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Effect of modifier oxides on absorption and emission properties of Eu^{3+} doped different lithium fluoroborate glass matrices

Y.C. Ratnakaram *, A. Balakrishna, D. Rajesh

Department of Physics, S.V. University, Tirupathi 517 502, A.P., India

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ABSTRACT

Eu^{3+} doped lithium fluoroborate glass with different modifier oxides ($Li_2B_4O_7$–BaF_2–NaF–MO where M=Mg, Ca, Cd and Pb) and combinations of modifier oxides ($Li_2B_4O_7$–BaF_2–NaF–MgO+CaO, $Li_2B_4O_7$–BaF_2–NaF–CdO+PbO) were prepared by means of melt quenching method. These glass samples were analyzed by absorption, photoluminescence and decay curve measurements. The relative merits of thermal correction to the spectral intensities originating from the ground state ($^7F_0$) of different absorption bands of Eu^{3+} are calculated. From the optical absorption measurements and using the Judd–Ofelt (J–O) theory, J–O parameters (Ω_λ λ=2, 4 and 6) have been obtained which are used to predict the radiative properties such as radiative transition probabilities (A), radiative life-times (τ_R), and branching ratios (β_r) for certain transitions in all the glass matrices. From the emission spectra, peak stimulated emission cross-sections (σ_P) are obtained for the emission transitions, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ of Eu^{3+} in lithium fluoroborate glass matrix with different modifier oxides. The fluorescence decay curves of the $^5D_0 \rightarrow {}^7F_2$ transition have been measured and analyzed for all the glass matrices.

1. Introducion

Rare earth doped glasses are well known candidates for many applications such as optical fiber amplification, up conversion laser and many other applications [1–3]. Among various rare earth ions, Eu^{3+} is an important ion for several studies due to its simple electronic energy level scheme [4–6]. Eu^{3+} ions exhibit pure magnetic and electric dipole transitions which make it a very sensitive probe for rare earth ion site symmetry. Eu^{3+} ions are more particularly used as luminescent probe in nuclear waste glasses [7,8]. Changes in the local environment of Eu^{3+} ions in glasses show strong modifications in optical properties. Recently, Stambouli et al. [9] reported energy transfer induced Eu^{3+} photoluminescence enhancement in tellurite glass. Ye et al. [10] reported luminescence and energy transfer of Eu^{2+}/Mn^{2+} co doped SiO_2–Al_2O_3–ZnO–K_2O glass ceramics for white LEDs. Luminescence and second harmonic generation in Eu^{3+}/Eu^{2+} embedded B_2O_3:$LiNbO_3$ non-linear glass ceramics were reported by Yadav et al. [11]. Optical and fluorescence spectroscopy of Eu_2O_3 doped P_2O_5–K_2O–KF–MO–Al_2O_3 (M=Mg, Sr and Ba) glasses were reported by Upendra Kumar et al. [12]. Mohapatra et al. [13] reported photoluminescence investigations of rare earth (Eu and Gd) doped nuclear waste glasses. Structral, optical and thermal studies of Eu^{3+} ions in lithium fluoroborate glasses were reported by Babu and Jayasankar [14]. Karunakaran et al. [15] reported structural, optical and thermal studies of Eu^{3+} ions in other lithium fluoroborate glasses. In the present work, spectroscopic investigations on Eu^{3+} doped lithium fluoroborate glass with different modifiers are reported. The present investigation also aims at a study of emission properties by the application of the Judd–Ofelt theory to interpret the local environment of Eu^{3+} ions in all the glass matrices studied.

Specifically, the present study focuses on exploring the effect of modifier oxides on Judd–Ofelt parameters (Ω_2, Ω_4, and Ω_6), radiative lifetimes (τ), branching ratios (β) and peak stimulated emission cross-sections (σ_P) in lithium fluoroborate glass matrix. From these studies, structural changes of the glass matrices and certain transitions which are useful for laser excitation in that glass matrix are reported.

