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Electronic polarizability and interaction parameter of gadolinium tungsten borate glasses with high WO_3 content

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ABSTRACT

Glasses with the compositions of $25Gd_2O_3$–xWO_3–$(75-x)B_2O_3$ with $x=25$–65 were prepared by using a conventional melt quenching method, and their electronic polarizabilities, optical basicities $\Lambda(n_o)$, and interaction parameters $A(n_o)$ were estimated from density and refractive index measurements in order to clarify the feature of electronic polarizability and bonding states in the glasses with high WO_3 contents. The optical basicity of the glasses increases monotonously with the substitution of WO_3 for B_2O_3, and contrary the interaction parameter decreases monotonously with increasing WO_3 content. A good linear correlation was observed between $\Lambda(n_o)$ and $A(n_o)$ and between the glass transition temperature and $A(n_o)$. It was proposed that Gd_2O_3 oxide belongs to the category of basic oxide with a value of $A(n_o)=0.044$ Å^{-3} as similar to WO_3. The relationship between the glass formation and electronic polarizability in the glasses was discussed, and it was proposed that the glasses with high WO_3 and Gd_2O_3 contents would be a floppy network system consisting of mainly basic oxides.

1. Introduction

One of the most important properties of materials, which is closely related to their applicability in the field of optics and electronics, is the electronic polarizability under light and electric fields. An estimate of the state of polarization of ions is obtained using the so-called polarizability approach based on the Lorentz–Lorenz equation [1–5]. Glasses are key materials, in particular in optical devices, e.g., lens and optical fibers, and thus it is extremely important to estimate the electronic polarizability for the design and control of optical properties in glasses. As a pioneering work, Duffy and Ingram [6,7] introduced the concept on the optical basicity of glasses and its estimation method. The optical basicity (Λ) of an oxide medium is a numerical expression of the average electron donor power of the oxide species constituting the medium, and it is used as a measure of the acid–base properties of oxides, glasses, alloys, slags, and molten salts. Furthermore, Duffy [8] proposed that an intrinsic relationship exists between electronic polarizability of the oxide ions ($\alpha_{O^{2-}}$) and optical basicity in oxide glasses. So far, various studies on the electronic polarizability and optical basicity of oxide glasses based on SiO_2, B_2O_3, P_2O_5, GeO_2, TeO_2, and Bi_2O_3 have been carried out, and the relationship between the optical basicity and glass structure or bonding state has been discussed (e.g., [1–5]).

Glasses containing tungsten oxide (WO_3) such as $NaPO_3$–BaF_2–WO_3 and K_2O–WO_3–TeO_2 have received much attention because of their unique thermal and optical properties such as photochromism [9–15]. Because WO_3 is a conditional glass-forming oxide, basically glasses containing WO_3 are prepared through the combination with glass-forming oxides such as B_2O_3 and P_2O_5 and glass modifiers such as Li_2O and K_2O. In the development of WO_3-based glasses, therefore, the design of glass system and chemical compositions are extremely important. Very recently, Taki et al. [16] synthesized the glasses with the compositions of $25Gd_2O_3$–xWO_3–$(75-x)B_2O_3$ (mol%) with high WO_3 contents of $x=25$–65 and found the formation of the nano-scale (2–3 nm) phase separation of tungsten-rich and boron-rich glassy phases prior to the crystallization in the glass with $x=40$ mol%. Wang et al. [17] also reported the glass formation in $22.5RE_2O_3$–$47.5WO_3$–$30B_2O_3$ (RE: Gd and Eu) and the crystallization of α-$Gd_2(WO_4)_3$ and α-$Eu_2(WO_4)_3$. Aleksandrov et al. [18] synthesized $25La_2O_3$–$50WO_3$–$25B_2O_3$ glass and the crystallization of $LaBWO_6$. As reported by Imaoka [19], it is difficult to form glasses in the binary system of WO_3–B_2O_3. Furthermore, as reported by Chakraborty et al. [20], glasses are not formed in the binary Gd_2O_3–B_2O_3 system, although clear glasses are obtained in the binary La_2O_3–B_2O_3 system [20,21]. It is, therefore, of extremely interest to clarify why such RE_2O_3–WO_3–B_2O_3 samples with high

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WO_3 contents of around 50 mol% and with extremely low B_2O_3 contents of around 10–15 mol% show the glass formation and also to estimate the electronic polarizability and optical basicity of those glasses. In this study, we estimated the electronic polarizability, optical basicity, and interaction parameter of $25Gd_2O_3$–xWO_3–$(75-x)B_2O_3$ glasses (mol%) with $x=25$–65 from density and refractive index measurements in order to clarify the feature of electronic and bonding states in the glasses with high WO_3 contents. To the best of our knowledge, the electronic polarizability of only WO_3–TeO_2 and La_2O_3–WO_3 glasses has been reported [2,22], although in particular the structure of various glasses containing WO_3 have been studied extensively.

