Europium doped Boro-Bismuth-Tellurite Glasses for Multicolor Phosphor Applications

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Abstract: The glass system $(50\text{-}x)B_2O_3\text{-}30Bi_2O_3\text{-}20TeO_2\text{-}xEu_2O_3$ (x = 0, 0.1, 0.5, 1.0, 1.5 and 2.0 mol%) have been prepared by conventional melt quenching method, their physical, optical and luminescence properties were investigated. The density of these glasses has been measured and the corresponding molar volume has also been calculated. The $(\alpha h\upsilon)^{1/n}$ vs $h\upsilon$ graph was plotted and it is well fitted to both direct (n=1/2) and indirect (n=2) band gaps. The direct and indirect band gap values are ranging from 2.57 to 2.94 eV and 1.74 to 2.58 eV respectively. The Urbach energy of the glass system was calculated and their values are ranging from 0.29 and 0.62 eV. Yellow, orange and red emissions have been observed through Photoluminescence (PL) spectroscopy excited at 464 nm and the obtained multicolor emissions have been demonstrated according to the Commission International de I'Eclairage France 1931 standards. The results of PL studies indicated the possibility towards the development of multicolor phosphor applications.

Keywords: Density; Optical properties; Photoluminescence.

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1. Introduction

Rare earth ions doped in different glass hosts to achieve favourable potential applications in a variety of optical devices such as lasers, fiber amplifiers, color displays solid state lighting

devices and development of phosphors for different applications[1–3]. Glasses contain rare earth ions have proved as efficient luminescent materials because they have good emission efficiency, while the emission is originated from both 4f-4f as well as 4f-5d electronic transition, the 4f-4f transitions gives sharp emission lines covering a wide range of spectral region, from the ultraviolet (UV) to the infrared region (IR). These sharp emissions attracted potential applications in solid state lasers, optical fiber amplifiers and three dimensional display devices[4]. Among the other rare earth ions, trivalent europium ions doped glasses are very prominent materials for efficient red phosphors and photonic applications, because these kind of glasses produces almost monochromatic light and long radiative lifetime[5]. The phonon energy of the host material and active ion concentration is playing a good role in the emission quantum efficiencies of rare earth ions. Recent years, a new direction has begun towards the borate glasses because of their structural peculiarities. The structure of pure borate glass made up of random networks of boroxyl BO_3 units[6]. However, borate glasses have high phonon energies due to the stretching vibrations of network forming oxides, resulting into the increase in non-radiative loss thereby a reduction in the luminescence efficiency. High phonon energies in the borate glasses can be reduced by the addition of heavy metal oxides such as bismuth and lead oxides. Moreover, heavy metal oxide containing glasses shows extremely high radioactive resistance because of their high density and atomic number. Bismuth trioxide alone cannot be considered as network former due to small field strength of Bi^{3+} ion[4]. Furthermore, introducing TeO_2 as a network modifier in the glass network improves low phonon energies and it helps to enhanced emission efficiency in the glass matrix. Also, it provides a high refractive index, low melting temperature, good chemical durability and good in IR transmission[7–10].

In this manuscript, we are reporting optical properties of europium doped boro bismuth-tellurite glasses studied by using UV-Visible spectrophotometer and Photoluminescence spectroscopy.

2. Experimental

The different compositions of europium doped boro bismuth tellurite glasses have been synthesized by conventional melt quenching method. The appropriate weights of Analar grade chemicals (H_3BO_3, Bi_2O_3, TeO_2 and Eu_2O_3) were taken in a mortar and grounded well by using a pestle for 15 min. The grounded mixture of samples was taken in an alumina crucible and placed in a furnace, set temperature at 900ºC for 2 hrs. After the completion of heat treatment, the molten liquid was cast onto a brass mould and quickly presses with another one. The result is in the form of pale yellow color transparent glass and these glass samples were cut into the appropriate dimensions with the thickness of 0.1~0.2 mm for optical measurements.

The glass structure was characterized by D-8 X-ray diffractrometer (Bruker AXS-Model) using 1.5406 Å from Cu K_α radiations in the scanning rate 2 º/min. The densities of the glass samples were measured at room temperature by using Archimedes method, with toluene as immersion liquid of stable density (ρ_t = 0.866 g/cm^3). The molar volume values of the glass samples were calculated by using the relation $V_m=M/\rho$, where M is the molar mass and ρ is the density of the glass samples. The optical absorption spectra were recorded at room temperature in the wavelength range from 450 to 600 nm by using a Perkin-Elmer lambda-30 UV-Visible spectrophotometer. The optical absorption coefficient $\alpha(\lambda)$ was calculated from the absorbance A, and the thickness of the sample d, by using the following relation,

$$\alpha(\lambda) = 2.303\frac{A}{d} \qquad (1)$$

Photoluminescence (PL) studies of the glass system have been performed by using F-2700 FL spectrophotometer with xenon flash lamp as a source. Emission and excitation spectra of the glasses were recorded at λ_{ex} = 464 nm and λ_{em} = 615 nm (and also λ_{em} = 590 nm) respectively.

