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X-RAYS LUMINESCENCE, OPTICAL AND PHYSICAL STUDIES OF BI_2O_3-B_2O_3-SM_2O_3 GLASSES SYSTEM

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ABSTRACT

Sm^{3+}-doped bismuth borate glasses of the composition (50-x) SiO_2: $50B_2O_3$: xSm_2O_3 (where x = 0.00, 0.50, 1.00, 1.50, 2.00 and 2.50 mol%) have been synthesized by conventional melt quenching technique. In order to understand the role of Sm_2O_3 in bismuth borate glasses, the density, molar volume, refractive index and optical absorption were investigated. The results show that density, molar volume and refractive index of glasses increased with increasing Sm_2O_3 concentration. The increase of molar volume with Sm_2O_3 concentration is due to the increase of Non-Bridging Oxygen (NBOs) in the glass matrix. The optical absorption spectra were measured in the wavelength range from 300-1100 nm and the optical band gaps were determined. It was found that the optical band gap decreased with the increase of Sm_2O_3 concentration. Moreover, the x-rays luminescence of Sm_2O_3 glasses samples were measured and shows emission band at ${}^4G_{5/2}\rightarrow{}^6H_{5/2}$ (569 nm), ${}^4G_{5/2}\rightarrow{}^6H^{7/2}$ (598 nm), ${}^4G_{5/2}\rightarrow{}^6H_{9/2}$ (641 nm) and ${}^4G_{5/2}\rightarrow{}^6H_{11/2}$ (705 nm). This investigation have been used as the basis for developing optical amplifier or glass scintillator.

Keywords: Sm_2O_3, X-Ray Luminescence, Glass, Optical Spectra, Optical Absorption, Molar Volume, Doped Bismuth Borate, Wavelength Range, Emission Band, Gap Decreased

1. INTRODUCTION

Boric oxide, B_2O_3, acts as one of the most important glass formers and flux materials. Melts with compositions rich in B_2O_3 exhibit rather high viscosity and tend to the formation of glasses. In crystalline form, on the other hand, borates with various compositions are of exceptional importance due to their interesting linear and nonlinear optical properties (Becker, 1998). The boron atom usually coordinates with either three or four oxygen atoms forming $[BO_3]^{3-}$ or $[BO_4]^{5-}$ structural units. Furthermore, these two fundamental units can be arbitrarily combined to form different B_xO_y structural groups (Xue *et al*., 2000). Among these borates, especially the monoclinic bismuth borate BiB_3O_6 shows up remarkably large linear and nonlinear optical coefficients (Hellwig *et al*., 1999; 2000). Calculations indicate that this can be mainly attributed to the contribution of the $[BiO_4]^{5-}$ anionic group (Xue *et al*., 1999; Lin *et al*., 2001). For the linear properties (refractive index) this anionic group should act in a similar way in an amorphous environment, i.e., in glass. Combining bismuth oxide with boric oxide thus allows tuning the optical properties in a wide range depending on the composition. Consequently, the properties of glasses of the system Bi_2O_3-B_2O_3 have attracted much interest (Becker, 2003). The trivalent samarium ion (Sm^{3+}) is one of the most important active ions in the RE family (cerium to lutetium) due to its convenient closely lying energy level structure (Carnall *et al*., 1968), that has been exploited in upconversion processes mainly in low phonon crystalline hosts and rarely in glasses (Kaczkan *et al*., 2001; Zhou *et al*., 2003; Biju *et al*., 2004; Farries *et al*., 1988; France *et al*., 2000). Hence very little is known about upconversion properties of Sm^{3+} in glasses. Within the Sm^{3+} ion energy scheme tricolor visible upconversion processes can take place from the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (green), $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (orange) and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (red) electronic transitions. Moreover, Sm^{3+} doped bismuth-borate glass has high density and radiation hard property. Also it is easy to made, can be produced with low cost and wide range of emission band. Therefore, it is a good candidate for radiation detector and possible to apply high energy and nuclear physics, medical imaging, homeland security and radiation detection. In this study, Sm^{3+}-doped bismuth borate glasses have been synthesized by conventional melt quenching technique and investigate on x-rays luminescence, optical and physical properties of glass samples.

