Preparation and Properties of Bi$_2$O$_3$-B$_2$O$_3$-Nd$_2$O$_3$ Glass System

K. Boonin$^{a,*}$, J. Kaewkhaob$^{b,c}$, T. Ratanab$^{d}$ and P. Limsuwan$^{a,c}$

$^a$Department of Physics, Faculty of Science, King Mongkut’s University of Technology Thonburi, Thailand, 10140
$^b$Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Thailand, 73000
$^c$Thailand Center of Excellence in Physics, CHE, Ministry of Education, Bangkok 10400, THAILAND
$^d$Department of Physics, Faculty of Science, Burapha University, Thailand, 20131

Abstract

In the present work Bi$_2$O$_3$-B$_2$O$_3$-Nd$_2$O$_3$ glasses have been prepared via melt quenching method. The composition has been fixed to 70 mol% B$_2$O$_3$, 30 mol% Bi$_2$O$_3$ which is a stable glass forming composition. In these glasses, Nd$_2$O$_3$ has been doped in replace of B$_2$O$_3$ concentration in glass formula. UV-VISIBLE-NIR studies have been performed in these glasses to examine the optical spectra and the result show eight absorption peaks. The transition energy levels vary with the Nd$_2$O$_3$ concentration and depend on covalency and the asymmetry of Nd-O local structure among these host matrices. In addition, the effect of Nd$_2$O$_3$ on these distributions has been examined in term of density, molar volume and basicity.

© 2011 Published by Elsevier Ltd.

Keywords: Glass, Nd$^{3+}$; Absorption spectra; Bismuth borate

1. Introduction

Glass is a promising host to investigate the influence of chemical environment on the optical properties of the rare earth ions. It affords considerable flexibility in size and shape, and can be doped at very high concentrations of activator ions with excellent uniformity. Rare earth-doped glasses have been studied and applied for several years in a variety of photonic applications, for example, as optical amplifiers and solid state lasers. Among the possible rare earth ions, Nd$^{3+}$ is one of the most studied rare earth ions and is also one of the most efficient candidates for photonic devices [1]-[3]. Recently, glass-ceramics containing neodymium oxide has been used for several purposes.

Firstly, Nd$_2$O$_3$ has been used for special glasses used in halogen lamps to absorb ultra-violet rays which are harmful to humans. Secondly, the glasses containing Nd$_2$O$_3$ can have high hardness and excellent chemical durability as refractory glasses. Thirdly, neodymium contained in glass can be used as a band rejection filter for...
image display devices, owing to absorption originating in the inter-transition within the 4f shell of the Nd³⁺ ion [4]-[5].

Boric oxide, B₂O₃, acts as one of the most important glass formers and flux materials. Melts with compositions rich in B₂O₃ 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 [6]. The boron atom usually coordinates with either three or four oxygen atoms forming [BO₃]³⁻ or [BO₄]⁵⁻ structural units. Furthermore, these two fundamental units can be arbitrarily combined to form different B₂O₃ structural groups [7]. Among these borates, especially the monoclinic bismuth borate BiB₃O₉ shows up remarkably large linear and nonlinear optical coefficients [8], [9]. Calculations indicate that this can be mainly attributed to the contribution of the [BiO₄]⁵⁻ anionic group [10], [11]. 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 Bi₂O₃–B₂O₃ have attracted much interest [12]. In this work we report on optical, physical and structural properties of Nd³⁺ ion-doped bismuth borate glass in formula (70-x)B₂O₃:30Bi₂O₃:xNd₂O₃ (where x = 0.0-2.5 mol%).

2. Materials and Method

Glasses from the system 30Bi₂O₃:(70-x)B₂O₃:xNd₂O₃ (x= 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 mol%) were prepared by melt quenching technique. Batch calculations were done and appropriate amounts of boric acid, Bi₂O₃, and Nd₂O₃ were weighed and thoroughly mixed together. The batch mixture was transferred to an alumina crucible and melted in electrical furnace at 1,100°C for 3 hr in normal atmosphere. The temperature was sufficient to produce clear, bubble free melt. The melt was then quenched on a pre-heated stainless steel mold to avoid thermal stresses produced by non-uniform rapid cooling of the glass. Clear, bubble free glass was obtained and characterization was carried out. For the absorption measurements, a Shimadzu, UV-3100 spectrophotometer was used working in the near ultraviolet, visible, and near infrared spectral region. The absorption data were measured on plate-shaped samples with a thickness of approximately 3 mm.