3. Results and Discussions

X-ray diffraction (XRD) pattern of the glass system as depicted in figure 1. It has been observed that a strong diffusion bands occurred in the pattern is due to the scattering of X-rays in the non-crystalline network and these obtained broad humps in the pattern confirms the amorphous nature of the glass system. Density and molar volume values are tabulated in the table 1 and their values were found to be in the range from 5.70 to 6.09 g/cm^3 and 34.14 to 36.28cm^{-3}, respectively. The density measurement is very crucial tool to examine the structure of the glass network. It can be seen that from table 1, the density values varies randomly, it may be due to the some sort of structural rearrangements takes place in the glass network with the addition of Eu_2O_3 mol%[11]. The variation of molar volume values are expected exactly opposite to that of density variation. The typical optical absorption spectra of the glass system as shown in figure 2, it consists five absorption peaks from 440 to 600 nm, located at 464, 525, 532, 578 and 585 nm corresponds to the electronic transitions of $^7F_0$-$^5D_2$, $^7F_0$-$^5D_1$, $^7F_1$-$^5D_1$, $^7F_0$-$^5D_0$ and $^7F_1$-$^5D_0$, respectively[5]. An expression of absorption coefficient α as a function of photon energy hv for direct and indirect inter-band electronic transition can be written as,

$$\alpha h\upsilon = B\left(h\upsilon - E_{opt}\right)^n \qquad (2)$$

where B is a constant and hv is the photon energy, E_{opt} is the optical energy band gap and n is a number which characterizes the transition process. The exponent, n takes the values: 1/2

and 2 for direct and indirect allowed transitions, respectively. The optical absorption coefficient values are well fitted to both direct and indirect band gaps and their values can be determined from the expression (2) by extrapolating the absorption coefficient to zero absorption in the $(\alpha h\upsilon)^2$ and $(\alpha h\upsilon)^{1/2}$ vs $h\upsilon$ plot at $(\alpha h\upsilon)^2=0$ and $(\alpha h\upsilon)^{1/2}=0$, as shown in figures 3. The respective values of direct and indirect band gaps vary from 2.57 to 2.94 eV and 1.74 to 2.58 eV; they are tabulated in table 1. It is observed that, there is an anomalous variation in both direct and indirect band gap values, these kind of variation in optical band gap values are also in reasonable agreement with the optical band gap values found in other Eu_2O_3 doped glasses[12,13]. As can be seen from the table 1, the values of direct and indirect band gap values increase at 0.1 mol% Eu_2O_3 and suddenly drops at 0.5 mol% Eu_2O_3. Further increasing the Eu_2O_3 content up to 2 mol%, both direct and indirect band gaps increase linearly. These kind of anomalous variation in both direct and indirect band gap values might be due to the some changes occurred in bonds and it may also arise from the photon-lattice interaction[14]. The shifting of the absorption band to a lower and higher energy can be related to the formation of non-bridging oxygen in the glass network. The shifting of the absorption band to the lower energy can be interpreted as the increase in non-bridging oxygen making the structure less rigid. Conversely, the shifting of the absorption band to the higher energy corresponds to the decrease in non-bridging oxygen making the structure more compact. Consequently, the obtained density and molar volume values are well agreeing to direct and indirect band gap values. The Urbach energy values are presented in table 1, which corresponds to the width of the band tail, caused by the localized states. The absorption at lower photon energy usually follows Urbach rule, the width of the band tail (E_{tail}) can be estimated by using the relation,

