X-RAYS LUMINESCENCE, OPTICAL AND PHYSICAL STUDIES OF BI$_2$O$_3$-B$_2$O$_3$-SM$_2$O$_3$ GLASSES SYSTEM

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ABSTRACT

Sm$^{3+}$-doped bismuth borate glasses of the composition (50-x) SiO$_2$: 50B$_2$O$_3$: xSm$_2$O$_3$ (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$_2$O$_3$ 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$_2$O$_3$ concentration. The increase of molar volume with Sm$_2$O$_3$ 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$_2$O$_3$ concentration. Moreover, the x-rays luminescence of Sm$_2$O$_3$ glasses samples were measured and shows emission band at $^4$G$_{5/2}$→$^6$H$_{5/2}$ (569 nm), $^4$G$_{5/2}$→$^6$H$_{7/2}$ (598 nm), $^4$G$_{5/2}$→$^6$H$_{9/2}$ (641 nm) and $^4$G$_{5/2}$→$^6$H$_{11/2}$ (705 nm). This investigation have been used as the basis for developing optical amplifier or glass scintillator.

Keywords: Sm$_2$O$_3$, X-Ray Luminescence, Glass, Optical Spectra, Optical Absorption, Molar Volume, Doped Bismuth Borate, Wavelength Range, Emission Band, Gap Decreased

1. INTRODUCTION

Boric oxide, B$_2$O$_3$, acts as one of the most important glass formers and flux materials. Melts with compositions rich in B$_2$O$_3$ 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$_x$O$_y$ structural groups (Xue et al., 2000). Among these borates, especially the monoclinic bismuth borate BiB$_3$O$_6$ 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$_2$O$_3$-B$_2$O$_3$ 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 $^4$G$_{5/2}$ $\rightarrow ^4$H$_{5/2}$ (green), $^4$G$_{5/2}$ $\rightarrow ^4$H$_{11/2}$ (orange) and $^4$G$_{5/2}$ $\rightarrow ^4$H$_{15/2}$ (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$_2$O$_3$; 50B$_2$O$_3$; xSm$_2$O$_3$ (x = 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 mol%). The batch was prepared from the AR grade of Bi$_2$O$_3$ (Fluka 99.99%), H$_3$BO$_3$ (Sigma-Aldrich, 99.99%) and Sm$_2$O$_3$ (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):

$$V_m = \frac{M}{\rho}$$

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, $\alpha(\nu)$, as a function of incident photon energy ($hv$) for direct and indirect optical transitions is given by (Abdel-Baki et al., 2006):

$$\alpha(\nu) = a_0(\nu - E_g)^n / \nu$$

where the exponent $n = 1/2$ for an allowed direct transition, while $n = 2$ for an allowed indirect transition, $a_0$ is a constant related to the extent of the band tailing and $E_g$ is the optical band gap energy. The absorption coefficient, $\alpha(\nu)$, 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 $(\alpha\nu)^{1/2}$ versus photon energy ($h\nu$) (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:

$$\left(\frac{n^2 - 1}{n^2 + 2}\right) = 1 - \frac{E_g}{20}$$

In order to measure the x-ray luminescence of the Sm$_2$O$_3$ 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 glass samples for different Sm$_2$O$_3$ concentrations are shown in Fig. 1. As seen in Fig. 1, density increase linearly with additional content of Sm$_2$O$_3$ into the network. Figure 2 shows the variation of the molar volume with Sm$_2$O$_3$ concentration. As
shown in Fig. 2, the molar volume increases with an increase in Sm$_2$O$_3$ content.

![Graph of density vs. Sm$_2$O$_3$ concentration](image1)

**Fig. 1.** Variation of density with Sm$_2$O$_3$ concentration

![Graph of molar volume vs. Sm$_2$O$_3$ concentration](image2)

**Fig. 2.** Variation of molar volume with Sm$_2$O$_3$ 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$_2$O$_3$ 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 show that the optical bandgap decreased with increasing of Sm$_2$O$_3$ 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$_2$O$_3$ concentration.

### 3.3. X-Rays Luminescence
Figure 7 showed x-rays luminescence spectra of \( \text{Sm}_2\text{O}_3 \) doped bismuth borate glasses. The emission wavelength observed at 569, 598, 641 and 705 nm.