By applying Archimedes principle, the weight of the prepared glass samples was measured in air and in xylene using a 4-digit sensitive microbalance (Denver, Pb214). The corresponding molar volume (V_M) was calculated using the relation, V_M = M_T / ρ, where M_T is the total molecular weight of the multi-component glass system given by

$$M_T = x_{Bi_2O_3}Z_{Bi_2O_3} + x_{B_2O_3}Z_{B_2O_3} + x_{Nd_2O_3}Z_{Nd_2O_3}$$

(1)

Where x_{Bi_2O_3}, x_{B_2O_3} and x_{Nd_2O_3} are the mole fractions of the constituent oxides, and Z_{Bi_2O_3}, Z_{B_2O_3} and Z_{Nd_2O_3} are the molecular weights of the constituent oxides.

In multi-component oxide glasses, the theoretical basicity, Λ_th, was calculated based on the basis of the equation given by

$$Λ_th = x_1Λ_1 + x_2Λ_2 + x_3Λ_3 + ...$$

(2)

where Λ_1, Λ_2 and Λ_3 are basicities of the oxide components, and x_1, x_2 and x_3 are their equivalent fractions (fraction of the total oxygen provided by the component oxide glass).

3. Results and Discussion

From table 1, although the relative molecular mass of Nd₂O₃ is higher than B₂O₃, density is found to not depend on Nd₂O₃ concentration. The molar volume of the glass systems under study changes with Nd₂O₃ content in a specific manner (figure 1). This variation of V_M can be divided into three regions. In the first region, V_M increases with increase in Nd₂O₃ content up to 0.5 mol%, which is attributed to the increase in the number of non-bridging oxygen (NBOs). In the second region (0.5-1.5 mol %), the rate of increase of V_M is very small and seems to have a constant value. This may be due to constancy in the number of NBOs. A probable explanation may be that a major part of Nd₂O₃ enters directly into the structure without the introduction of additional NBOs. In the third region (since 1.5 mol %), V_M again increases again. A further addition of Nd₂O₃ may accordingly result in an extension of the network [13]. The change in molar volume depends on the rates of change of both density and molecular weight. However, the rate of the increase in molecular weight is greater than the rate of increase in density [14]. This would be accompanied by an increase in V_M, as can be seen from figure 1.
Table 1 Densities, molar volumes and basicity of of Bi₂O₃-B₂O₃-Nd₂O₃ glass system

| % Nd₂O₃ | Density (g/cm³) | V_M (cm³/mol) | \( \Lambda_{th} \) |
|---------|----------------|---------------|-------------------|
| 0.00    | 4.207          | 45.261        | 0.654             |
| 0.50    | 4.147          | 46.184        | 0.657             |
| 1.00    | 4.153          | 46.447        | 0.660             |
| 1.50    | 4.175          | 46.523        | 0.663             |
| 2.00    | 4.171          | 46.883        | 0.666             |
| 2.50    | 4.180          | 47.097        | 0.669             |

Figure 1 Molar volume of Bi₂O₃-B₂O₃-Nd₂O₃ glass system

Theoretical optical basicity serves in the first approximation as a measure of the ability of oxygen to donate a negative charge in the glasses. The theoretical optical basicity can be used to classify the covalent/ionic ratios of the glasses since an increasing \( \Lambda_{th} \) indicates decreasing covalency [15]. It is clear from Tables 1, the values of \( \Lambda_{th} \) lie in the range 0.654–0.669 and is found to increase as concentration of Nd₂O₃ increases. As optical basicity depends on both, so the overall result is increase in basicity. In the glass system in which Nd₂O₃ replaces B₂O₃ is having large value of basicity than the system where Nd₂O₃ replaces B₂O₃. This is because as B₂O₃ is highly acidic and its replacement by a base will increase the optical basicity.
Absorption spectra of Nd$^{3+}$ doped in bismuth borate glasses are shown in figure 2. The optical absorption edges are not sharply defined in glass samples under study, in accordance with their amorphous nature [16]. It can be seen that the transition energy levels vary with the Nd$_2$O$_3$ concentration and depend on covalency and the asymmetry of Nd-O local structure among these host matrices [17]. It is observed that the absorption intensity of the observed bands increase with the increase of Nd$_2$O$_3$ concentration. The absorption bands of Nd$^{3+}$ correspond to transitions from the $^4$I$_{9/2}$ ground state to various excited levels. These transitions were assigned by comparing the band positions in the absorption spectra with a standard wavelength chart for the Nd$^{3+}$ ion [18]. The various spectroscopic transitions observed are as follows: $^4$F$_{3/2}$ (877 nm), $^5$F$_{5/2}$ + $^2$H$_{9/2}$ (803 nm), $^4$S$_{3/2}$ + $^4$F$_{7/2}$ (745 nm), $^4$F$_{9/2}$ (684 nm), $^5$H$_{11/2}$ (630 nm) $^4$G$_{5/2}$ + $^2$G$_{7/2}$ (583 nm), $^5$K$_{13/2}$ + $^4$G$_{7/2}$ (526 nm) $^4$G$_{9/2}$ (519 nm) $^4$I$_{9/2}$ transitions were not clearly observed for the bismuth borate glass.