$$\alpha(\upsilon) = Bexp\left(\frac{h\upsilon}{E_{tail}}\right) \quad (3)$$

The E_{tail} values vary from 0.29 to 0.62 eV as can be seen from table 1 and these values are well matched with amorphous semiconductors (0.046 to 0.66 eV) as reported in the literature[15]. The excitation spectra of Eu^{3+} doped boro bismuth tellurite glasses were monitored at λ_{em} = 590 and 615 nm of $^5D_0$-$^7F_1$ and $^5D_0$-$^7F_2$ transitions are depicted in figure 4. It is quite similar to the spectra obtained with other oxide glass hosts doped with trivalent europium[16]. The spectral range from 250 to 570nm consists of sharp lines, which is attributed from transitions between the 4f energy levels of Eu^{3+} ions, in that excitation spectrum shows strongest peak at 464 nm. Figure 5 shows the emission spectra at λ_{ex} = 464 nm of Eu^{3+} ions and we observed that two emission bands centered at 590 ($^5D_0$-$^7F_1$) and 615 nm ($^5D_0$-$^7F_2$) due to the magnetic (ΔJ=1) and electric (ΔJ=2) dipole transition of Eu^{3+} ions. It is found that, the emission centered at 615 nm ($^5D_0$-$^7F_2$) for the glass system, which is the most efficient then the other transitions. It can also be seen that, the maximum emission intensity of the glass system observed at 1 mol% of Eu_2O_3. Furthermore, increasing the concentration of Eu_2O_3 up to 2 mol%, the luminescence intensity reduces contrarily owing to the concentration quenching effect. Therefore, the optimum dopant concentration of Eu^{3+} ions in the boro bismuth tellurite glass system was about 1 mol%. The concentration quenching occurs in the glass matrix may be due to the addition of Eu^{3+} ions increase the phonon energies. As we know that, the phonon energy is very significant for emission quantum efficiencies of RE^{3+} ions. Luminescence colors of the glass system (λ_{ex}= 464 nm) were characterized by CIE (Commission International de I'Eclairage France) chromaticity diagram and as shown in figure 6. The chromaticity coordinates have been calculated from the emission spectra by using the 1931 CIE method and their chromaticity coordinates of BB1, BB2, BB3, BB4 and BB5 are (0.49, 0.48), (0.55, 0.43), (0.60, 0.39), (0.58, 0.41) and (0.54, 0.44) respectively. From these results confirms that the obtained highest chromaticity coordinates (0.60, 0.39) of europium doped boro bismuth tellurite glasses produce efficient

red light and the other coordinates are appearing in the range of yellow, orange and red region.

4. Conclusion

The glasses of different compositions of boro bismuth tellurite glasses doped with trivalent europium ions have been successfully prepared by conventional melt quenching method. The prepared glasses are found to be in pure amorphous phase and calculated density and molar volume values are well agreeing with the band gap values. The studied glasses show an anomalous variation in both direct and indirect band gap values. These kind of variation in band gap values due to the some structural rearrangement takes place with the addition of Eu_2O_3 content in the glass matrix, which leads to the significant changes in the optical properties of the studied glass system. The PL spectrum of the glass system shows the bright red luminescence peak at 1 mol% of Eu^{3+} ions. The CIE chromaticity coordinates of the glass system almost appeared in the yellow, orange and red region. These kind of glasses widely used as multicolor phosphor applications.

5. Acknowledgement

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6. References

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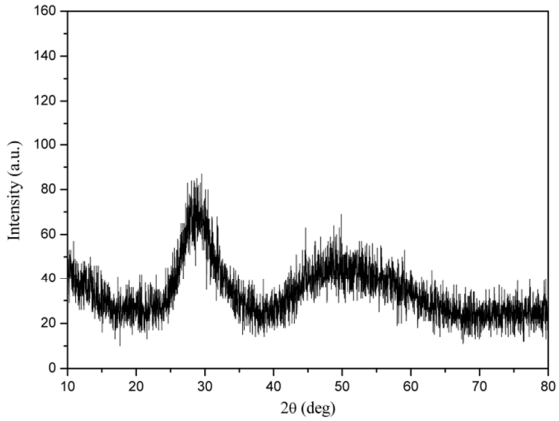

Figure 1. Typical XRD pattern of europium doped boro bismuth-tellurite glass.

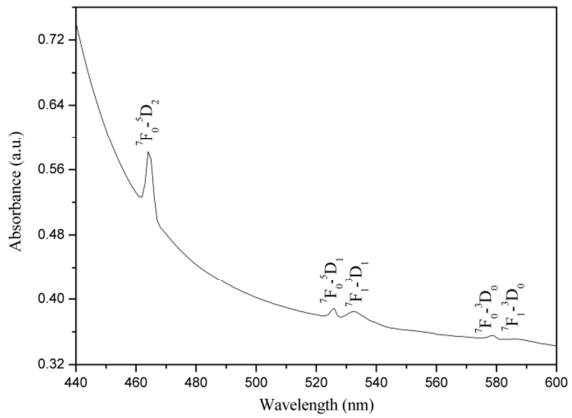

Figure 2. The optical absorbance spectra of B_2O_3-Bi_2O_3-TeO_2-Eu_2O_3 glass system.