![Absorption Spectra](image)

Fig. 3. Typical absorption spectra of \( \text{Sm}_2\text{O}_3 \) doped in bismuth borate glass
Fig. 4. Typical Tauc’s plot of Sm$_2$O$_3$ doped in bismuth borate glass

Fig. 5. Variation of optical band gap (for indirect allow transition) with Sm$_2$O$_3$ concentration
4. DISCUSSION

4.1. Density and Molar Volume

From the increasing of density results, indicates that replacing B$_2$O$_3$ by addition of Sm$_2$O$_3$ is effects to increase of the average molecular weight due to Sm$_2$O$_3$ has a higher relative molecular weight than that of B$_2$O$_3$. As shown in Fig. 2, the molar volume increases with an increase in Sm$_2$O$_3$ 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$_2$O$_3$ 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 ($^4I_{15/2}$ + $^4I_{13/2}$), $^4F_{15/2}$ and $^4F_{9/2}$ respectively. From optical band gap result show that, when increase Sm$_2$O$_3$, 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$_2$O$_3$ doped bismuth borate glass were identified as $^4G_{5/2} → ^6H_{5/2}$ (569 nm), $^4G_{5/2} → ^6H_{7/2}$ (598 nm), $^4G_{5/2} → ^6H_{9/2}$ (641 nm) and $^4G_{5/2} → ^6H_{11/2}$ (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$_2$O$_3$ doped sample is approximately.

5. CONCLUSION

In this study, Sm$^{3+}$-doped bismuth borate glasses of the composition (50-x) SiO$_2$: 50B$_2$O$_3$: xSm$_2$O$_3$ (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$_2$O$_3$ concentration. The increase of molar volume with Sm$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ concentration. The x-rays luminescence of Sm$_2$O$_3$ doped glasses samples shows emission band at $^6G_{5/2}$→$^6H_{5/2}$ (569 nm), $^6G_{5/2}$→$^6H_{7/2}$ (598 nm), $^6G_{5/2}$→$^6H_{9/2}$ (641 nm) and $^6G_{5/2}$→$^6H_{11/2}$ (705 nm).

6. REFERENCES

Abdel-Baki, M., F. El-Diasty and F.A.A. Wahab, 2006. Optical characterization of xTiO$_2$-(60-x)SiO$_2$-40Na$_2$O glasses: II. Absorption edge, Fermi level, electronic polarizability and optical basicity. Opt. Commun., 2: 65-70. DOI: 10.1016/j.optcom.2005.11.056

Becker, P., 1998. Borate materials in nonlinear optics. Adv. Mater., 10: 979-992. DOI: 10.1002/(SICI)1521-4095(199809)10:13<979::AID-ADMA979>3.0.CO;2-N

Becker, P., 2003. Thermal and optical properties of glasses of the system Bi$_2$O$_3$-B$_2$O$_3$. Cryst. Res. Technol., 38: 74-82. DOI: 10.1002/crat.200310009

Biju, P.R., G. Jose, V. Thomas, V.P.N. Nampoori and N.V. Unnikrishnan, 2004. Energy transfer in Sm$^{3+}$:Eu$^{3+}$ system in zinc sodium phosphate glasses. Opt. Mater., 24: 671-677. DOI: 10.1016/S0925-3467(03)00183-6

Carnall, W.T., P.R. Fields and K. Rajnak, 1968. Electronic energy levels in the trivalent lanthanide aquo ions. I. Pr$^{3+}$, Nd$^{3+}$, Pm$^{3+}$, Sm$^{3+}$, Dy$^{3+}$, Ho$^{3+}$, Er$^{3+}$ and Tm$^{3+}$. J. Chem. Phys., 49: 4424-4442. DOI: 10.1063/1.1669893

Dimitrov, V. and T. Komatsu, 2002. Classification of simple oxides: A polarizability approach. J. Solid State Chem., 163: 100-112. DOI: 10.1006/jssc.2001.9378

Eraiah, B. and S.G. Bhat, 2007. Optical properties of samarium doped zinc-phosphate glasses. J. Phys. Chem. Solids, 68: 581-585. DOI: 10.1016/j.jpcs.2007.01.032

Farries, M. C., R.P. Morkel and J. E. Townsend, 1988. Samarium$^{3+}$-doped glass laser operating at 651nm. Elect. Lett., 24: 709-711.