2. Experimental

In the present work, all the glass samples were prepared using standard melt quenching technique using the analytical grade chemicals, $Li_2B_4O_7$, BaF_2, NaF, $CdCO_3$, Pb_3O_4, $MgCO_3$, $CaCO_3$, and Eu_2O_3. The glass compositions studied in the present work are $48Li_2B_4O_7+20BaF_2+10NaF+x$ (where $x=20MgCO_3$, $20CaCO_3$, $20CdCO_3$, $20Pb_3O_4$, $10MgCO_3+10CaCO_3$ and $10CdCO_3+10Pb_3O_4$) $+0.5Eu_2O_3$. The details of experimental methods are given in our

* Corresponding author. Tel./fax: +91 9440751615.
E-mail address: ratnakaramsvu@gmail.com (Y.C. Ratnakaram).

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earlier articles [12,13]. Melting temperatures and times of melt are in the range 950–1050 °C and 1–1.5 h for different modifier oxides in the above glass matrix. The samples were polished to obtain a smooth transparent and uniform surface for optical measurements. The densities of the glass samples were determined by Archimedes method using xylene as the immersion liquid and they are accurate to ± 0.001 g/cm^3. The refractive indices of the glass samples were measured using an Abbe refractometer at sodium wavelength (589.3 nm). These values are in the range 1.653–1.656 for different lithium fluoroborate glass matrices. Absorption spectra in the wavelength range 300–2300 nm were measured using JASCO V570 spectrophotometer with a spectral resolution of 0.1 nm. Emission spectra and decay curve measurements were measured using a JOBIN YVON Fluorolog-3 fluorimeter using xenon flash lamp.

3. Results and discussion

3.1. Absorption spectra and energy values

Optical absorption spectra of Eu^{3+} doped different lithium fluoroborate glasses recorded in the UV–vis and NIR regions are shown in Fig. 1a and b respectively. The observed absorption bands have been divided into two groups depending on the spectra recorded in the regions 350–550 nm and 1900–2300 nm. The observed absorption bands and their energies of Eu^{3+} ions in different (Mg, Ca, Cd, Pb, Mg–Ca and Cd–Pb) fluoroborate glass matrices studied in the present work are shown in Table 1. In the present work, nine absorption peaks are observed in which seven peaks are in the UV–vis region and two peaks are in the NIR region. Though there is no much variation in the peak positions of different absorption bands, there is variation in the spectral profiles of absorption peaks. Since the closely spaced ^7F_J ($J=0$, 1, 2, 3, 4, 5 and 6) levels of Eu^{3+} have energy level differences of the order of KT, where K is the Boltzmann constant and T is the absolute temperature, they are thermally populated at room temperature unlike the other lanthanides. Hence, in the absorption spectrum of Eu^{3+} ion, the transitions start from both $^7F_0$ and $^7F_1$ levels. Because of the overlapping of these levels, the absorption spectra are to be recorded at lower temperature (77 K) or the spectral intensities at room temperature are to be corrected to thermalization effect. In the present work, spectral intensities were calculated for all the absorption bands in all the glass matrices and the corrected spectral intensities were also obtained considering the thermalization effect using the formulae given in Ref. [16]. Spectral intensities and the corrected spectral intensities of all the observed absorption bands are presented in Table 2. From the table it is observed that the spectral intensities of the transitions, $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5L_7$ (as the spectral profiles of these two transitions are broad) are highest in calcium and lowest in cadmium glass matrix among the four glass matrices (Mg, Ca, Cd and Pb) indicating highest and lowest asymmetries of the glass matrices. In the case of mixed glass matrices (Mg–Ca and Cd–Pb), the spectral intensities were found increasing which indicates increasing asymmetry of the glass matrices.

