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Approach to thermal properties and electronic polarizability from average single bond strength in $ZnO–Bi_2O_3–B_2O_3$ glasses

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ABSTRACT

The glass transition temperature (T_g), density, refractive index, Raman scattering spectra, and X-ray photoelectron spectra (XPS) for xZnO–yBi$_2$O$_3$–zB$_2$O$_3$ glasses (x=10–65, y=10–50, z=25–60 mol%) are measured to clarify the bonding and structure features of the glasses with large amounts of ZnO. The average electronic polarizability of oxide ions (α_{O2-}) and optical basicity (Λ) of the glasses estimated using Lorentz–Lorenz equation increase with increasing ZnO or Bi_2O_3 content, giving the values of α_{O2-}=1.963 Å^3 and Λ=0.819 for 60ZnO–10Bi$_2$O$_3$–30B$_2$O$_3$ glass. The formation of B–O–Bi and B–O–Zn bridging bonds in the glass structure is suggested from Raman and XPS spectra. The average single bond strength ($B_{M–O}$) proposed by Dimitrov and Komatsu is applied to the glasses and is calculated using single bond strengths of 150.6 kJ/mol for Zn–O bonds in ZnO_4 groups, 102.5 kJ/mol for Bi–O bonds in BiO_6 groups, 498 kJ/mol for B–O bonds in BO_3 groups, and 373 kJ/mol for B–O bonds in BO_4 groups. Good correlations are observed between T_g and $B_{M–O}$, Λ and $B_{M–O}$, and T_g and Λ, proposing that the average single bond strength is a good parameter for understanding thermal and optical properties of $ZnO–Bi_2O_3–B_2O_3$ glasses.

1. Introduction

Zinc oxide (ZnO) is one of the important constituent components in the formation of oxide glasses, and in particular, it is known that glasses containing large amounts of ZnO have low melting temperatures. Because low melting glasses with large amounts of PbO, which have been used widely in various commercial devices, are now unfavorable from the environment point of view, the importance of low melting glasses with large amounts of ZnO and with no PbO is increasing largely. Indeed, for instance, $ZnO–B_2O_3$ glasses with high ZnO contents have been used as a sintering aid for the fabrication of low temperature co-fired ceramics [1,2]. Recently, Pinckney [3] succeeded in synthesizing of transparent crystallized glasses consisting of ZnO nanocrystals in $K_2O–ZnO–Al_2O_3–SiO_2$ glasses. Nagai et al. [4] succeeded in patterning lines consisting of ZnO crystals by laser irradiations in borosilicate glasses with a high ZnO content of 65.5 mol%. Glasses with high ZnO contents, therefore, are very attractive materials.

Many studies on the structure and properties of ZnO-containing glasses have been studied so far. However, information on the coordination and bonding states of Zn^{2+} ions in glasses with high ZnO contents is extremely poor. Almost 60 years ago, Sun [5] has proposed the bond energy criterion for the glass formation based on the dissociation energy of the oxides. He reported the data for the single bond strength of a chemical bond M–O in an oxide MO_x obtained by dividing the dissociation energy of the oxide by the coordination number of the metal M. The data reported by Sun are well known among the glass scientists, because they provide a good basis for separating oxides into glass-formers, intermediates and modifiers. Recently, based on Sun's approach, Dimitrov and Komatsu [6] have proposed that the average single bond strength $B_{M–O}$ of binary glass with general formula $xA_pO_q(1-x)B_rO_s$ could be expressed by the following equation:

$$B_{M-O} = xB_{A-O} + (1-x)B_{B-O} \quad (1)$$

where x is the mole fraction of A_pO_q, B_{A-O} and B_{B-O} are single bond strengths of M–O in the corresponding individual oxide. They demonstrated that there is a good correlation among electronic oxide polarizability (i.e., optical basicity) and average single bond strength of several oxide glasses including $La_2O_3–P_2O_5$, $Na_2O–SiO_2$, $PbO–SiO_2$, $Na_2O–GeO_2$, $R_2O–TeO_2$ (R=Li, Na, K), $Bi_2O_3–B_2O_3$, $Sb_2O_3–B_2O_3$ glasses as well as some vanadate glasses [6–10]. That is, in general the electronic oxide polarizability increases with decreasing single bond strength of glasses. Since the pioneering works by Duffy and Ingram [11,12], it has been recognized that electronic polarizability is one of the most important properties of materials in the field of optics and electronics. The data reported by Dimitrov and Komatsu [6–10] propose a close link between optical

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and thermodynamic properties of glasses. It is of interest to approach thermal properties and electronic polarizability of glasses with high ZnO contents from the point of view of average single bond strength.