2. MATERIALS AND METHODS

2.1. Experimental

The compositions of glass are (50-x) Bi_2O_3: $50B_2O_3$: xSm_2O_3 (x = 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 mol%). The batch was prepared from the AR grade of Bi_2O_3 (Fluka 99.99%), H_3BO_3 (Sigma-Aldrich, 99.99%) and Sm_2O_3 (Sigma-Aldrich, 99.99%). The glasses were melted in a high alumina crucible at 1,100°C in air atmosphere. The molten glass was cast into a stainless steel plate and properly annealed. The glass thus obtained was cut and polished for optical measurement. The density was measured by the Archimedes method using xylene as immersion liquid. Density of xylene at the experimental temperature was found to be 0.863 g/cm^3. The corresponding molar volume, V_m, was calculated using the following Equation (1) (Limkitjaroenporn *et al*., 2011):

$$V_m = M / \rho \quad (1)$$

where, M is the molecular weight of the multi-component glass system.

The UV-Vis absorption spectra were obtained with a double-beam spectrophotometer (Variance, Cary-50). According to Davis and Mott, the absorption coefficient, $\alpha(v)$, as a function of incident photon energy (hv) for direct and indirect optical transitions is given by (Abdel-Baki *et al*., 2006):

$$a(v) = a_0(hv - E_g)^n / hv \quad (2)$$

where the exponent n = 1/2 for an allowed direct transition, while n = 2 for an allowed indirect transition, α_0 is a constant related to the extent of the band tailing and E_g is the optical band gap energy. The absorption coefficient, $\alpha(v)$, can be determined near the absorption edge of different photon energies for all glass sample. It is well known that for amorphous materials a reasonable fit of Equation (2) with n = 2 is achieved. Therefore, the values of optical band gap energy (E_g) can be determined from the plot of $(\alpha hv)^{1/2}$ versus photon energy (hv) (Tauc's plot), for allowed indirect transitions.

Refractive index of these glasses has been calculated by using the relation proposed by (Dimitrov and Komatsu, 2002; Eraiah and Bhat, 2007) Equation 3:

$$\frac{(n^2-1)}{(n^2+2)} = 1 - \sqrt{\frac{E_g}{20}} \quad (3)$$

In order to measure the x-ray luminescence of the Sm_2O_3 doped bismuth borate glass samples at room temperature, x-ray tube (DRGEM Co.) was used and faces of the glass sample were wrapped with several layers of Teflon tape excepting the one for attaching to the optical fiber. Signals from the glass sample by the induced x-ray were measured using a QE65000 spectrometer (Ocean Optics Co.) The QE65000 was cooled to-15 to reduce thermal noise in the CCD. It was used to plot the x-ray emission spectrum of the glass sample by window based-software (Kim *et al*., 2011; Rooh *et al*., 2009).

3. RESULTS

3.1. Density and Molar Volume

The measured density of Sm^{3+} doped bismuth borate glass samples for different Sm_2O_3 concentrations are shown in **Fig. 1**. As seen in **Fig. 1**, density increase linearly with additional content of Sm_2O_3 into the network. **Figure 2** shows the variation of the molar volume with Sm_2O_3 concentration. As shown in **Fig. 2**, the molar volume increases with an increase in Sm_2O_3 content.

