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Kinetics of fluorescence properties of Eu^{3+} ion in strontium-aluminium-bismuth-borate glasses

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Abstract: Eu^{3+} doped strontium-aluminium-bismuth-borate glasses with the chemical composition $(50–x)B_2O_3+20Bi_2O_3+7AlF_3+8SrO+15SrF_2+xEu_2O_3$ (where x=0.1 mol.%, 0.5 mol.%, 1.0 mol.% and 1.5 mol.%) were prepared by the conventional melt quenching technique. Structural properties of the prepared glasses were analysed through X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and Raman spectral techniques. Thermal stability of glass was analysed by differential thermal analysis (DTA) curve. Photoluminescence characteristics were studied using excitation, emission spectra and decay curves of Eu^{3+} doped strontium-aluminium-bismuth-borate glasses. The Judd-Ofelt (J-O) intensity parameters, Ω_λ (λ=2, 4 and 6) were obtained using emission spectra and was used to identify the nature of Eu^{3+} ions with their surrounding ligands. Using J-O parameters the transition probabilities (A), stimulated emission cross-sections σ_P^E, branching ratios (β_R) and radiative lifetimes (τ_{meas} and τ_{cal}) were evaluated for the $^5D_0\rightarrow{}^7F_J$ (J=0, 1, 2, 3 and 4) transition of Eu^{3+} ions in the present glasses. The decay profiles were found to be non exponential for all the concentrations and the measured lifetimes (τ_{meas}) were obtained from the decay profiles. The higher values of A, σ_P^E, β_R and quantum efficiency (η) for $^5D_0\rightarrow{}^7F_2$ emission transition at 617 nm confirmed the present glass was as active medium for red laser emission applications.

Keywords: absorption; photoluminescence; Judd-Ofelt analysis; decay curves; rare earths

Trivalent rare earth ion doped glasses are good optical materials, which are used for optical wave guides in optical fiber communication systems, laser devices, and optical amplifiers[1–3]. The luminescence of rare earth doped materials is due to the 4f-4f transitions. This luminescence is due to the shielding effect of the outer orbital (5s and 5p) on the 4f electrons[4]. Among various glasses, borate glasses are excellent host matrices because boric oxide (B_2O_3) acts as a good glass former and flux material[5]. Glasses containing bismuth oxide have a wide range of practical applications. The introduction of heavy metal compounds such as Bi_2O_3, PbO, PbF_2, etc., in conventional glasses like silicate and borate glasses, decreases the host phonon energy and thereby improves the effective fluorescence[6,7] and also the addition of AlF_3 minimizes the phonon energy of the host glass matrix[8]. The Bi_2O_3 content in the glass host improves chemical durability of glass[9]. Even though Bi_2O_3 is not a classical network former, it has some superior physical properties like high density and high refractive index. Rare earth ion doped glasses are not only extended up to infrared region, but also interested in visible region for some optical device applications[10,11].

Eu^{3+} ion has great importance to study many optical properties due to its simple electronic energy level scheme[12–14]. Eu^{3+} ion doped glasses are widely used for visible laser devices, phosphors and LEDs, they emit orange or red colour light having high intensity and monochromaticity[15–18]. Judd-Ofelt[19,20] intensity parameters are calculated from emission transitions $^5D_0\rightarrow{}^7F_2$, $^7F_4$ and $^7F_6$ by Peng and Izumitani[21]. But these parameters are evaluated from absorption transitions $^7F_0\rightarrow{}^5D_2$, $^5D_4$ and $^5L_6$ by Van Deun et al.[22]. In the present study, the authors followed the method put forward by Peng and Izumituni[21] in the characterization of Eu^{3+} doped glasses. Recently, Arunkumar and Marimuthu[23] have reported the structural and luminescence studies of Eu^{3+} doped B_2O_3–Li_2O–MO–LiF (M=Ba, Bi_2, Cd, Pb, Sr_2 and Zn) Glasses. Pavani et al.[24] have reported photoluminescence characteristics of Eu^{3+} doped calcium fluoroborate glasses with different concentrations of Eu_2O_3, Stambouli et al.[25] have reported optical and spectroscopic properties of Eu-doped tellurite glasses and glass ceramics. Maheshwaran and Marimuthu[26] have reported concentration dependent Eu^{3+} doped boro-tellurite glasses—structural and optical investigations. Ratnakaram et al.[27] reported effect of modifier oxides on absorption and emission properties of Eu^{3+} doped different lithium fluoroborate glass matrices.