In this study, we focus our attention on $ZnO–Bi_2O_3–B_2O_3$ glasses containing ZnO contents of 10–60 mol%. Since the first report by Dumbaugh [13] on Bi_2O_3-based glasses, it is well established that the addition of Bi_2O_3 has a strong effect on lowering of melting temperatures in glasses. It is also noted that glasses containing Bi_2O_3 exhibit large third order nonlinear optical susceptibilities $\chi^{(3)}$ of the order 10^{-11} esu [14,15]. Glasses based on the $ZnO–Bi_2O_3–B_2O_3$ system are, therefore, very interesting in the field of solid state materials science and technology. In the present study, we measured the glass transition temperature, density, refractive index, Raman scattering spectra, and X-ray photoelectron spectra (XPS) for $ZnO–Bi_2O_3–B_2O_3$ glasses and tried to characterize their thermal properties and electronic polarizability (optical basicity) from the point of view of average single bond strength.

2. Experimental

The chemical compositions of $ZnO–Bi_2O_3–B_2O_3$ glasses prepared in the present study are given in Table 1. Glasses were prepared using a conventional melt quenching technique. Commercial powders of reagent grade ZnO, Bi_2O_3, and H_3BO_3 were melted in a platinum crucible at 1000 °C for 30 min in an electric furnace. The melts were poured onto an iron plate and pressed to a thickness of ~1.5 mm by another iron plate. Glass transition temperatures (T_g) were determined using differential thermal analyses (DTA) at a heating rate of 10 K/min. Densities of glasses were determined with the Archimedes method using distilled water as an immersion liquid. Refractive indices at a wavelength of 632.8 nm (He–Ne laser) were measured at room temperature with a prism coupler (Metricon Model 2010).

Raman scattering spectra at room temperature for the glasses were measured with a laser microscope (Tokyo Instruments Co., Nanofinder) operated at Ar^+ laser (wavelength: $\lambda=488$ nm). In this apparatus, the data below 250 cm^{-1} cannot be measured due to the use of an edge filter. XPS measurements were carried out with a *JEOL JPS-9010TR* electron spectrometer which has Al conical anode for charge control. Non-monochromatic 240 W Mg$K\alpha$ X-ray provided the excitation radiation. During experiments the pressure inside the analyzer chamber was about 10^{-7} Pa. The drift of the electron binding energy due to surface charging effect was calibrated by utilizing the C1*s* peak (binding energy=284.6 eV) of the contamination of the pumping oil at the sample introduction chamber.

Table 1
Compositions, glass transition temperature T_g, density d, refractive index at 642.8 nm n, molar volume V_m, and atom packing density V_p for $ZnO-Bi_2O_3-B_2O_3$ glasses. The experimental uncertainties of T_g, d, and n are ± 2 °C, ± 0.003 g/cm^3, and ± 0.001, respectively.

Composition (mol%)				T_g (°C)	d (g/cm^3)	n	V_m (cm^3/mol)	V_p
Sample	ZnO	Bi_2O_3	B_2O_3					
Glass A	30	10	60	515	4.209	1.748	26.80	0.583
Glass B	40	10	50	499	4.529	1.784	25.17	0.574
Glass C	50	10	40	471	4.842	1.815	23.78	0.557
Glass D	60	10	30	449	5.152	1.851	22.58	0.534
Glass E	65	10	25	440	5.292	1.870	22.10	0.519
Glass F	30	20	50	482	5.445	1.895	27.99	0.578
Glass G	40	20	40	462	5.688	1.933	27.01	0.555
Glass H	50	20	30	435	5.964	1.968	25.95	0.532
Glass I	20	30	50	440	5.993	1.986	31.85	0.563
Glass J	30	30	40	421	6.192	2.021	31.01	0.539
Glass K	40	30	30	398	6.497	2.059	29.75	0.522
Glass L	20	40	40	397	6.798	2.095	33.91	0.545
Glass M	10	50	40	376	7.151	2.155	37.61	0.537

