{3+} doped 1EPbFB lead fluoroborate glass shown in Fig. 1 as a representative case exhibit a broad scattering at lower angle suggesting a structural disorder which confirms the amorphous nature of the present xEPbFB glasses.

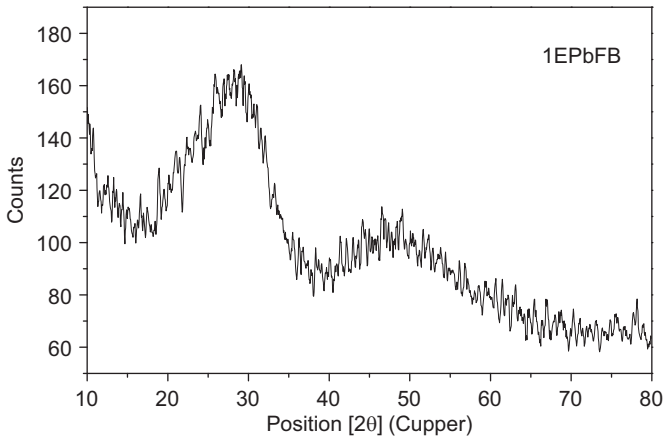

Fig. 1. XRD pattern of the Eu^{3+} doped 1EPbFB lead fluoroborate glass.

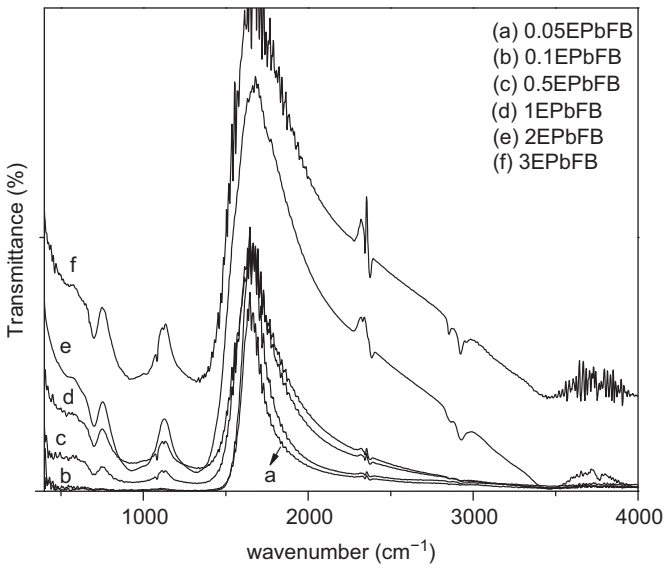

Fig. 2. FTIR spectra of the Eu^{3+} doped lead fluoroborate glasses.

Table 1
Sample code and compositions, refractive index and density of the Eu^{3+} doped lead fluoroborate glasses.

Sample code	Compositions	Refractive index	Density (ρ) (g/cm^3)
0.05EPbFB	$49.95B_2O_3+20PbO+20PbF_2+10ZnO+0.05Eu_2O_3$	1.901	3.731
0.1EPbFB	$49.9B_2O_3+20PbO+20PbF_2+10ZnO+0.1Eu_2O_3$	1.915	3.846
0.5EPbFB	$49.5B_2O_3+20PbO+20PbF_2+10ZnO+0.5Eu_2O_3$	1.928	3.878
1EPbFB	$49B_2O_3+20PbO+20PbF_2+10ZnO+1Eu_2O_3$	1.937	3.902
2EPbFB	$48B_2O_3+20PbO+20PbF_2+10ZnO+2Eu_2O_3$	1.945	3.937
3EPbFB	$47B_2O_3+20PbO+20PbF_2+10ZnO+3Eu_2O_3$	1.951	3.979