Journal of Luminescence 132 (2012) 2259–2267

Contents lists available at SciVerse ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Concentration dependent Eu^{3+} doped boro-tellurite glasses—Structural and optical investigations

K. Maheshvaran, K. Marimuthu *

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

ARTICLE INFO

Article history:
Received 9 January 2012
Received in revised form
8 April 2012
Accepted 16 April 2012
Available online 23 April 2012

Keywords:
Absorption
Photoluminescence
Judd–Ofelt analysis
Band tailing parameter
Urbach energy

ABSTRACT

Eu^{3+} doped boro-tellurite glasses with the chemical composition $(40-x)B_2O_3+30TeO_2+15MgO+15K_2O+xEu_2O_3$ (where $x=0.01$, 0.1, 1, 2 and 3 wt%) have been prepared by following the conventional melt quenching technique. Structural and optical behavior of the prepared Eu^{3+} doped boro-tellurite glasses were studied and compared with reported literature. The XRD pattern confirms the amorphous nature and the FTIR spectral studies explore the presence of B–O stretching vibrations, $O_3B–O–BO_3$ bond bending vibrations along with the bending vibration of Te–O–Te linkages in the prepared glasses. Through the optical absorption spectra, bonding parameters ($\overline{\beta}$, δ) were calculated to identify the ionic/covalent nature of the glasses. Judd–Ofelt (JO) parameters have been calculated from the luminescence spectral measurements. The JO parameters (Ω_λ, $\lambda=2$, 4 and 6) were used to calculate the radiative properties like transition probability (A), stimulated emission cross-section (σ_P^E), radiative lifetime (τ_{rad}), and branching ratios (β_R) for the $^5D_0\rightarrow{}^7F_J$ ($J=0$, 1, 2, 3 and 4) emission transitions of the Eu^{3+} ions. The local site symmetry around the Eu^{3+} ions were calculated through the luminescence intensity ratio (R) of the $^5D_0\rightarrow{}^7F_2$ to $^5D_0\rightarrow{}^7F_1$ transitions. The experimental lifetime of the $^5D_0$ level in the Eu^{3+} doped boro-tellurite glasses has also been calculated and compared with similar Eu^{3+} glasses. The lifetime of the $^5D_0$ level is found to be less than the reported glasses and it may be due to the presence of OH^- groups in the prepared glasses. The Optical band gap (E_{opt}), band tailing parameter (B) and the Urbach energy (ΔE) values of the prepared glasses were calculated from the absorption spectral measurements and the results were discussed and reported.

1. Introduction

Optical properties of various rare earth (RE) ions doped with oxide glasses have been studied extensively over the past few decades due to their potential technological and commercial applications. The spectral properties of the B_2O_3, P_2O_5 and alkali halide based rare earth doped glasses showing optical non-linearity have been studied and reported [1–4]. Borate based glasses have been studied extensively due to their special physical properties like high transparency, low melting point, high thermal stability and good rare earth ions solubility which manifest an interesting structural particularities as the occurrence of boron anomaly [5]. Being good shield against infrared radiation, these borate glasses are often used as dielectric and insulating materials. Among the oxide glasses, tellurite glasses possess encouraging properties like good mechanical strength, chemical durability, low process temperature, high dielectric constant and excellent transmission in the visible and IR wavelength regions. They also have lower phonon energy and larger refractive index, compared to other oxide glasses [6]. Since the TeO_2 belongs to an intermediate glass forming oxide, and does not form a glass readily on its own, but it does so when it is mixed with other oxides like B_2O_3, P_2O_5, SiO_2 along with a small amount of alkali oxide which act as a network modifier in order to obtain good quality optical glasses. The presence of TeO_2 in the alkali borate glass matrix decreases its hygroscopic nature, improves the glass quality and enhances the IR transmission [7].