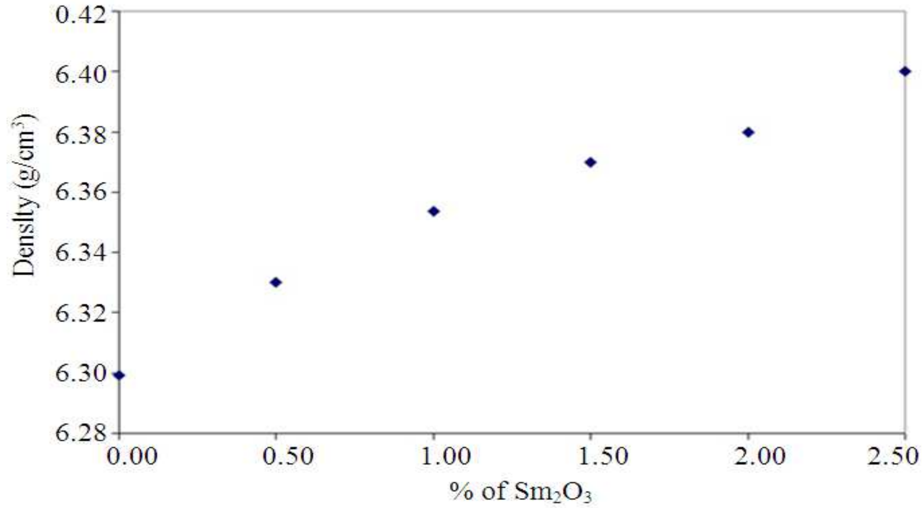

Fig. 1. Variation of density with Sm_2O_3 concentration

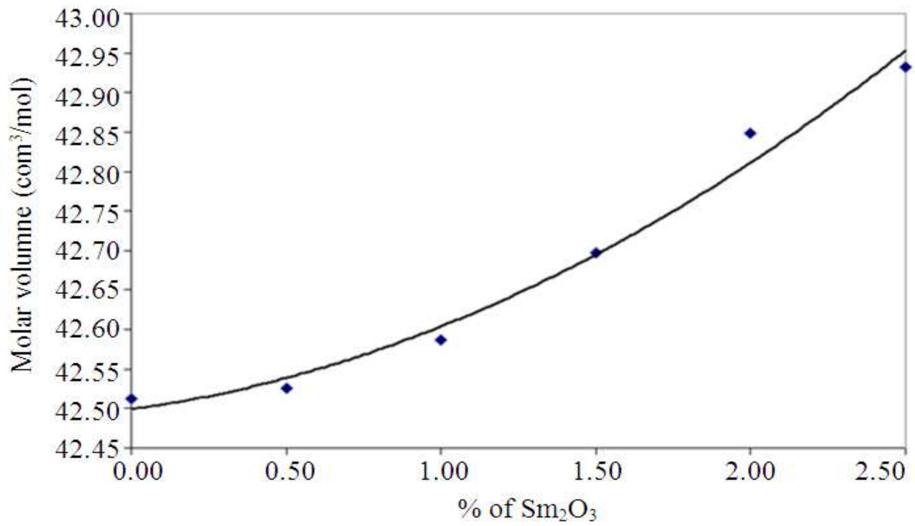

Fig. 2. Variation of molar volume with Sm_2O_3 concentration

3.2. Optical Spectra, Optical Band Gap and Refractive Index

The absorption spectra of Sm^{3+} doped bismuth borate glasses in the UV-VIS region at room temperature are shown in **Fig. 3**. It is clearly observed that the absorption intensity of the absorption bands increases with the increase of Sm_2O_3 concentration. Three absorption bands peaked at 474 nm, 950 nm and 1083 nm were observed. From absorption spectra, the optical band gap were evaluated by Tauc's plot using Equation (2) and shown in **Fig. 4**. the results shows that the optical bandgap decreased with increasing of Sm_2O_3 concentration (**Fig. 5**). Refractive index of these glasses has been calculated by using Equation 3 and show in **Fig. 6**. The result show refractive index of glasses increased with increasing of Sm_2O_3 concentration.

3.3. X-Rays Luminescence

Figure 7 showed x-rays luminescence spectra of Sm_2O_3 doped bismuth borate glasses. The emission wavelength observed at 569, 598, 641 and 705 nm.