2. Experimental

Glasses with the nominal (batch) compositions of $25Gd_2O_3$–xWO_3–$(75-x)B_2O_3$ with $x=25$–65 mol% were prepared using a conventional melt quenching technique [16]. Commercial powders of reagent grade Gd_2O_3 (purity 99.9%, Kojyundo Chemicals Laboratory (KCL) Co.), WO_3, (purity 99.9%, KCL Co.), and B_2O_3 (purity 99.9%, KCL Co.) were used as starting materials and were melted in a platinum crucible at 1200 °C for 30 min in an electric furnace. The batch weight was 5 g. The melts were poured onto an iron plate and pressed to a thickness of ~1.5 mm by another iron plate. Chemical compositions of the glasses obtained by a melt-quenching method have not been analyzed at this moment, and we use the nominal compositions (batch compositions) as the chemical compositions of the glasses obtained through this paper. The glass transition (T_g) and crystallization peak (T_p) temperatures of the glasses (sample: bulk) were determined using differential thermal analysis (DTA) (Rigaku Thermo Plus TG8120) at heating rate of 10 K/min in air. Densities (d: g/cm^3) of glasses were determined with the Archimedes method using distilled water as an immersion liquid, in which measurements were repeated five times and the average value was used. Refractive indices (n) at a wavelength of 632.8 nm (He–Ne laser) were measured at room temperature with a prism coupler (Metricon Model 2010). Optical absorption spectra for the glasses with well-polished plate shapes (thickness: ~1 mm) were measured by using a spectrophotometer (Shimadzu UV-3150). 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 which the laser power is 25 mW, the spot size of laser is 3 μm, and the confocal is realized by using a pinhole. Silicon single crystal is used for the calibration of Raman shift. In this apparatus, the data below 250 cm^{-1} cannot be measured due to the use of an edge filter.

3. Results and discussion

3.1. Thermal and optical properties of glasses

Optically transparent glasses were obtained in all compositions of $25Gd_2O_3$–xWO_3–$(75-x)B_2O_3$ with $x=25$–65, as reported in the previous paper [16]. The DTA patterns of some bulk glasses are shown in Fig. 1. Endothermic dips due to the glass transition and exothermic peaks due to the crystallization are clearly observed. It is seen that the glass transition and crystallization temperatures decrease with increasing WO_3 content. It is obvious that the substitution of WO_3 for B_2O_3 induces the crystallization toward more low temperatures. The values of T_g and T_p for the glasses are summarized in Table 1. For instance, the glass with $WO_3=25$ mol% has the values of $T_g=666$ °C and $T_p=874$ °C and the glass with $WO_3=65$ mol% shows the values of $T_g=612$ °C and $T_p=724$ °C. The

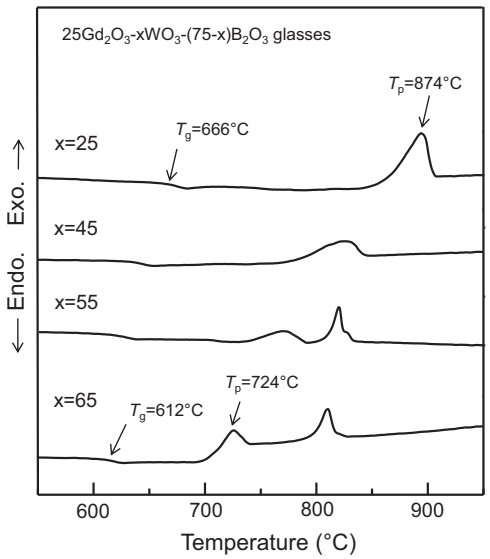

Fig. 1. DTA patterns in air for the bulk $25Gd_2O_3$–xWO_3–$(75-x)B_2O_3$ glasses with $x=25$, 45, 55, and 65. T_g and T_p are the glass transition and crystallization peak temperatures, respectively. Heating rate was 10 K/min.

Table 1
Chemical composition, the glass transition temperature (T_g), crystallization peak temperature (T_p), density (d), and refractive index (n) at 632.8 nm for $25Gd_2O_3$–$(75-x)WO_3$–$75B_2O_3$ glasses with $x=25$–65. The experimental uncertainties of T_g, T_p, d, and n are ±2 °C, ±2 °C, ±0.003 g/cm^3, and ±0.01, respectively.

Sample no.	Composition (mol%)			T_g (°C)	T_p (°C)	d (g/cm^3)	n
	Gd_2O_3	WO_3	B_2O_3				
1	25	25	50	666	874	5.640	1.82
2	25	30	45	654	888	5.662	1.83
3	25	35	40	650	883	5.793	1.85
4	25	40	35	640	850	5.929	1.86
5	25	45	30	633	819	6.152	1.88
6	25	50	25	631	783	6.326	1.90
7	25	55	20	624	773	6.490	1.91
8	25	60	15	614	752	6.617	1.93
9	25	65	10	612	724	6.773	1.94

thermal stability against the crystallization is usually evaluated simply from the degree of the difference between the crystallization and glass transition temperatures, i.e., $\Delta T=T_p-T_g$. As seen in Fig. 1, the value of ΔT decreases with increasing WO_3 content, indicating that the substitution of a large amount of WO_3 for B_2O_3 in Gd_2O_3–WO_3–B_2O_3 glasses deteriorates the thermal stability and enhances the crystallization at low temperatures. As reported by Taki et al. [16], $25Gd_2O_3$–$40WO_3$–$35B_2O_3$ glass shows the formation of the α-$Gd_2(WO_4)_3$ crystalline phase in its initial crystallization. Wang et al. [17] reported the formation of α-$Gd_2(WO_4)_3$ crystals in $22.5Gd_2O_3$–$47.5WO_3$–$30B_2O_3$ glass.

Optical absorption spectra at room temperature for the glasses with $x=25$ and 50 are shown in Fig. 2. The absorption edge for the glass with $x=25$ is ~356 nm (i.e., 3.48 eV), and that for the glass with $x=50$ is ~365 nm (i.e., 3.40 eV), indicating that the absorption edge tends to shift toward the longer wavelength side with increasing WO_3 content. Similar optical absorption spectra were obtained for other glasses with $x=30$–65. All glass samples are colorless in the visible light region (Fig. 2), suggesting that the valence of W ions in $25Gd_2O_3$–xWO_3–$(75-x)B_2O_3$ glasses with $x=25$–65 is mainly W^{6+}. Even if W^{5+} ions are present in the glasses, their amount would be very small.

The values of density and refractive index at room temperature for the glasses are summarized in Table 1. It is seen that both