France, P.W., M.G. Drexhage, J.M. Parker, M.W. Moore and S.F. Carter, 2000. Fluoride Glass Optical Fibers. 1st Edn., CRC Press, Boca Raton, FL.

Hellwig, H., J. Liebertz and L. Bohaty, 1999. Exceptional large nonlinear optical coefficients in the monoclinic bismuth borate BiB$_2$O$_6$ (BIBO), Solid State Commun., 109: 249-251. DOI: 10.1016/S0038-1098(98)00538-9

Hellwig, H., J. Liebertz and L. Bohaty, 2000. Linear optical properties of the monoclinic bismuth borate BiB$_2$O$_6$. J. Applied Phys., 88: 240-244. DOI: 10.1063/1.373647

Kaczkan, M., Z. Frukacz and M. Malinowski, 2001. Infra-red-to-visible wavelength upconversion in Sm$^{3+}$-activated YAG crystals. J. Alloys Comp., 49: 4424-4442. DOI: 10.1016/S0925-8388(01)01066-0

Kim, M.J., H.J. Kim, H. Park, S. Kim and J.I. Kim, 2011. Characterization of BaCl$_2$ scintillation crystal at low temperature. Nucl. Instruments Methods Phys. Res. A, 632: 47-51. DOI: 10.1016/j.nima.2010.12.226

Lin, Z., Z. Wang, C. Chen and M.H. Lee, 2001. Mechanism for linear and nonlinear optical effects in monoclinic bismuth borate (BiB$_2$O$_6$) crystal. J. Applied Phys., 90: 5585-5590. DOI: 10.1063/1.1413711

Rooh, G., H. Kang, H.J. Kim, H. Park and S. Kim, 2009. The growth and scintillation properties of Cs$_2$NaCeCl$_6$ single crystal. J. Crystal Growth, 311: 2470-2473. DOI: 10.1016/j.jcrysgro.2009.01.091

Sindhu, S., S. Sanghi, A. Agarwal, V.P. Seth and N. Kishore, 2005. Effect of Bi$_2$O$_3$ content on the optical band gap, density and electrical conductivity of MO•Bi$_2$O$_3$•B$_2$O$_3$ (M = Ba, Sr) glasses. Mate. Chem.
Som, T. and B. Karmakar, 2008. Infrared-to-red upconversion luminescence in samarium-doped antimony glasses. J. Luminescence, 128: 1989-1996. DOI: 10.1016/j.jlumin.2008.06.011

Xue, D., K. Betzler, H. Hesse and D. Lammers, 1999. Origin of the large nonlinear optical coefficients in bismuth borate BiB\textsubscript{3}O\textsubscript{6}. Phy. Stat. Solids (a), 176: R1-R2. DOI: 10.1002/(SICI)1521-396X(199912)176:2<R1::AID-PSSA99991>3.0.CO;2-H

Xue, D., K. Betzler, H. Hesse and D. Lammers, 2000. Nonlinear optical properties of borate crystals. Solid State Commun., 144: 21-25. DOI: 10.1016/S0038-1098(99)00579-7

Yusov, A.B., A.M. Fedosseev, G.B. Andreev and I.B. Shirokova, 2011. Luminescence properties of solid Eu, Sm, Tb and Dy compounds with the molybdoaluminate ion Al(\textsubscript{6}OH\textsubscript{6})Mo\textsubscript{6}O\textsubscript{18}. Mendeleev Commun., 11: 86-87. DOI: 10.1070/MC2001v011n03ABEH001427

Zhou, Y., J. Lin and S. Wang, 2003. Energy transfer and upconversion luminescence properties of \textit{Y}_2\textit{O}_3: Sm and \textit{Gd}_2\textit{O}_3: Sm phosphors. J. Solid State Chem., 171: 391-395. DOI: 10.1016/S0022-4596(02)00219-0