The pure borate based glasses possess high phonon energy in the order of 1300–1500 cm^{-1}, and when these glasses were added with TeO_2 and an alkali oxide would result in significant reduction in the phonon energy in the order of 600–800 cm^{-1}. Further, optical properties like high refractive index and high optical non-linearity, the B_2O_3–TeO_2 glasses are also of great interest for the fabrication of various new optical devices. Boro-tellurite glass represents favorable compromise between the requirements of low phonon energy and a relatively high thermal stability, high chemical durability and ease of fabrication. Therefore, in the present work such an ideal low phonon energy optical host matrix have been chosen to dope it with Eu^{3+} ion. The selection of trivalent europium ion has proved to be worthy for the study of disordered materials, because of its simple energy level structure with non-degenerate ground $^7F_0$ and emitting $^5D_0$

* Corresponding author. Tel.: +91 451 2452371; fax: +91 451 2454466.
E-mail address: mari_ram2000@yahoo.com (K. Marimuthu).

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http://dx.doi.org/10.1016/j.jlumin.2012.04.022

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

Sl. no.	Physical properties	0.01EBT	0.1EBT	1EBT	2EBT	3EBT
1	Density ρ (g/cm^3)	4.010	5.347	4.047	4.228	4.048
2	Refractive index n_d (589.3 nm)	1.603	1.616	1.627	1.639	1.651
3	Rare earth ion concentration N (10^{20} ions/cm^3)	0.044	0.582	4.314	8.790	12.316
4	Polaron radius r_p (Å)	24.63	10.40	5.33	4.21	3.76
5	Inter ionic distance r_i (Å)	61.13	25.80	13.24	10.44	9.33
6	Field strength F (10^{14} cm^{-2})	0.080	0.451	1.713	2.753	3.447
7	Electronic polarizability α_e (10^{-22} cm^3)	187.39	14.33	1.96	0.98	0.71
8	Molar refractivity R_m (cm^3)	6.525	4.990	6.617	6.381	6.933
9	Dielectric constant (ε)	2.570	2.611	2.647	2.686	2.726
10	Reflection losses R (%)	5.366	5.545	5.697	5.863	6.030

states [8–10]. The optical properties of the Eu^{3+} ion are well known to be highly sensitive to environment in which it is surrounded. Though, there is enough information available on Eu-doped borate and tellurite glasses [1,3,4,6,10], it will be of interest to find out the variation of optical properties of Eu^{3+} ions in boro-tellurite glasses by varying its concentration.

Judd–Ofelt (JO) theory [11,12] has not been applied uniformly to characterize the spectroscopic properties of Eu^{3+} ion doped glasses. Peng and Izumitani [13] used $^5D_0 \rightarrow {}^7F_2$, $^7F_4$ and $^7F_6$ emission transitions of the Eu^{3+} ions to obtain the JO parameters whereas, Van Deun et al. [14] used $^7F_0 \rightarrow {}^5D_2$, $^5D_4$ and $^5L_6$ transitions of the absorption spectrum. In the present work, employing the method followed by Peng and Izumitani [13], the JO parameters have been evaluated. Sooraj Hussain et al. analyzed the absorption and emission spectral measurements and reported the stimulated emission cross-section for the lithium boro-tellurite glasses [15]. Supriya and Buddhudu [16] have investigated the emission properties of TeO_2–B_2O_3–P_2O_5–Li_2O glasses. Yang et al. [17] have reported the structural and optical properties of Er^{3+}, Eu^{3+} single-doped Na_2O–ZnO–B_2O_3–TeO_2 glasses. Reddy et al. [18] have reported the radiative properties of rare earth doped B_2O_3–TeO_2–BaO–R_2O glasses.

The aim of the present study is to (i) examine the structure of the title glasses through XRD and to identify the local structural groups through FTIR spectra; (ii) calculate the bonding ($\overline{\beta}$ and δ) parameters, JO parameters and oscillator strengths; (iii) determine the radiative properties for the significant levels and to compare with similar results; (iv) determine the experimental decay time of the $^5D_0$ level and to compare the results with the calculated lifetime values; and (v) finally to calculate the optical band gap and Urbach energy values of the prepared glasses and to compare with similar reported literature.

