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Effect of ZnO on Physical and Optical Properties of Bismuth Borate Glasses

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This paper presents the results and observations obtained from a study of the effects of zinc oxide on the optical properties of B_2O_3-Bi_2O_3-ZnO glasses. In this study, we prepared glasses with the composition, 2xZnO-(50-x)[$B_2O_3 \cdot Bi_2O_3$], (x=0, 5, 10, 15), and analyzed their physical, thermal and optical properties. The systematic variation in the density and molar volume in these glasses indicates the effect of ZnO on the glass structure. Differential thermal analysis (DTA) studies showed that the glass transition temperature (T_g) decreases from 423°C to 390°C as the content of ZnO increases. The values of the optical band gap and theoretical optical basicity are also investigated.

Keywords: bismuth borate glass, zinc oxide, non-bonding oxides, optical properties, physical properties

1. INTRODUCTION

In recent years, borates have attracted the attention of researchers due to their useful physical properties, which makes them promising for practical use.[1] Among them, bismuth borates are of most interest.[2,3]

The interest in heavy metal oxide glasses is due to their long infrared cut-off and optical non-linearity.[4,5] Bismuth based oxide glasses have attracted the attention of the scientific community, due to their important applications in the field of glass ceramics, thermal and mechanical sensors, reflecting windows, etc.[6] A survey of the literature shows that there are many reports available on ternary bismuth borate glasses.[7-12]

Recently, attention has been given to the investigation of glasses containing transition metal cations. The investigation of the structure of such materials is essential to obtain a better insight into their structure–property relations. The property of each type of glass depends on the concentration of the oxide itself.[13-18] Especially, zinc oxide based glasses/ceramics have special applications in the areas of varistors, dielectric layers and transparent dielectric and barrier ribs in plasma display panels.[19,20] However, the number of studies in which zinc is added is very limited.[21,22]

Therefore, the present work was carried out to investigate the effect of ZnO on the physical and optical properties of B_2O_3-Bi_2O_3 glasses.

2. EXPERIMENTAL PROCEDUR

Glass samples from the system 2xZnO-(50-x)[$B_2O_3 \cdot Bi_2O_3$] (x=0, 5, 10, 15) were prepared using B_2O_3, Bi_2O_3 and ZnO with purities higher than 99.9%. All of the prepared chemical powders were finely mixed for 10 minutes. Each batch was melted in an alumina crucible in an electrical furnace at 1000°C for 30 minutes. These melts were quenched on steel plates and annealed in an electrical furnace at 350°C for 1 hour to release the thermal stress in the glasses. The glasses were polished to obtain a mirror surface.

The amorphous nature of all of the samples was confirmed by the absence of any Bragg's peak in the X-ray diffraction pattern (Rigaku X-ray diffractometer, Cu-Kα, 30 kV 20 mA) (Fig. 1). The density of the glass samples was determined at room temperature by the Archimedes method (AND GH-200) with water as the immersion liquid. The thermal stability was measured by differential thermal analysis (Shimadzu, DTG-60H) at a heating rate of 5°Cmin^{-1} in platinum

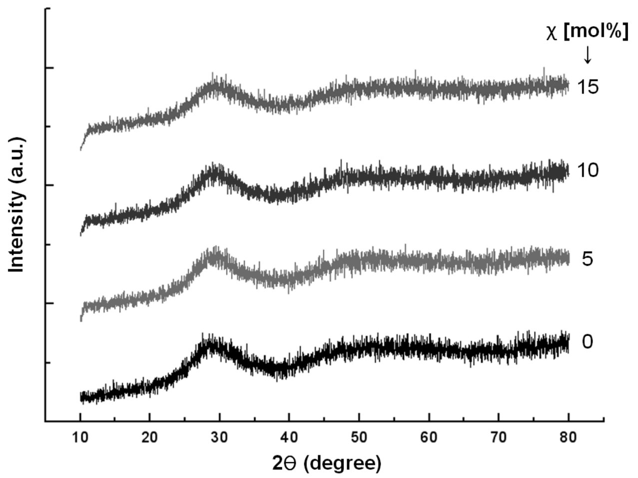

Fig. 1. XRD spectra of 2xZnO-(50-x)[$B_2O_3 \cdot Bi_2O_3$] glasses.

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pans. The transmittance spectra of the glasses were recorded on a UV-Visible spectrometer [Agilent 8453, halogen-lamp]. The thickness of all of the sample glasses was about 2mm. The optical band gap energy was calculated from the experimental transmittance spectra.

