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Temperature dependence of refractive index and electronic polarizability of RO–TeO$_2$ glasses (R=Mg, Ba, Zn)

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ABSTRACT

The refractive indices (n) and densities (ρ) of xRO – (100 – x)TeO$_2$ glasses (R = Mg, Ba, and Zn) with x = 10–40 are measured in the temperature range of 50–150 °C in order to clarify thermo-optic coefficients (dn/dT) and the temperature dependence of the electronic polarizability of oxide ions ($\alpha_{O^{2-}}$) and optical basicity (Λ). It is found that the values of n, $\alpha_{O^{2-}}$, and Λ increase almost linearly with increasing temperature. The values of dn/dT are between 7.32 and 9.69 × 10^{-5} K^{-1} and tend to decrease with increasing RO content. Contrary, the values of d$\alpha_{O^{2-}}$/dT and dΛ/dT are almost constant irrespective of RO content. It is suggested that the electronic polarizability has an important contribution on thermo-optic coefficients, but the contribution of volume thermal expansion on thermo-optic coefficients is not ignored. In the analyses of electronic polarizabilities of RO–TeO$_2$ glasses, the concept of group optical basicity for TeO$_3$ and TeO$_4$ structural units is also applied. It is explained that large thermo-optic coefficients in RO–TeO$_2$ glasses are composed of oxides having small average single bond strengths and large optical basicities.

1. Introduction

Since the first report on glasses based on tellurium dioxide (TeO$_2$) by Stanworth [1], numerous studies on their structure and properties have been carried out so far. Unique properties observed in TeO$_2$-based glasses such as low phonon energy, low melting temperature, high solubility of rare-earth oxides, high dielectric constant, wide infrared transmittance, high linear and nonlinear refractive indices are in contrast with SiO$_2$- or B$_2$O$_3$-based glasses [2–7] and would be closely related to the large electronic polarizability (i.e., large optical basicity) of TeO$_2$ itself and small single bond strength of Te–O bond [8–15]. Electronic polarizability of ions demonstrates the easy deformation of their electronic clouds by applying of an electromagnetic field. The temperature dependence of refractive indices, n, i.e., dn/dT, is called the thermo-optic coefficient, where T is the temperature. An in-depth understanding of electronic polarizability and thermo-optic coefficient of TeO$_2$-based glasses is, therefore, of importance for their optical device applications.

Because it is difficult to synthesize a clear homogeneous glass in TeO$_2$ itself, other metal oxides such as Na$_2$O, BaO, ZnO, La$_2$O$_3$, Nb$_2$O$_5$, and WO$_3$ are added to prepare thermally stable TeO$_2$-based glasses, i.e., multi-component TeO$_2$-based glasses. The basic TeO$_2$-based glasses are synthesized with the addition of alkaline metal oxides such as Li$_2$O and Na$_2$O, alkaline earth oxides such as BaO, and divalent oxides such as ZnO, meaning the scientific importance of the understanding of electronic polarizability and thermo-optic coefficient for such TeO$_2$-based glasses. Recently, the temperature dependence of refractive index and electronic polarizability of Li$_2$O–TeO$_2$ and Na$_2$O–TeO$_2$ glasses have been reported, and its feature has been analyzed from the structure and bonding state of those glasses [14].

The purpose of the present study is to evaluate the temperature dependence of refractive indices and to approach electronic polarizabilities of binary RO–TeO$_2$ glasses (R = Mg, Ba, and Zn). So far, many studies on the structure and properties of RO–TeO$_2$ based glasses such as BaO–TeO$_2$ and ZnO–TeO$_2$ have been carried out [16–20]. For instance, Sakida et al. [20] reported comprehensive data on the structure of RO–TeO$_2$ glasses obtained by means of ^{125}Te nuclear magnetic resonance (NMR) spectroscopy. However, there has been no report on the temperature dependence of electronic polarizability of RO–TeO$_2$ glasses.

