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Structural and luminescence studies of Eu^{3+}: TeO_2–B_2O_3–AO–AF_2 (A = Pb, Ba, Zn, Cd, Sr) glasses

S. Selvi, K. Marimuthu, G. Muralidharan*

Department of Physics, Gandhigram Rural University, Gandhigram 624302, India

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ABSTRACT

Eu^{3+} doped oxyfluoro boro-tellurite (TBXFE) with molar composition 29 TeO_2–30B_2O_3–20AO–20-AF_2–1Eu_2O_3 (where A = Pb, Ba, Zn, Cd, Sr) glasses were prepared and investigated by XRD, FTIR, UV–Vis–NIR, luminescence and decay measurements. XRD patterns confirm the glassy nature of the prepared glasses. The influence of metal ions on the structure of boro-tellurite glasses were investigated through FTIR spectra. The intra band (4f-4f) transitions of Eu^{3+} ions are discussed through UV–Vis–NIR absorption spectra. The covalent nature around the Eu^{3+} ions with ligands are discussed using the bonding parameter (δ) and nephelauxetic ratio (β). The fundamental absorption edge, direct, indirect band gap, Urbach energy and band tailing parameters are reported. A bright red emission at 616 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions could be observed in the title glasses. Judd-Ofelt parameters were estimated from the emission spectra of Eu^{3+} ions. The dependence of these parameters on the composition of the glass is discussed. Judd-Ofelt parameters were used to derive the radiative parameters such as transition probabilities (A, s^{-1}), branching ratios (β_R), radiative lifetime (τ_{rad}) and stimulated emission cross-section (σ_P^E) for the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3 and 4) transitions. The luminescence intensity ratio (LIR) of $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ transitions was estimated to analyze the local site symmetry around the Eu^{3+} ions in the present glasses. The chromaticity coordinates and colour purity were calculated from the emission spectra and analyzed with Commission International de l'Eclairage (CIE) 1931 diagram. The experimental lifetime of $^5D_0$ level could be fitted to a single exponential indicating the absence of energy transfer between the Eu^{3+} ions in the present glasses.

1. Introduction

Over the last few years, the heavy metal oxide based materials are drawing much attention due to their interesting optical, electrical and magnetic properties. In addition, these materials have a wide band gap and large exciton binding energy making them potential candidates for the development of optoelectronic devices, UV emitting lasers, solar energy converters and gas sensors [1]. The heavy metal oxides present in the glass matrices could enhance radiative parameters of rare earth ions. Glasses based on heavy metal oxides such as, PbO, ZnO, CdO, Bi_2O_3 and Ga_2O_3 find wide applications in the field of glass ceramics, optical and electronic devices [2]. Luminescence of rare earth ions (RE^{3+}) in oxyfluoride glasses is attracting large interest of researchers, for it improves the glass forming ability of heavy metal oxide glass matrices. The oxyfluoride glasses combine the advantages of high mechanical strength of oxide glasses and low phonon energy of fluoride glasses [3,4]. Among the oxide glasses, tellurite glasses have been identified as a best choice for the fabrication of photonic devices due to their high RE ion solubility, high refractive index and moisture resistance. But, pure TeO_2 does not form a glass unless it is doped with other elements such as borate or phosphate and other glass forming materials [4]. Borate glasses possess the shielding property against infrared radiation, so it is used as a dielectric media and enhances the glass stability [5]. But, it has some drawbacks such as hygroscopic nature and high phonon energy (1300–1500 cm^{-1}) leading to non-radiative transitions. These drawbacks have been overcome by the addition TeO_2. The combination of borate and tellurite glasses exhibit low phonon energy, high chemical durability, high dielectric constant, excellent transparency in a wide spectral region (0.3–6.0 μm) and ease of fabrication [5]. Also, the alkaline earth oxides such as BaO and SrO increase the thermal stability of the glasses. Further, the addition suitable fluorides

* Corresponding author.
E-mail address: muraligru@gmail.com (G. Muralidharan).

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(PbF_2, BaF_2, ZnF_2, BaF_2, SrF_2) to these glasses is known to decrease the phonon energy of the host. This is expected to bring down the non-radiative decay rates, shorten the interionic distance which favours the energy transfer process and improve the emission efficiency [6]. These oxyfluoride glasses exhibit excellent optical and spectral performance due to the ease of incorporation of RE^{3+} ions.