In the present work, different concentrations of Eu_2O_3 doped strontium-aluminium-bismuth-borate glasses (SABiB) were prepared and investigated their structural

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and optical properties. The XRD and Raman spectroscopy were used to identify glass nature and structural groups present in the SABiB glass respectively. Surface morphology of the SABiB glass was examined by SEM image. Elemental composition of the present glass matrices was confirmed based on EDS spectra. Thermal stability of glass samples was estimated by DTA traces. Photoluminescence studies were used to calculate J-O parameters (Ω_2 and Ω_4), transition probabilities (A), effective linewidths ($\Delta\nu_{eff}$), branching ratios (β), stimulated emission cross-sections (σ_p^E), radiative lifetimes (τ_{cal} and τ_{meas}) of the excited state $^5D_0$ and quantum efficiency (η).

1 Experimental

1.1 Glass preparation

The Eu^{3+} doped strontium-aluminium-bismuth-borate glasses with composition, $(50–x) B_2O_3+20Bi_2O_3+7AlF_3+8SrO+15SrF_2+xEu_2O_3$ (where x=0.1 mol.%, 0.5 mol.%, 1.0 mol.%, 1.5 mol.% referred to as SABiBEu01, SABiBEu05, SABiBEu10, and SABiBEu15 glasses respectively) were prepared by melt quenching method. The high purity starting chemicals H_3BO_3, Bi_2O_3, AlF_3, Sr_2CO_3, SrF_2 and Eu_2O_3 were weighed about 8 g, thoroughly ground in an agate mortar and melted in an electric furnace at 1150 ºC for 45 min. During melting the chemicals in the crucible were stirred for bubble free and homogenous mixing. The melt was then poured on to a preheated brass plate, to get uniform thickness which was pressed by another brass plate. Then the glasses were annealed at 350 ºC for 3 h to improve the mechanical strength.

1.2 Measurements

The density of samples was measured by the Archimedes principle using xylene as immersion liquid. The refractive indices were measured by using an Abbe refractometer with sodium vapour lamp (589.3 nm) and 1-monobromonapthalin ($C_{10}H_7Br$) as contact liquid. The physical parameters like concentration of rare earth ion, density, thickness, refractive index, dielectric constant, reflection losses, polaron radius and inter-ionic distance are calculated for all the glass matrices and these are presented in Table 1.

X-ray diffraction patterns were obtained by using an INEL C120 diffractometer employing Co Kα radiation which conform the amorphous nature of the glass sample. To analyse surface morphology and to confirm elemental compositions of present SABiB glass samples, the SEM image and EDS spectrum were recorded by using a Carl Zeiss EV0-MA15 scanning electron microscope. To confirm structural groups in the present glass samples, Raman spectrum was recorded using a Horiba Jobin Yvon No. HR 800 Raman spectrophotometer with spectral resolution of 1 cm^{-1}. The DTA was studied by TA-Q20-2047 Differential Scanning Calorimeter in nitrogen purge in the temperature range 20–900 ºC with an increasing rate of 10 ºC/min. The excitation, emission spectra and decay spectral profiles of Eu^{3+} doped glasses were recorded using a JOBIN YVON Fluorolog-3 spectrophotometer with spectral resolution of 0.1 nm by exciting with the xenon lamp at 465 nm wavelength. All the spectral measurements were carried out at room temperature only.

Table 1 Physical properties of Eu^{3+} ion doped strontium-aluminum-bismuth-borate glass (for 1.0 mol.%)

S. No	Physical properties	Value
1	Density/(g/mL)	4.271
2	Thickness/cm	0.194
3	Refractive index (n)	1.652
4	Dielectric constant (ε)	2.729
5	Concentration N/(10^{19} ions/cm^3)	1.598
6	Reflection losses R/%	6.044
7	Polaron radius r_p/nm	1.599
8	Inter-ionic distance r_i/nm	3.9701

2 Theory

2.1 Physical properties

Rare earth ion concentration effects the laser action of the host material. The number of ions per cubic centimetre or density of ions is

$$N(\text{ions/cm}^3) = \frac{x\rho N_A}{M} \tag{1}$$

where x is the mol fraction of rare earth oxide, ρ is the density of the glass, N_A is the Avogadro number and M is the average molecular weight or molar mass of the glass.

2.2 Oscillator strengths

According to the Judd-Ofelt theory[19,20], the oscillator strength, f_{Cal} (ΨJ, $\Psi' J'$) of an electric dipole absorption transition from the initial (ground) state ΨJ, to the final (excited) state $\Psi' J'$, are calculated using,

$$f_{cal}(\psi J, \psi' J') = \frac{8\pi^2 mc\nu}{3h(2J+1)}\left[\frac{(n^2+2)^2}{9n}\right] \sum_{\lambda=2,4,6} \Omega_\lambda \left(\psi J \| U^\lambda \| \psi' J'\right)^2 \tag{2}$$

where m is the mass of the electron, c is the velocity of light in vacuum, h is the Planck's constant, ν is the mean energy of the transition (cm^{-1}), J is the total angular momentum of the ground state, ($2J$+1) is the degeneracy of the ground state, and n is the refractive index of host medium, $\frac{(n^2+2)^2}{9n}$ is the Lorentz local field correction term for