4. Conclusion
In this research, glasses from the system 30Bi$_2$O$_3$·(70-x)B$_2$O$_3$·xNd$_2$O$_3$ (x= 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 mol%) were prepared by melt quenching technique. The absorption peaks at $^4$F$_{3/2}$ (877 nm), $^4$F$_{5/2}$ + $^2$H$_{9/2}$ (803 nm), $^4$S$_{3/2}$ + $^4$F$_{7/2}$ (745 nm), $^4$F$_{9/2}$ (684 nm), $^5$H$_{11/2}$, (630 nm) $^4$G$_{5/2}$ + $^2$G$_{7/2}$ (583 nm), $^5$K$_{13/2}$ + $^4$G$_{7/2}$ (526 nm) $^4$G$_{9/2}$ (519 nm) of Nd$_2$O$_3$ in bismuth borate glasses were observed. The molar volume were increased with increasing of Nd$_2$O$_3$, indicates that increase of NBOs. An increase of NBOs in the structure generally leads to an increase average atomic separation due to more ionic bond are created, which will break the bonds of host glass, and then the spaces into the network will increase. The increase of basicity with Nd$_2$O$_3$ show more ability of oxygen to donate a negative charge in the glasses.
Acknowledgments

The authors wish to thanks Commission of Higher Education (NRU Project) and Research and Development Institute, Nakhon Pathom Rajabhat University for financial support.

References

[1] K. Gatterer, G. Pucker, W. Jantscher, H.P. Fritzer and S. Arafa, Journal of Non-Cryst, Sol., vol. 231, pp. 189-199, 1998.
[2] W.A. Pisarski, T. Goryczka, B. Wodecka-Dus, M. Plonska and J. Pisarska, Mat. Sci. and Eng., vol. 122, pp. 94-99, 2005.
[3] Maumita Das, K. Annappurna, P. Kundu, R.N. Dwivedi and S. Buddhudu, Mat. Lett., vol. 60, pp. 222, 2006.
[4] M. Shaweta, S.T. Kulwant, S. Gopi and G. Leif, Spect. Act., vol. 70, pp. 1173, 2008.
[5] L.R. Moorthy, T.S. Rao, M. Rayasimhadri, A. Radhapathy and D.V.R. Murthy, Spect. Act., vol. 60, pp. 2449.8, 2004.
[6] P. Becker, Adv. Mat, vol. 10, pp. 979, 1998.
[7] D. Xue, K. Betzler, H. Hesse, D. Lammers, Solid State Communications, vol. 114, pp.21, 2000.
[8] H. Hellwig, J. Liebertz and L. Bohaty, Solid State Communications, vol. 109, pp. 249, 1999.
[9] H. Hellwig, J. Liebertz and L. Bohaty, J. of Appl. Phy., vol. 88, pp. 240, 2000.
[10] D. Xue, K. Betzler, H. Hesse and D. Lammers, Phy. Stat. Solidi (a), vol. 176, pp. R1-R2, 1999.
[11] Z. Lin, Z. Wang, C. Chen and M.-H. Lee, J. of Appl. Phy., vol. 90, pp. 5585, 2001.
[12] P. Becker, Cryst. Res.and Tech., vol. 1, pp. 74, 2003.
[13] A. Bishay and C. Maghrabi, Phys. Chem. Glasses., vol. 10, pp. 1, 1969.
[14] S. Sindhu, S. Sanghi, A. Agarwal, V.P. Seth and N. Kishore, Mat. Chem. Phys., vol. 90, pp. 83, 2005.
[15] S. Sindhu, S. Sanghi, A. Agarwal, N. Kishore and V.P. Seth, J. Alloys Comp, vol. 428 pp. 206, 2007.
[16] B. Eraiah and Sudha G. Bhat, J. of Phy. Chem. of Sol., vol. 68, pp. 581, 2007.
[17] B. Karthikeyana, S. Mohanb and M.L. Baesso, Physica B., vol. 337, pp. 249, 2003.
[18] G.H. Dieke, Spectra and Energy Levels of Rare-Earth Ions in Crystals, vol. 1, 1968.