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Emission analysis of CdO–Bi_2O_3–B_2O_3 glasses doped with Eu^{3+} and Tb^{3+}

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Abstract

This article reports on the emission properties of cadmium bismuth borate (CdBiB) glasses as a function of doping concentrations of Eu^{3+} and Tb^{3+} ions. The functional groups present in the glasses have been identified by analyzing FT-IR spectra. The emission spectra of Eu^{3+} and Tb^{3+}:CdBiB glasses have shown reddish green emissions at 616 nm ($^5D_0 \rightarrow {}^7F_2$) under the excitation at 465 nm and at 547 nm ($^5D_4 \rightarrow {}^7F_5$) under the excitation at 485 nm, respectively. The Judd–Ofelt (J–O) theory was applied to evaluate the J–O intensity parameters from the absorption and the emission spectra; by using the J–O intensity (Ω_λ) parameters, spontaneous emission transition probability (A), total radiative transition rate (A_T), radiative lifetime (τ_R) and branching ratios (β) of the various emission transitions have been computed for both Eu^{3+} and Tb^{3+}:CdBiB glasses. The quenching behavior in the emission intensity with increased concentration of Eu^{3+} and Tb^{3+} was observed, which could be useful for optimizing the compositions toward practical applications.

Keywords: C. Optical properties; D. Glass

1. Introduction

Inorganic luminescent compounds such as bismuth borate glasses are known to have advantageous characteristics such as physical and chemical stability, high refractive index, extensive glass formation range, low melting temperature, long infrared (IR) cutoff for large third order nonlinear optical susceptibility. The dopant controllability and transparency in the IR range have deserved extensive research works in recent years [1]. Further research interests in bismuth borate glasses is also due to their engineering applications in the fields of thermal and mechanical sensors, optical fiber amplifiers, laser materials, optoelectronics and magneto optical devices, electro-optic switches, solid state laser materials, photonic switches, reflecting windows, glass ceramics and layers for optical and electronic devices etc. [2,3]. In cadmium bismuth borate glasses, B_2O_3 could be found as a network former (NWF) and other oxides such as Bi_2O_3 and CdO are used as the network modifiers (NWM) when those were added to the B_2O_3 based structure. The small field strength of Bi^{3+} ions limits the role of Bi_2O_3 into a network modifier in general whereas, in combination with B_2O_3, there is a possibility for the glass formation over a reasonably large composition range [4]. Glasses are considered as the fine host materials because of their properties such as good mechanical and thermal stability, flexibility to add rare earth ions in different concentrations, easy preparation, possibility of easily obtaining bulk samples and the low cost. Moreover, the preparation of rare earth ions doped glasses has also engrossed the researchers, because of their applications in solid state lasers, channel waveguides, infrared to visible up-converters, field emission displays and optical fiber amplifiers for optical communications [5,6]. In the rare earth family, one of the vital luminescent activator ion is Eu^{3+} with reddish emission at 612 nm in various host lattices via the transition from $^5D_0$ to $^7F_2$. Furthermore,

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Eu^{3+} doped red phosphors are exceptionally useful in the preparation of white light emitting diodes and the relevant field emission devices [7]. Another imperative ion among the rare earth elements is Tb^{3+} which shows an intense green emission in different hosts useful for the development of efficient green emitting phosphors and scintillator materials. Previously, we have reported optical absorption, NIR emission spectra, and the analysis based on the Judd–Ofelt (J–O) theory of Nd^{3+}, Er^{3+}, Sm^{3+} and Dy^{3+}:CdBiB glasses [8–11]. In this article, we reports on the emission properties of different concentrations of Eu^{3+} and Tb^{3+} ions doped CdBiB glasses and also the J–O theory was applied to evaluate the intensity parameters and radiative properties of the various emission transitions of Eu^{3+} and Tb^{3+}:CdBiB glasses.

2. Experimental studies

Eu^{3+} and Tb^{3+}:CdBiB glasses were prepared by the melt quenching method. The starting chemicals used were reagent grade of H_3BO_3, Bi_2O_3, CdO, Eu_2O_3 and Tb_2O_3. The chemical compositions of the prepared glasses are as follows:

$$(30-x)Bi_2O_3–60B_2O_3–10CdO–xEu_2O_3/Tb_2O_3$$

where x=0.25, 0.5, 1.0, 2.0 and 2.5 mol%.