3.2. Emission spectra and Judd–Ofelt parameters

The photoluminescence spectra of Eu^{3+} doped different lithium fluoroborate glass matrices obtained by exciting the samples with 395 nm at room temperature are shown in Fig. 2.

Table 1
Energies (υ) (cm^{-1}) of the observed absorption bands of Eu^{3+} doped lithium fluoroborate glass matrix with different modifier oxides.

S. no.	Transition	Mg	Ca	Cd	Pb	Mg–Ca	Cd–Pb
1	$^7F_1 \rightarrow {}^7F_6$	4546	4530	4542	4542	4551	4526
2	$^7F_0 \rightarrow {}^7F_6$	4778	4790	4778	4793	4790	4756
3	$^7F_1 \rightarrow {}^5D_1$	18,444	18,444	18,460	18,425	18,463	18,426
4	$^7F_0 \rightarrow {}^5D_1$	18,909	18,862	18,965	18,909	18,909	18,909
5	$^7F_1 \rightarrow {}^5D_2$	20,860	20,837	20,880	20,888	20,811	20,877
6	$^7F_0 \rightarrow {}^5D_2$	21,678	21,637	21,696	21,704	21,652	21,653
7	$^7F_0 \rightarrow {}^5D_3$	24,196	24,178	24,178	24,242	24,156	24,248
8	$^7F_0 \rightarrow {}^5L_6$	25,542	25,519	25,599	25,585	25,542	25,542
9	$^7F_0 \rightarrow {}^5L_7$	26,780	26,885	–	26,820	26,740	26,740

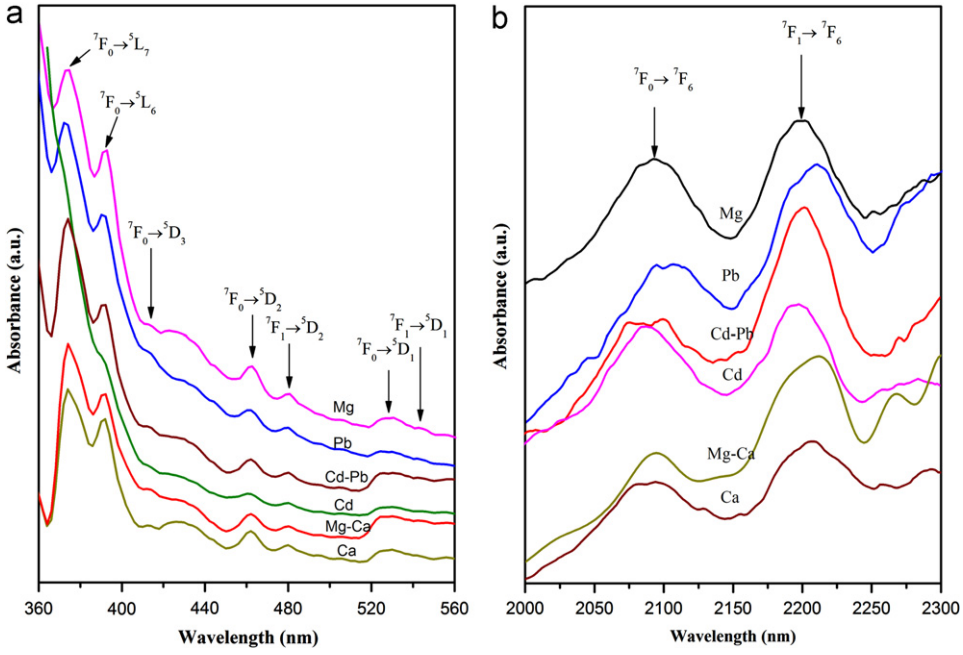

Fig. 1. (a) Optical absorption spectra of Eu^{3+} doped lithium fluoroborate glass matrix with different modifier oxides (UV–vis region).(b) Optical absorption spectra of Eu^{3+} doped lithium fluoroborate glass matrix with different modifier oxides (NIR region).