3. RESULTS AND DISCUSSION

3.1. Physical properties

The densities (ρ) of the glass samples determined in the present study are given in Table 1. The molar volume (Vm) of the glass samples was calculated from the molecular weight (M) and density (ρ) using the following relation:

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

and these values are included in Table 1. The oxygen packing density (O), ionic concentration (N) of Zn^{2+} ions and inter ionic distance (R) are calculated using the following relations and are presented in Table 1:

$$O = (\rho / M) \times n \quad (2)$$

$$N = (6.023 \times a \times b) / V_m \quad (3)$$

$$R = (1 / N)^{1/3} \quad (4)$$

where n is the number of oxygen atoms per formula unit, *a* is the mol% of cations and *b* is the valency of the cations.

The variation of the density, molar volume and oxygen packing density with the composition of ZnO is shown in Table 1. This could be explained by considering the fact that the density of the present glass system increases and the oxygen packing density increases, whereas the molar volume decreases, with increasing content of ZnO. This is an expected result since, although Bi_2O_3 has a high relative molecular mass, it has a larger ionic radius than ZnO and small cation unit field strength, which provides a fairly open structure in the glass matrix.

3.2. Thermal analysis

Fig. 2 shows the glass transition temperature (T_g) of the samples. The T_g of the samples decreases from 423°C to 390°C with increasing ZnO content. Generally, the decrease in the oxygen packing density, which is a measure of the tightness of packing of the oxide network, can be used to explain the decrease in T_g. This indicates that the structure becomes loosely packed. However, in this result, although the oxygen packing density is increased, T_g is decreased. The decrease in T_g may be due to the increase in the number of non-bridging oxygens (NBOs) as the ZnO content increases. The electronic shell of the O^2 ions is affected by the polarizing action of the modifying cation, i.e., Zn^{2+}. Therefore, increasing the ZnO concentration results in a progressive increase in the number of NBOs, which in turn decreases the number of bridging oxygens.

3.3. Optical Properties

The observed value of the cut-off wavelength (λ_c) is shifted towards a higher wavelength as the content of ZnO increases (Fig. 3). The value of the optical band gap (E_{opt}) is dependent on the ZnO content in a systematic manner (Table

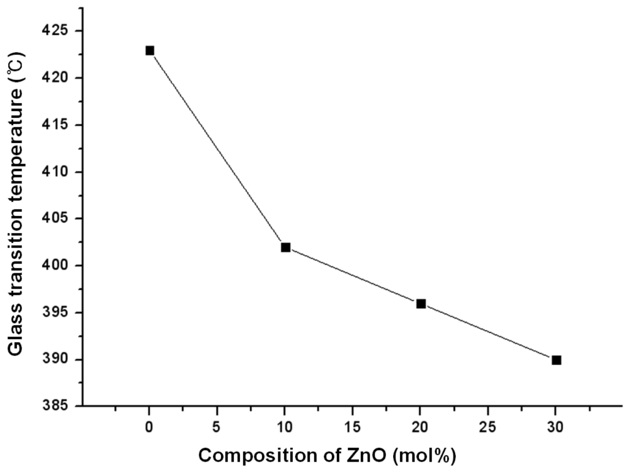

Fig. 2. Variation of glass transition temperature (Tg) with composition of ZnO.

Table 1. Physical parameters of the glass

Parameter	x=0	x=5	x=10	x=15
Density, (g/cc)	6.2178	6.3847	6.4053	6.5206
Average molecular weight, M(g/mole)	267.79	249.15	230.51	211.87
Molar volume, V_m(cc/mole)	43.068	39.023	35.987	32.492
Oxygen packing density, O(g atm/l)	69.657	71.753	72.246	73.863
Zn2+ ion concentration, N($\times 10^{21}$/cc)	0	3.087	6.694	11.122
Inter ionic distance, R(Å)	0	6.868	5.305	4.48
Cut-off wave length (nm)	484	490	497	502
Optical band gap (eV)	2.562	5.531	2.495	2.47
Optical basicity	0.808	0.809	0.810	0.811