The starting chemicals were finely powdered in an appropriate stoichiometric ratio and then mixed thoroughly before each batch (~10 g) was melt by using alumina crucibles in an electric furnace at 950 °C for an hour. These melts were quenched in between two brass plates and thus have grown to form optical glasses with a uniform thickness of 0.3 cm covering 2–3 cm diameter.

FT-IR spectra were recorded on a Perkin-Elmer Spectrum1 spectrometer with KBr pellets over a broad range (4000–450 cm^{-1}). The prepared glass samples were shaped and polished to get thickness of 0.30 cm before the measurements on their physical and optical properties. The refractive indices (n) were measured using an Abbe′s refractometer at sodium wavelength of 589.3 nm with 1-bromonapthlin (C10H7Br) as contact liquid. The refractive indices were found to be 1.942 and 1.937 for 1.0 mol% of Eu^{3+} and Tb^{3+}:CdBiB glasses, respectively. The densities of the samples, measured by the Archimedes method using distilled water as an immersion liquid, were estimated to be 5.01 and 5.28 for 1.0 mol% of Eu^{3+} and Tb^{3+}:CdBiB glasses, respectively. The physical properties of 1.0 mol% of Eu^{3+} and Tb^{3+}:CdBiB glasses are further summarized in Table 1. The optical absorption spectra were recorded by using an UV–vis–NIR spectrophotometer (Varian Cary 5E) in the wavelength region of 450–2500 nm. Room temperature excitation and emission spectra were recorded by Jobin Yvon Fluorolog-3 spectrofluorometer with xenon flash lamp as an excitation source.

3. Results and discussion

3.1. Eu^{3+}:CdBiB glasses

Fig. 1 presents the FT-IR spectrum of (1.0 mol%) Eu^{3+}:CdBiB glass. From this spectrum the functional groups present in the glass composition have been identified. The IR absorption band at 518 cm^{-1} is assigned to Bi–O–Bi stretching vibrations; the band at 707 cm^{-1} is due to B–O–B bending vibrations; the asymmetric stretching vibrations of the B–O bonds are located at 996 cm^{-1}; the absorption band at 1318 cm^{-1} is due to the symmetric stretching vibrations of B–O bonds in BO_3 units [12]. The absorption band at 1635 cm^{-1} is assigned to the asymmetric stretching relaxation of the B–O bond of the BO_3 units [13]. The bands at 2857 cm^{-1} and 2915 cm^{-1} represents the presence of hydrogen bonding and the broad band at 3431 cm^{-1} is duo to the O–H stretching vibrations and confirms the presence of OH^- groups [14].

Absorption spectrum of (1.0 mol%) Eu^{3+}:CdBiB glass measured at room temperature in the visible and NIR regions are shown in Figs. 2 and 3, respectively. From the absorption spectra in Fig. 2 four weak absorption bands are observed at 464 nm, 526 nm, 533 nm, and 579 nm which correspond to the transitions $^7F_0\rightarrow{}^5D_2$, $^7F_0\rightarrow{}^5D_1$, $^7F_1\rightarrow{}^5D_1$, and $^7F_0\rightarrow{}^5D_0$ whereas two intense bands at 2092 nm and 2207 nm in Fig. 3 are associated with the transitions $^7F_0\rightarrow{}^7F_6$ and

Table 1
Physical properties of 1.0 mol% of Eu^{3+} and Tb^{3+}:CdBiB glasses.

Physical quantities (unit)	Eu^{3+}:CdBiB glass	Tb^{3+}:CdBiB glass
Sample thickness (cm)	0.30	0.30
Refractive index (n)	1.942	1.937
Density (gm/cm^3)	5.01	5.28
Concentration (mol/l)	0.265	0.279
Concentration (ions $cm^{-3}\times10^{20}$)	1.599	1.684
Average molecular weight (g)	188.58	188.72
Dielectric constant (ε)	3.771	3.752
Molar volume V_m (cm^3/mol)	37.641	35.742
Glass molar refractivity (cm^{-3})	18.074	17.101
Electronic polarizability α_e ($\times10^{-24}$ cm^3)	7.88	6.781
Reflection losses R (%)	10.252	10.177
Polaron radius r_p (Å)	5.450	7.296
Interionic distance r_i (Å)	20.832	18.10
Field strength F ($\times10^{14}$ cm^{-2})	10.097	5.630