







Study of Eu^{3+} – Gd^{3+} co-doped Ba–Bi–B glasses for red-laser applications: Physical, structural, photoluminescence and time-resolved spectral characteristics

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Abstract

A series of Eu^{3+} and $\text{Eu}^{3+}/\text{Gd}^{3+}$ co-doped barium-bismuth-borate (Ba–Bi–B) glasses were prepared by melt-quench technique. And deliberated the physical, structural, and spectroscopic properties of all glasses and explored the energy transfer process from Gd^{3+} to Eu^{3+} ions. The density of glasses increased with increasing of Gd^{3+} concentration in co-doped glasses. Characteristics of steady-state and time-resolved photoluminescence (PL) of Eu-doped and Eu^{3+} - Gd^{3+} co-doped glasses under different excitation wavelengths suggested the prospects of the investigated glass system for display device applications. PL spectrum displays a strong red emission peak centered at 612 nm due to the Eu^{3+} : ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition. Less intense emissions centered at 577 nm (${}^7\text{F}_0$), 590 nm (${}^7\text{F}_1$), 651 nm (${}^7\text{F}_3$) and 700 nm (${}^7\text{F}_4$) are also observed from the radiative transitions of the excited state ${}^5\text{D}_0$ of Eu^{3+} ions. The values of radiative parameters such as transition probability, branching ratios, and stimulated emission cross-sections were obtained from Judd–Ofelt theory analysis and

indicated the aptness of the Ba–Bi–B glasses for optical devices. A 5-fold enhancement in the PL intensity was observed in 1.0 mol% Eu^{3+} and 3.0 mol% Gd^{3+} co-doped glass under $\lambda_{\text{Exci.}}=394\text{nm}$ excitation. The calculated commission Internationale de l'éclairage color coordinates and correlated color temperature values show that the Ba–Bi–B glasses are useful for red-laser and display device applications.

Introduction

Trivalent rare-earth (RE^{3+})-doped optical materials, glasses, crystals, phosphors, etc., play a significant role in photonic applications such as display devices, fiber lasers, up-conversion lasers, optical amplifiers, laser gain media and scintillators [[1], [2], [3], [4], [5], [6]]. In the last few decades, glass materials have attracted researchers due to the ease of fabrication on large scale with required shape and sizes, optical homogeneity, high thermal stability, chemical stability, and also the large coefficient with the combination of RE^{3+} ions in the glass matrix.

The spectral behavior of RE (4f-4f) transitions and their performance for various applications depends on the composition of the glass host. Among the RE ions, the Eu^{3+} ion is special and has unique properties to examine the local ion symmetry of RE^{3+} ions in different glass systems. Eu^{3+} ions as optically active dopants predominantly produce the intense reddish-orange emission at 612 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$). This intense emission is a hypersensitive electronic transition (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$) whose spectral characteristics have been investigated in different host matrices to obtain laser emission in the red spectral region and display devices [[7], [8], [9], [10]].

In the recent past, different types of Eu^{3+} -doped glass materials were developed for optical displays, plasma display panels, visible lasers, and scintillation applications. For example, Nakamori et al. [11] prepared the Eu^{3+} -activated $\text{TeO}_2\text{--Al}_2\text{O}_3\text{--SrO}$ glasses and studied scintillation properties. Yang et al. [12] investigated Eu^{3+} doped silicate glasses to improve the efficiency of silicon solar cells. Venkatramu et al. [13] detailed optical and fluorescence properties of borate and fluoro borate doped zinc and lead glasses, Marimuthu et al. deliberated alkali borate glasses [14]. Similarly, several other glass systems as zinc-aluminum-bismuth borate glasses [15], $20\text{PbO}\text{--}5\text{CaO}\text{--}5\text{ZnO}\text{--}10\text{AF}\text{--}59\text{B}_2\text{O}_3\text{--}1\text{Eu}_2\text{O}_3$ alkali borate glasses [16], alkali fluoroborate glasses [17], $\text{SiO}_2\text{--B}_2\text{O}_3\text{--CaF}_2\text{--NaF--Na}_2\text{O}$ glasses [18], tantalum oxide doped phosphate glass [9], zinc fluorophosphate glasses [19], boro-phosphate glasses [20], zinc-tungsten-antimonite glasses [21], titanium lead phosphate glasses [22], $\text{TeO}_2\text{--Lu}_2\text{O}_3\text{--WO}_3$ [23], etc., have been reported. Moreover, Zhao et al. [6] reported the heavy tellurite ($70\text{TeO}_2\text{--}20\text{ZnO}\text{--}10\text{Lu}_2\text{O}_3$) doped with different Eu^{3+}

concentrations for scintillation applications. Nandyala et al. [24] explored the time-resolved and PL performance of Eu^{3+} doped borosilicate ($50\text{B}_2\text{O}_3-20\text{SiO}_2-20\text{Na}_2\text{O}-10\text{CaO}$) glasses for display applications. Mariselvam et al. [25] studied spectral properties of Eu^{3+} -doped barium bismuth fluoroborate glasses.