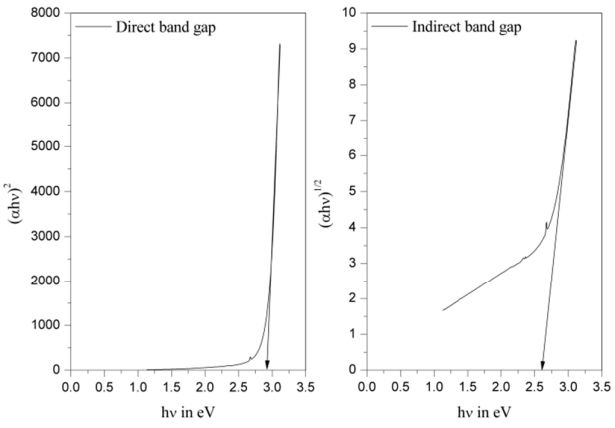

Figure 3. Typical plot of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) respectively.

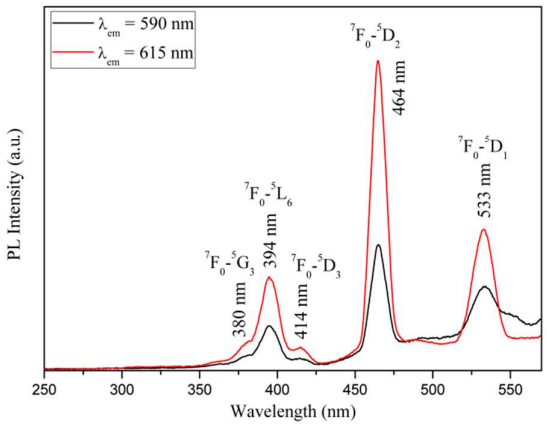

Figure 4. Excitation spectra of Eu^{3+} doped boro bismuth tellurite glass at λ_{em} = 590 and 615 nm.

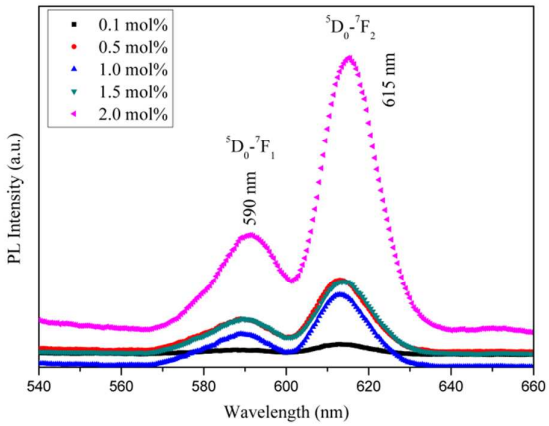

Figure 5. PL emission spectra of Eu^{3+} doped boro bismuth tellurite glasses excited with λ_{ex} = 464 nm.

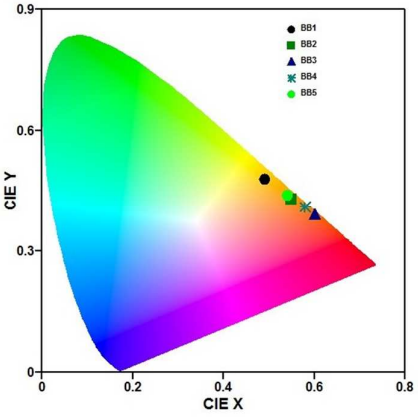

Figure 6. Commission International de I'Eclairage (CIE) chromaticity diagram of emission for samples upon 464 nm excitation of the B_2O_3-Bi_2O_3-TeO_2-Eu_2O_3 glass system.

Table 1: Density (ρ), molar volume (V_m), direct (E_g^d) and indirect (E_g^i) band gap and Urbach energy (E_{tail}) of (50-x)B_2O_3-30Bi_2O_3-20TeO_2-xEu_2O_3 glasses.

Glass series code	ρ (g/cm^3)	V_m (cm^{-3})	E_g^d (eV)	E_g^i (eV)	E_{tail} (eV)
BB0 (x=0.0)	5.89	35.06	2.76	2.31	0.38
BB1 (x=0.1)	5.70	36.28	2.81	2.37	0.34
BB2 (x=0.5)	6.09	34.14	2.57	1.74	0.62
BB3 (x=1.0)	6.03	34.71	2.71	2.06	0.54
BB4 (x=1.5)	5.95	35.42	2.87	2.45	0.33
BB5 (x=2.0)	5.82	36.45	2.94	2.58	0.29