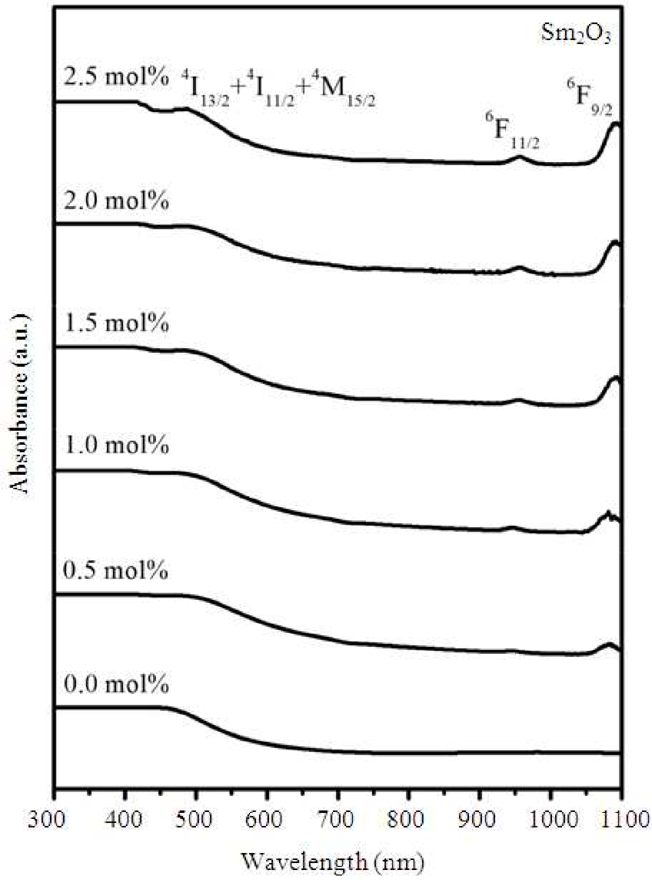

Fig. 3. Typical absorption spectra of Sm_2O_3 doped in bismuth borate glass

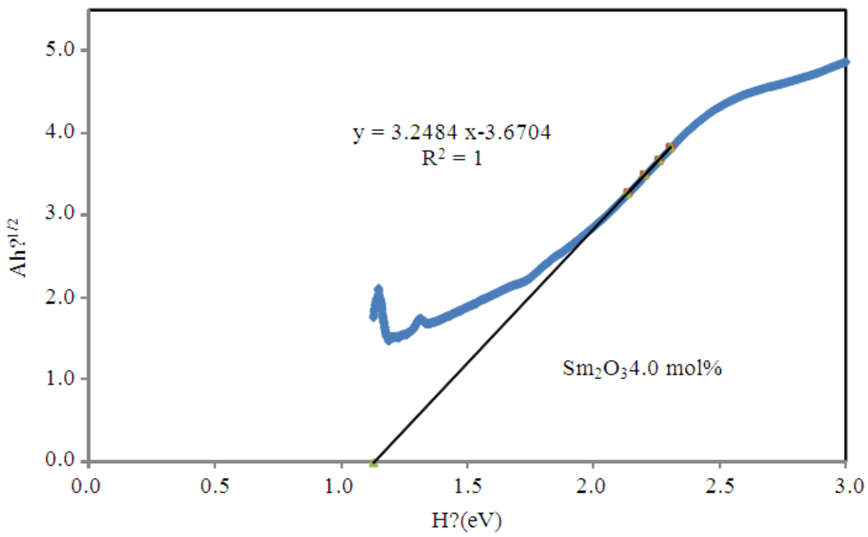

Fig. 4. Typical tauc's plot of Sm_2O_3 doped in bismuth borate glass

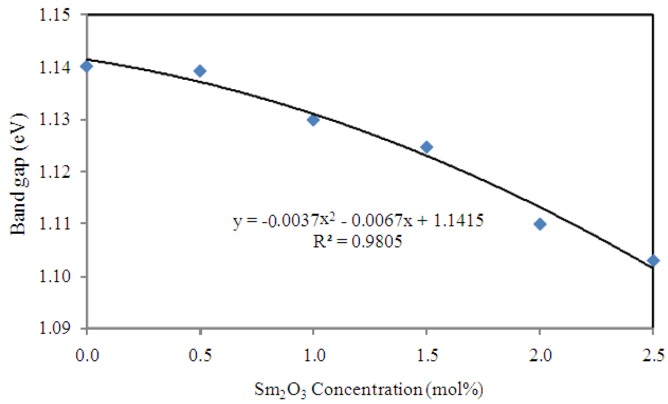

Fig. 5. Variation of optical band gap (for indirect allow transition) with Sm_2O_3 concentration