In this present barium-bismuth-borate (Ba-Bi-B) glasses, Gd^{3+} ions act as sensitizer and Eu^{3+} ions act as acceptors. Gd^{3+} ions have a half-filled 4f shell with a stable ground state ($^8\text{S}_{7/2}$) and can be excited by ultra-violet (UV) light, and the accessible excitation states are $^6\text{P}_j$, $^6\text{I}_j$, and $^6\text{D}_j$ [[10], [11], [12]]. The energy transfer (ET) is the capability of energy interchange between the optically active ions. In recent years, ET made from Gd^{3+} to Eu^{3+} ions has been explored in several different glass hosts [[26], [27], [28], [29], [30], [31]]. Yasutaka et al. [26] studied ET in Eu^{3+} - Gd^{3+} co-doped soda-lime silicate glasses and investigated time-resolved luminescence. Natalia et al. [27] reported the structural and optical properties of $\text{Eu}^{3+}/\text{Gd}^{3+}$ ions in silica xerogels, Wantana et al. [28] investigated the energy transfer emission analysis of Eu^{3+} doped $\text{Gd}_2\text{O}_3-\text{CaO}-\text{SiO}_2-\text{B}_2\text{O}_3$ glasses for laser applications, Khan et al. [29] developed oxyfluoride glasses for efficient ET ($\text{Gd} \rightarrow \text{Eu}$) to produce intense red emission for solid-state laser applications. Damdee et al. [30] studied Gd_2O_3 concentration on X-ray and photoluminescence properties of borate-based Eu-doped glasses for radiation detection materials and display device applications. Ramakrishna et al. [31] studied structural and radiative properties in Gd/Eu co-doped $\text{Li}_2\text{O}-\text{ZnO}-\text{SrO}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses. Yue Zi et al. [8] deliberated heavy Eu^{3+} -doped boroaluminate ($20\text{Al}_2\text{O}_3-60\text{B}_2\text{O}_3-(20-x)\text{Gd}_2\text{O}_3$) glasses for x-ray detection applications.

Based on the review of literature, to obtain better characteristics for practical applications, the glass host as well as impurity concentration is crucial. The authors have been choosing new glass composition $45\text{B}_2\text{O}_3-15\text{Bi}_2\text{O}_3-30\text{BaF}_2-10\text{TiO}_2$ with RE^{3+} (Eu^{3+} , and Gd^{3+}). Generally, borate glasses are one of the efficient luminescent materials with high thermal and chemical stability, and a high coefficient of combination of the RE ions [14,15]. The heavy metal oxides (HMO), bismuth oxide (Bi_2O_3), barium oxide (BaO), lead oxide (PbO), and titanium dioxide (TiO_2) are considered as intermediates in the glass matrices and are used for enhancing the optical properties via the formation of the glass structure [7,10,15]. The inclusion of TiO_2 in the glass systems can improve the linear refractive index and non-linear properties along with the thermal stability, chemical durability, and mechanical strength of the glasses [32,33]. Moreover, adding HMO leads to a decrease in the phonon energy and improves the luminescence properties of glass matrices [34,35]. The addition of barium fluoride (BaF_2) signifies the low phonon energy that causes less non-radiative (NR) relaxation rates and higher quantum efficiency of RE^{3+} in glass matrices [36,37].

In this direction, we investigated the structural and optical properties of Eu^{3+} -doped Ba–Bi–B glasses with different Gd_2O_3 compositions. The structural characteristics have been detailed by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopic studies. The Judd–Ofelt (J–O) [38,39] intensity parameters were evaluated and used to obtain radiative characteristics of the emission transition of Eu^{3+} - Gd^{3+} co-doped glasses. The ET mechanism from Gd^{3+} to Eu^{3+} ions by studying the behavior of PL profiles and time-resolved measurements of prepared glasses has been proposed.

Section snippets

Experimental details

The glass samples of the composition $(44-x)\text{B}_2\text{O}_3-15\text{Bi}_2\text{O}_3-30\text{BaF}_2-10\text{TiO}_2-1\text{Eu}_2\text{O}_3-x\text{Gd}_2\text{O}_3$ (where $x=0, 0.5, 1.0, 2.0, 3.0, 4.0$ and $5.0\text{mol}\%$) were prepared by using melt quenching technique. All chemicals were mixed carefully and grounded to get the homogeneity of the powders and then placed in a high purity crucible (Al_2O_3) to be melted at 1050°C for 1 h. Then the glass melt was quenched in air preheated brass plate and followed by annealing at 400°C for 8 h. The glass samples were sliced and...

Physical characteristics

Calculations of physical factors, for instance, the average mol. weight ($\text{Mol}_{\text{Avg.}}$), density (ρ), molar volume (V_m), and oxygen packing density (OPD) for all studied glasses were performed based on the data of elemental composition and their respective values are presented in Table 2a (i) [40,41].

The density (ρ) values are found in the range of ($4.253-4.421\text{g}/\text{cm}^3$), Mol_{Avg} ($161.807-173.416\text{g}/\text{mol}$), V_m ($38.225-39.226\text{cm}^3/\text{mol}$), are found to be increasing with increasing concentration of Gd^{3+} ...

Conclusions

In summary, structural, PL, and time-resolved activities of Eu^{3+} - Gd^{3+} co-doped Ba–Bi–B glasses were investigated. XRD results of the powder sample reveal the non-crystalline nature of the studied glasses. Optical band gaps were evaluated in direct ($2.883-3.062\text{eV}$), and indirect ($2.756-2.939\text{eV}$) configurations for all E1–E1G3.0 glasses. The band gaps were

found to increase with increasing Gd^{3+} ions concentration (0–3.0mol%) of the glasses under investigation.

J-O parameters are found in range $\Omega_2...$

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper...

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