Among the RE^{3+} ions, the trivalent europium ($4f^6$) ions are known to emit narrow band, monochromatic light with longer lifetime in the optically active state and it provides the red light with high efficiency [7]. Europium (Eu^{3+}) ion is the one of the best candidate to be used as a spectroscopic probe to investigate the local structure around Ln ions in condensed matter [8]. Eu^{3+} ions are used as a red emitting phosphors for field emission technology due to the narrow and monochromatic nature of the $^5D_0 \rightarrow {}^7F_2$ transition at 616 nm. In addition, persistent spectral hole burning can be performed in the $^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+} ions at room temperature which is used in high density optical storage materials [9]. The non-degenerate excited state of $^5D_0$ and the ground state of $^7F_0$ of Eu^{3+} ions provide information about the symmetry/inhomogeneity around the host matrices. The Eu^{3+} ions effectively absorb vacuum ultraviolet (via $Eu^{3+} \rightarrow F^-$ charge transfer transition) or ultraviolet/near ultraviolet (via $Eu^{3+} \rightarrow O^{2-}$or $Eu^{3+} \rightarrow S^{2-}$ charge transfer transitions) in fluoride, oxide or sulfide materials [10]. Earlier, Lourenco et al. [11] reported the europium doped SiO_2–B_2O_3–PbO_2 glasses which are used for silicon photodetectors and solar cells. The Eu^{3+} doped borate glasses modified with Zn^{2+}, Ca^{2+} and Pb^{2+} cations were investigated by Abdul Azeem et al. [12]. They found that the Ca^{2+} modified Eu^{3+} doped borate glasses have higher covalency and larger stimulated emission cross-section compared to the Zn^{2+} and Pb^{2+} modified Eu^{3+} doped borate glasses. Kesavulu et al. [8] analyzed the Eu^{3+} doped lead fluorophosphate glasses and they found the addition of PbF_2 to suppress the non-radiative losses which in turn leads to increase in the emission cross-section. The effect of modifiers on the fluorescence and absorption of Eu^{3+} in alkali and alkaline earth silicate glasses were investigated by Nageno et al. [13]. They observed that the intensity (red/orange) ratio yields a maximum with the addition of alkaline oxides in alkali silicate glasses. Murali Mohan et al. [14] reported the Eu^{3+} ions in K–Nb–Si glasses and the addition of K_2O in these glasses modify the cation field strength and improve the mechanical strength. Tripathi et al. [15] studied the effect of barium carbonate on the Eu^{3+} doped calibo glass and they found that the Judd-Ofelt parameters (Ω_2, Ω_4, Ω_6) were decreased by the addition of BaO. The influence of heavy metal oxide and activator concentration of Eu^{3+}, Dy^{3+}, Tb^{3+} doped lead borate glasses were reported by Zur et al. [16]. They found the Ln-Ln interaction to increase as the activator concentration increases. This has led to the shortening of the luminescence decay time.

In the present work, the detailed spectroscopic properties of Eu^{3+} in oxyfluoro borotellurite glasses are reported and the influence of modifier cations, Pb, Ba, Zn, Cd, Sr in the present glass system has been explored. Further, to investigate the structural and optical properties of Eu^{3+} ions in oxyfluoro boro-tellurite glasses XRD, FTIR, optical absorption, luminescence spectra and decay time measurements have been carried out. Estimated JO parameters are used to determine the radiative transition parameters for the excited levels of Eu^{3+} ions. Decay time of $^5D_0$ level has been compared with the theoretical values.

2. Experimental methods

Eu^{3+} doped oxyfluoro boro-tellurite glasses were prepared through melt quenching technique with the following chemical composition (in wt %):

29 TeO_2–30B_2O_3–20PbO–20PbF_2–1Eu_2O_3: TBLFE

29 TeO_2–30B_2O_3–20BaO–20BaF_2–1Eu_2O_3: TBBFE

29 TeO_2–30B_2O_3–20ZnO–20ZnF_2–1Eu_2O_3: TBZFE

29 TeO_2–30B_2O_3–20CdO–20CdF_2–1Eu_2O_3: TBCFE

29 TeO_2–30B_2O_3–20SrO–20SrF_2–1Eu_2O_3: TBSFE

15 g batches of above chemical compositions were mixed and thoroughly ground in an agate mortar. Then the mixture was heated for 30 min in a porcelain crucible around 1025 °C in an electrical furnace. The melt was stirred frequently for homogeneous mixing of all chemical constituents. The melt was then quickly quenched to 370 °C in air by pouring the melt into a preheated brass plate. The glass samples were annealed at 370 °C for 8 h to eliminate thermal strains that arise during the sudden quench and to improve the mechanical strength. Before measurement of their physical and spectroscopic properties the prepared glass samples were well polished.

X-ray diffraction studies of the samples were performed by PANalytical XPERT- PRO X-Ray diffractometer with CuKα radiation. The Infrared absorption spectra of TBXFE glasses were recorded in the range of 4000–400 cm^{-1} using Perkin-Elmer BX spectrometer by KBr pellet technique. The UV–Vis–NIR absorption spectral measurements were made on Jasco V- 670 spectrophotometer in the wavelength range 200–2700 nm with a resolution of 0.5 nm. The luminescence spectra of the glass samples excited at 465 nm were recorded using Perkin Elmer LS55 spectrophotometer with a spectral resolution of 1.0 nm in the spectral range of 550–740 nm. The decay curves were measured by digital storage oscilloscope (Tektronix TDS 1001B) coupled with personal computer. The density of the TBXFE glasses was measured using Archimedes principle with xylene as the immersion liquid. The refractive index of the glasses was obtained at 589.3 nm (sodium wavelength) using Abbe refractometer with monobromonaphthalene as the contact liquid.

Table 1
Physical properties of Eu^{3+} doped oxyfluoro boro-tellurite glasses.

Sl. No	Physical properties	TBLFE	TBBFE	TBZFE	TBCFE	TBSFE
1	Density ρ (g/cm^3)	5.550	4.748	4.844	4.843	4.489
2	Refractive index n_d (589.3 nm)	1.776	1.738	1.788	1.779	1.716
3	Rare earth ion concentration N(10^{20} ions/cm^3)	4.126	4.003	5.541	4.700	2.956
4	Polaron radius r_p(A°)	5.412	5.467	4.906	5.182	6.049
5	Inter ionic distance r_i (A°)	13.43	13.57	12.17	12.86	15.01
6	Field strength F (10^{14} cm^{-2})	1.663	1.629	2.024	1.814	1.331
7	Electronic polarizability α_e (10^{-22} cm^3)	2.419	2.402	1.822	2.130	3.178
8	Molar refractivity R_m (cm^3)	1.135	1.272	1.309	1.305	1.314
9	Dielectric constant (ε)	3.154	3.021	3.197	3.165	2.945
10	Reflection losses R (%)	7.814	7.265	7.989	7.858	6.949