3. Results and discussion

3.1. Glass transition temperature of glasses

The melt-quenched samples for all compositions of $ZnO–Bi_2O_3–B_2O_3$ examined in this study are optically transparent. The amorphous state in the as-quenched samples was confirmed from XRD patterns, in which halo patterns were observed. The DTA patterns for xZnO–10Bi_2O_3–(90−x)B_2O_3 glasses with $x=40$–60 are shown in Fig. 1 as examples. Endothermic peaks due to the glass transition were clearly observed, giving the values of $T_g=499$ °C for the glass with $x=40$, $T_g=471$ °C for the glass with $x=50$, and $T_g=449$ °C for the glass with $x=60$. In the glasses with $x=50$ and 60, exothermic peaks due to the crystallization are observed, giving the crystallization peak temperatures (T_p) of $T_p=673$ °C for the glass with $x=50$ and $T_p=593$ °C for the glass with $x=60$. These results indicate that thermal stability against crystallization in xZnO–10Bi_2O_3–(90−x)B_2O_3 glasses decreases with the substitution of ZnO for B_2O_3. The endothermic peak due to the glass transition was observed in other glasses, and the values of T_g estimated from DTA curves are given in Table 1. The glasses of $ZnO–Bi_2O_3–B_2O_3$ show the values of $T_g=376$–515 °C, and it is seen that the values of T_g decrease with increasing ZnO or Bi_2O_3 content and decreasing B_2O_3 content. For instance, the glass of 40ZnO–20Bi_2O_3–40B_2O_3 has the value of $T_g=462$ °C, and the glass of 20ZnO–40Bi_2O_3–40B_2O_3 shows the value of $T_g=397$ °C. It should be, therefore, pointed out that Bi_2O_3 has a stronger effect for lowering the glass transition temperature, i.e., weakening the glass network structure, of ternary $ZnO–Bi_2O_3–B_2O_3$ glasses compared with ZnO.

The values of density, d, and refractive index, n, at room temperature for the glasses are given in Table 1. It is seen that both values increase with increasing ZnO or Bi_2O_3 content and decreasing B_2O_3 content. As similar to the glass transition temperature, Bi_2O_3 has a stronger effect for the density and refractive index compared with ZnO. For instance, the glass of 40ZnO–20Bi_2O_3–40B_2O_3 has the values of $d=5.688$ g/cm^3 and $n=1.933$, and the glass of 20ZnO–40Bi_2O_3–40B_2O_3 shows the values of $d=6.798$ g/cm^3 and $n=2.155$.

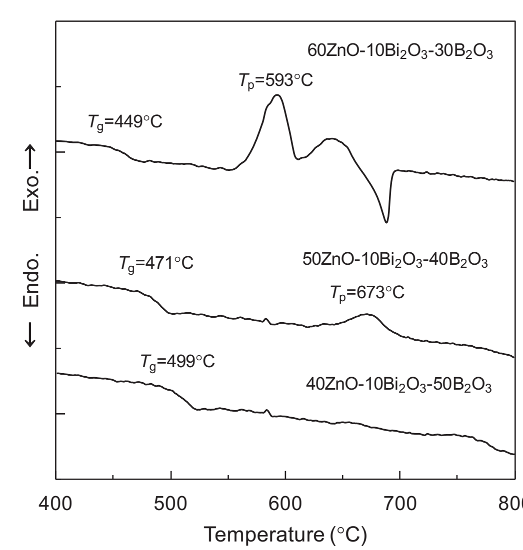

Fig. 1. DTA patterns for xZnO−10Bi_2O_3−(90−x)B_2O_3 glasses with $x=40$–60. Heating rate was 10 K/min.