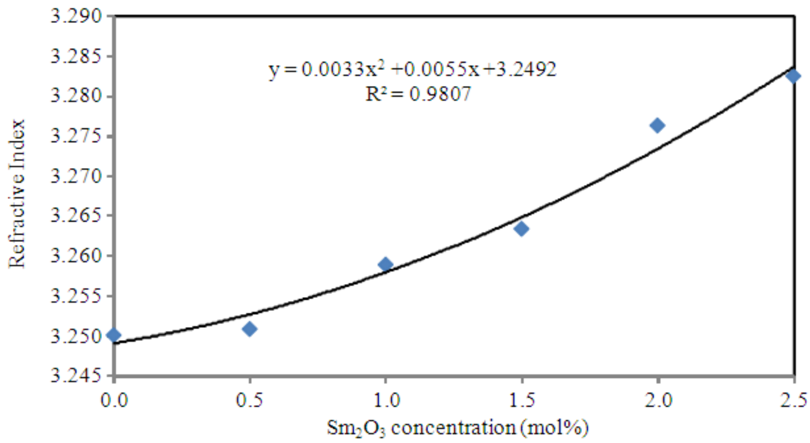

Fig. 6. Variation of refractive index with Sm_2O_3 concentration

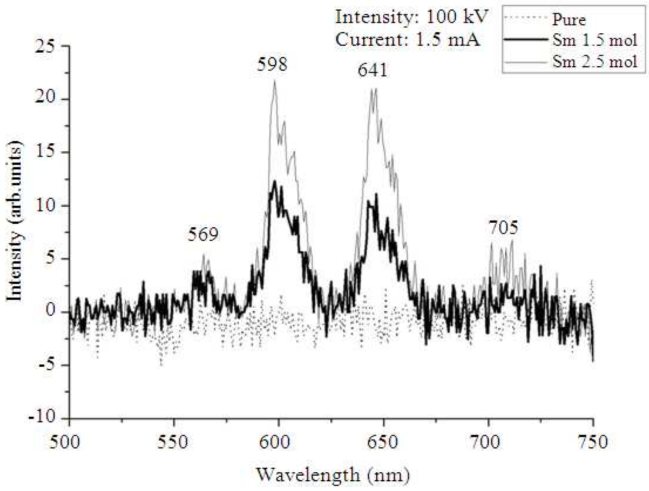

Fig. 7. X-rays luminescence spectra of Sm_2O_3 doped bismuth borate glasses

4. DISCUSSION

4.1. Density and Molar Volume

From the increasing of density results, indicates that replacing B_2O_3 by addition of Sm_2O_3 is effects to increase of the average molecular weight due to Sm_2O_3 has a higher relative molecular weight than that of B_2O_3. As shown in **Fig. 2**, the molar volume increases with an increase in Sm_2O_3 content, which is attributed to the increase in the number of Non-Bridging Oxygen (NBOs). The increase of NBOs in the structure generally leads to an increase in average atomic separation. The results obtained indicate that the samarium oxide enters the glass network as a modifier by occupying the interstitial space in the network and generating the NBOs to the structure. It can also be concluded that the addition of Sm_2O_3 may accordingly result in an extension of glass network (Sindhu *et al*., 2005).

4.2. Optical Spectra, Optical Band Gap and Refractive Index

All absorption band spectra are characteristics of Sm^{3+}-doped oxide glasses (Som and Karmakar, 2008) and the observed absorption bands were assigned to appropriate f-f electronic transitions of Sm^{3+} ions from the $^6H_{5/2}$ ground state to ($^4I_{13/2}$ + $^4I_{11/2}$ + $^4M_{15/2}$), $^6F_{11/2}$ and $^6F_{9/2}$ respectively. From optical band gap result show that, when increase Sm_2O_3, bonding defect and non-bridging oxygen were increased. These leads to increase in the degree of localization of electrons there by increasing the donor center in the glass matrix. The increasing presence of donor center, therefore, decreases the optical band gap. As a result of this, band gap are decreased as shown in **Fig. 5**, for indirect allow transition. For this case the refractive index of glasses were increased. This result is effects from increasing of density and polarizability of Sm^{3+} doped bismuth borate glass.

4.3. X-Rays Luminescence

The x-rays luminescence spectra of the Sm_2O_3 doped bismuth borate glass were identified as $^4G_{5/2}\rightarrow{}^6H_{5/2}$ (569 nm), $^4G_{5/2}\rightarrow{}^6H_{7/2}$ (598 nm), $^4G_{5/2}\rightarrow{}^6H_{9/2}$ (641 nm) and $^4G_{5/2}\rightarrow{}^6H_{11/2}$ (705 nm) (Yusov *et al*., 2011). The intensity of luminescence was increase with increasing doping concentration and intensity at 598 nm of 2.5 mol% of Sm_2O_3 doped sample is approximately

5. CONCLUSION

In this study, Sm^{3+}-doped bismuth borate glasses of the composition (50-x) SiO_2: $50B_2O_3$: xSm_2O_3 (where x = 0.00, 0.50, 1.00, 1.50, 2.00 and 2.50 mol%) have been synthesized by conventional melt quenching technique The results show that density, molar volume and refractive index of glasses increased with increasing Sm_2O_3 concentration. The increase of molar volume with Sm_2O_3 concentration is due to the increase of Non-Bridging Oxygen (NBOs) in the glass matrix. It can also be concluded that the addition of Sm_2O_3 may accordingly result in an extension of glass network. The optical absorption spectra were measured in the wavelength range from 300-1100 nm and three absorption bands peaked at

474 nm, 950 nm and 1083 nm were observed. The optical band gap decreased with the increase of Sm_2O_3 concentration. The x-rays luminescence of Sm_2O_3 doped glasses samples shows emission band at $^4G_{5/2}\rightarrow{}^6H_{5/2}$ (569 nm), $^4G_{5/2}\rightarrow{}^6H_{7/2}$ (598 nm), $^4G_{5/2}\rightarrow{}^6H_{9/2}$ (641 nm) and $^4G_{5/2}\rightarrow{}^6H_{11/2}$ (705 nm).

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