2. Experimental

Eu^{3+} doped boro-tellurite glasses have been prepared by following the conventional melt quenching technique. The starting materials used are H_3BO_3, TeO_2, Mg_2CO_3, K_2CO_3 and Eu_2O_3 of analytical grade (Sigma Aldrich) with 99.99% high purity. The batch compositions (in wt%) and the sample codes of the prepared glasses are as follows:

$$39.99B_2O_3 + 30TeO_2 + 15MgO + 15K_2O + 0.01Eu_2O_3 \rightarrow 0.01EBT$$

$$39.9B_2O_3 + 30TeO_2 + 15MgO + 15K_2O + 0.1Eu_2O_3 \rightarrow 0.1EBT$$

$$39B_2O_3 + 30TeO_2 + 15MgO + 15K_2O + 1Eu_2O_3 \rightarrow 1EBT$$

$$38B_2O_3 + 30TeO_2 + 15MgO + 15K_2O + 2Eu_2O_3 \rightarrow 2EBT$$

$$37B_2O_3 + 30TeO_2 + 15MgO + 15K_2O + 3Eu_2O_3 \rightarrow 3EBT$$

About 15 g of the batch compositions were thoroughly mixed and ground in an agate mortar. The homogeneous mixture was taken into a porcelain crucible and melted in an electrical furnace at a temperature of 850 °C for 30 min. The melt was poured onto a preheated brass plate and annealed at 300 °C for about 7 h to remove strains, avoid the formation of air bubbles and to improve the mechanical strength. The prepared glasses were slowly allowed to reach room temperature (RT). By polishing on both sides good optical quality glasses of about 1.5 mm thickness were obtained before further optical measurements.

X-ray diffraction analysis was carried out using JEOL 8530C X-ray diffractometer employing CuK_α radiation to confirm the amorphous nature of the prepared glasses. The local structural units were explored through FTIR spectral measurements recorded in the range 400–4000 cm^{-1} using Perkin–Elmer Peragon 500 FTIR spectrophotometer with a spectral resolution of ± 4.0 cm^{-1}. The absorption spectral measurements were recorded using CARY 500 UV–vis–NIR spectrometer in the range 350–2300 nm with a resolution of ± 0.1 nm. The photoluminescence measurements were made using Perkin–Elmer LS55 spectrophotometer with a resolution of ± 1.0 nm. The decay time measurements were made through Scientech modular spectrophotometer using xenon flash lamp as an excitation source. All these measurements were carried out at room temperature.

The refractive indices were measured using Abbe refractometer at sodium wavelength (589.3 nm) using mono-bromonapthalin ($C_{10}H_7Br$) as the contact liquid. The density of the prepared glasses has been determined employing Archimedes principle using xylene as an immersion liquid. The calculated physical properties of the title glasses are presented in Table 1.

3. Results and discussion

3.1. Structural analysis

The XRD pattern of the Eu^{3+} doped boro-tellurite glasses recorded in the range $5^\circ \leq \theta \leq 80^\circ$ does not exhibit any diffraction lines which confirms the amorphous nature of the prepared glasses and as a representative case, XRD pattern of the Eu^{3+}:1EBT boro-tellurite glass is shown in Fig. 1.

The FTIR spectra of the Eu^{3+} doped boro-tellurite glasses presented in Fig. 2 contain several peaks which include several stretching vibrations of BO_3, BO_4 units, B–O–B linkages and Te–O, TeO_3 units at around 1636, 1377, 1236, 1039, 724 and 448 cm^{-1}. The peak positions and their assignments are presented in Table 2. The vibrational modes of the borate network are active in three infrared regions. The first group of bands observed at 1200–1600 cm^{-1} are due to the asymmetric stretching relaxation of the B–O bond of trigonal BO_3 units. The second group of bands observed at around 800–1200 cm^{-1} are attributed to the B–O