2. Experimental

Glasses with the compositions of xMgO – (100 – x)TeO$_2$ (x = 10, 15, and 20), xBaO – (100 – x)TeO$_2$ (x = 10, 15, and 20), and

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xZnO – (100 – x)TeO_2 (x = 20, 30, and 40) were prepared by using a conventional melt-quenching method. Commercial powders of reagent grade $MgCO_3$, $BaCO_3$, ZnO, and TeO_2 were mixed together and melted in a platinum crucible at 900 °C for 20 min in an electric furnace. The melts were poured onto an iron plate and pressed to a thickness of 1–2 mm by another iron plate. Densities of the glasses (ρ) at room temperature were determined with the Archimedes method using distilled water as an immersion liquid. Linear thermal expansion coefficients (TECs) of the glasses in the temperature range of 30–150 °C were measured using a laser-type thermal expansion equipment (ULVAC Model LIX2), and the temperature dependence of densities were calculated under the assumption that the volume change is expressed by three times of linear TECs. Refractive indices (n) at a wavelength of 632.8 nm (He–Ne laser) were measured in the temperature range of 30–150 °C with a prism coupler (Metricon Model 2010) in which heaters are attached.

3. Results

3.1. Electronic polarizability and optical basicity at room temperature

The values of the refractive index, n, and density, ρ, at room temperature for RO–TeO_2 glasses (RO = MgO, BaO, and ZnO) measured in the present study are given in Table 1. The electronic polarizability of the glasses was evaluated using the following Lorentz–Lorenz equation giving the relationship between the molar refraction, R_m, and the refractive index and density [21]:

$$R_m = \left[\frac{(n^2-1)}{(n^2+2)}\right]\left(\frac{M}{\rho}\right) = \left[\frac{(n^2-1)}{(n^2+2)}\right] V_m = \frac{4\pi\alpha_m N}{3} \quad (1)$$

where M is the molecular weight, V_m the molar volume, α_m the molar polarizability, and N the Avogadro's number. The Lorentz–Lorenz equation allows calculating the electronic polarizability of oxide ions, $\alpha_{O^{2-}}(n)$, by subtracting the cation polarizability from the molar polarizability α_m, using the following equation:

$$\alpha_{O^{2-}}(n) = \left[\frac{R_m}{2.52} - \sum \alpha_i\right]\left(N_{O_{2-}}\right)^{-1} \quad (2)$$

where $\Sigma\alpha_i$ denotes molar cation polarizability and $N_{O^{2-}}$ denotes the number of oxide ions in the chemical formula. The values of α_{Mg} = 0.094 Å^3 for Mg^{2+} ions, α_{Ba} = 1.595 Å^3 for Ba^{2+} ions, α_{Zn} = 0.283 Å^3 for Zn^{2+} ions and α_{Te} = 1.595 Å^3 for Te^{4+} ions are used [10]. An intrinsic relationship exists between the electronic polarizability of oxide ions and the optical bacisity (Λ) of the glasses as indicated in the following equation [22]:

$$\Lambda = 1.67\left(1 - \frac{1}{\alpha_{O^{2-}}}\right) \quad (3)$$

As shown in Table 1, all glasses prepared in this study have large refractive indices of n = 2.01–2.12, large electronic polarizabilities of oxide ions of $\alpha_{O^{2-}}$ = 2.28–2.40 Å^3, and large optical basicities of Λ = 0.94–0.97. The large values of n, $\alpha_{O^{2-}}$, and Λ obtained in RO–TeO_2 glasses suggest that these glasses are basic in nature [11,15]. The values of n, ρ, and α_m decrease clearly with increasing RO content in the glasses. On the other hand, it should be pointed out that the values of $\alpha_{O^{2-}}$ and Λ in each RO–TeO_2 system are almost constant, with weak compositional dependence. Similar compositional dependences have been reported in Refs. [8] and [11].