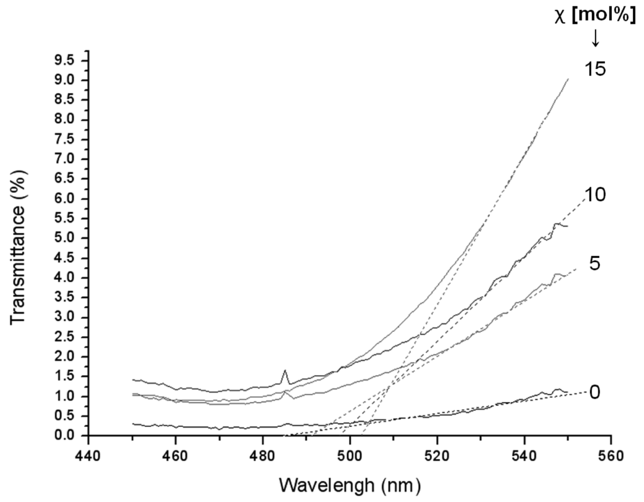

Fig. 3. Transmittance spectra of glasses.

1). It can be understood that, as the ZnO content increases, E_{opt} decreases. The increase in the number of NBOs means that the number of bridging oxygens decreases. It is known that the NBOs are bonded to only one framework cation, B^{3+}, in three or four co-ordination and that the bridging oxygens are bonded to two network cations.[23] Thus, the creation of NBOs seems to be the reason for the shift of λ_c towards a longer wavelength.

The theoretical optical basicity (Λ_{th}) for the glass system under study was calculated using the relation,

$$\Lambda_{th} = X(ZnO)\Lambda(ZnO) + X(Bi_2O_3)\Lambda(Bi_2O_3) + X(Bi_2O_3)\Lambda(Bi_2O_3) \quad (5)$$

where X(ZnO), $X(Bi_2O_3)$, $X(B_2O_3)$ are the equivalent fractions of the different oxides, i.e., the proportion of the oxide atoms that contributes to the glass system, and Λ(ZnO), $\Lambda(Bi_2O_3)$, $\Lambda(B_2O_3)$ are the optical basicity values of the constituent oxides. Here, the values Λ(ZnO)=0.82, $\Lambda(Bi_2O_3)$=1.19 and $\Lambda(B_2O_3)$=0.425 were taken from the literature.[24]

The optical basicity expresses the basicity of the glass in terms of the electron density carried by oxygen. Many physical and chemical properties of oxide glasses are related to their basicity. From Table 1, it can be observed that the calculated theoretical optical basicity values increase with increasing ZnO content. This may be understood from the following relation.[25]

$$\Lambda_{th} = 1.67\left[1 - \frac{1}{\alpha_0^{2-}}\right] \quad (6)$$

where α_0^{2-} is the oxide ion polarizability. This equation shows that as the polarizability increases, the basicity also increases. Furthermore, the optical band gap in the present glass system is found to decrease with increasing optical basicity (Fig. 4). Therefore, as the number of NBOs increases, the ZnO content increases, which causes a decrease in E_{opt} and an increase in the optical basicity.

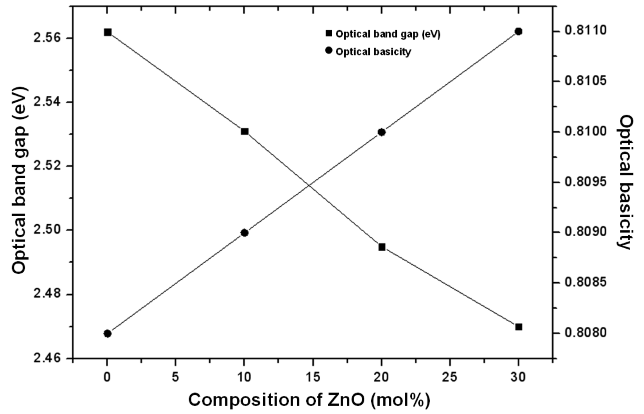

Fig. 4. Variation of glass optical basicity and optical band gap with composition of ZnO.

4. CONCLUSIONS

In this study, we analyzed the physical, thermal and optical properties of the B_2O_3-Bi_2O_3-ZnO glass system, in order to determine the effects of zinc oxide. The variation in the density and molar volume with the ZnO content indicates that the effect of ZnO on the glass structure is dependant on its concentration. The differential thermal analysis studies showed that the glass transition temperature decreases as the content of ZnO increases. The values of the theoretical optical basicity increases and the optical band gap decreases as the ZnO content increases. Therefore, increasing the ZnO concentration of the present glass system results in a progressive increase in the number of Non-Bonding Oxides, which in turn decreases the number of bridging oxygens.

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