Table 1
Values of density ρ, refractive index n, molar polarizability α_m, electronic polarizability of oxide ions $\alpha_{O^{2-}}$, and refractive index based optical basicity Λ at room temperature (30 °C) for xRO – (100 – x)TeO_2 glasses. The uncertainties of ρ, n, and Λ are ±5 × 10^{-3} g/cm^3, ±3 × 10^{-4}, and ±0.002, respectively.

x (mol%)	ρ (g/cm^3)	n	α_m (Å^3)	$\alpha_{O^{2-}}$ (Å^3)	Λ	B_{M-O} (kJ/mol)
MgO						
x = 10	5.388	2.1252	5.863	2.329	0.953	272
x = 15	5.312	2.0930	5.603	2.291	0.941	265
x = 20	5.211	2.0932	5.472	2.324	0.951	259
BaO						
x = 10	5.573	2.1264	6.106	2.377	0.968	270
x = 15	5.550	2.0972	6.019	2.394	0.973	263
x = 20	5.512	2.0615	5.922	2.407	0.976	256
ZnO						
x = 20	5.499	2.1026	5.529	2.335	0.955	258
x = 30	5.445	2.0605	5.151	2.326	0.952	245
x = 40	5.430	2.0144	4.729	2.289	0.941	231

3.2. Temperature dependence of electronic polarizability and optical basicity

The values of refractive indices for RO–TeO_2 glasses (RO = MgO, BaO, and ZnO) glasses are shown in Figs. 1–3 as a function of temperature. All glasses show the almost linear increase in the refractive index with increasing temperature (30–150 °C). The temperature dependence of the refractive indices for these glasses, dn/dT, is evaluated using the least square fitting method and is given in Table 2. It is noted that the glasses show large temperature dependences of dn/dT = 8.90–9.69 × 10^{-5} K^{-1} for MgO–TeO_2, dn/dT = 7.32–8.54 × 10^{-5} K^{-1} for BaO–TeO_2, and dn/dT = 8.75–8.97 × 10^{-5} K^{-1} for ZnO–TeO_2.

The linear thermal expansion coefficients (TEC) for RO–TeO_2 glasses were measured in the temperature range of 30–150 °C, and the values of the mean volume thermal expansion coefficient β were calculated using the values of TEC, i.e., 3×TEC. The values of β calculated are given in Table 2. It is seen that the glasses show large volume expansion coefficients of β = 3.09–4.36 × 10^{-5} K^{-1}. The densities of the glasses in the temperature range of 30–150 °C were evaluated using the densities at room temperature

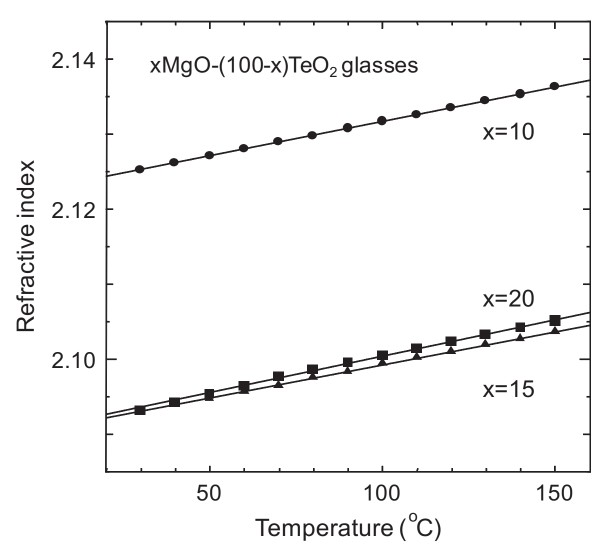

Fig. 1. Temperature dependence of refractive indices (n) for xMgO – (100 – x)TeO_2 glasses in the temperature range of 30–150 °C. The uncertainty of n is ±3 × 10^{-4}.