Refractive Index and Its Dispersion of Na₂O-GeO₂ Glasses

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Na₂O-GeO₂ 系ガラスの屈折率と分散

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[Received March 13, 1995; Accepted June 16, 1995]

Accurate refractive indexes of Na₂O-GeO₂ glasses containing 5-30 mol% Na₂O were measured in the wavelength range of 0.334 to 1.710 μ m using the minimum deviation method. The influence of glass structure on the refractive index and its dispersion has been discussed in terms of the number of the oxygen ion in a unit volume and the apparent refractivity of the oxygen ion. With the addition of Na₂O, the refractive index n_d increased at 5 < Na₂O < 15 mol%, showed a maximum around 15 mol% Na₂O, and decreased with further addition. The Abbe number v_d decreased monotonically. The variations of n_d and v_d with Na₂O content were related to the oxygen coordination number of Ge ions.

Key-words: Germanate glass, Refractive index, Dispersion, Number of the oxygen ion, Apparent refractivity of the oxygen ion, Oxygen coordination number

1. Introduction

For alkali germanate glasses, the existence of maxima in the variations of refractive index and density with alkali oxide content is well-known. For example, a maximum appears at 15-16 mol% Na₂O in Na₂O-GeO₂ glasses.^{1,2)} This phenomenon is so-called "germanate anomaly" being also observable for several physical properties such as the third-order non-linearity,³⁾ molar refractivity,⁴⁾ elastic constant,⁵⁾ viscosity⁶⁾ and thermal expansion.⁷⁾ It has been explained as being due to the variation of oxygen coordination number of Ge ions between four-fold and six-fold. The identification of four-fold Ge ions as well as six-fold Ge ions has been corroborated by Raman scattering,⁸⁾ X-ray diffraction,^{9,10)} neutron diffraction¹¹⁾ and X-ray emission spectroscopy.¹²⁾ These measurements may conclude for Na₂O-GeO₂ glasses that the fraction of six-fold Ge ions increases with the addition of Na₂O, shows a maximum of 20-25% at about 15-20 mol% Na₂O, and then decreases to zero around 35 mol% Na₂O. Some researchers also reported that non-bridging oxygen ions were produced above 15-20 mol% Na₂O.^{8,9,13)}

Borate glasses also show anomalous dependences of properties on composition such as molar

refractivity,¹⁴⁾ refractive index dispersion,¹⁴⁾ and apparent refractivity of the oxygen ion.¹⁵⁾ Although there are a large number of studies of the properties such as the refractive index and its dispersion for borate glasses, a few papers^{1),2),4)} have dealt with those of germanate glasses.

In this work we measured accurate refractive indexes for Na₂O-GeO₂ glasses in the wavelength from 0.334 to 1.710 μ m using the minimum deviation method. We discuss the influence of change in glass structure on refractive index and its dispersion in terms of the refractivity and the number of the ion in a unit volume for each glass component and compare with the previous results of BaO-B₂O₃¹⁶⁾ and Na₂O-SiO₂¹⁷⁾ glasses.

2. Experimental procedure

2.1 Glass preparation

Glasses were prepared using Na₂CO₃ (99.5%) and GeO₂ (99.999%) as raw materials. Table 1 shows the glass compositions of Na₂O-GeO₂ glasses. This table also shows the compositions of BaO-B₂O₃¹⁶⁾ and Na₂O-SiO₂¹⁷⁾ glasses to compare with Na₂O-

Table 1. Compositions of Na₂O-GeO₂, BaO-B₂O₃¹⁶⁾ and Na₂O-SiO₂¹⁷⁾ Glasses Examined in This Study

Glass systems	Composition (mol%)				
	Na ₂ O	BaO	GeO ₂	B ₂ O ₃	SiO ₂
Na ₂ O-GeO ₂	5		95		
	10		90		
	15		85		
	20		80		
	25		75		
	30		70		
BaO-B ₂ O ₃ ¹⁶⁾		20		80	
		22.5		77.5	
		25		75	
		27.5		72.5	
		30		70	
		32.5		67.5	
		35		65	
		37.5		62.5	
Na ₂ O-SiO ₂ ¹⁷⁾	4.9				95.1
	9.7				90.3
	14.5				85.5
	19.1				80.9
	24.2				75.8
	26.7				73.3

GeO₂ glasses in latter discussion. Mixed batches of 2.0×10^{-2} kg for Na₂O–GeO₂ glasses were melted in Pt crucibles without a lid at 1250–1270°C for 2h in air. Each glass was poured into a graphite mold heated at the glass transition temperature and subsequently annealed at near the glass transition temperature. Prisms having about 10 × 20 mm faces were cut and optically polished in our laboratory.

2.2 Refractive index and density measurements

Refractive index was measured with a precision spectrometer (Model GMR-1, Kalnew, Nagano, Japan) at 23°C in the wavelength range of 0.334 to 1.710 μm using Hg, Cd, H₂ and He lamps as spectral sources. The errors for the refractive indexes were 1.0×10^{-4} at the He d-line, which were dependent on striae in glass samples.

To evaluate the dispersion characteristics, Abbe number $v_d = (n_d - 1) / (n_F - n_C)$ was determined,¹⁸⁾ where n_d , n_F , and n_C are the refractive indexes at 0.5876 μm (He d-line), 0.4861 μm (H₂ F-line) and 0.6563 μm (H₂ C-line). This definition concludes that large Abbe number means low dispersion.

Density was determined by the Archimedes method using kerosene as an immersion liquid.

2.3 Ionic refractivity and number of the ion in a unit volume

Refractive index n is given in terms of the density d , the average molecular weight M , and the molar refractivity R using the Lorentz-Lorenz formula.

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = R$$

This formula indicates that refractive index is affected by two factors, that is, the packing and polarization of a glass. The number of the ion in a unit volume and the ionic refractivity for each component in a glass were determined to evaluate the packing and the polarization of a glass. In this study we used these parameters to understand the factors affecting refractive index and its dispersion.

The apparent refractivity of the oxygen ion^{15), 19)} was calculated from the ionic refractivities of the cations and the molar refractivity of a glass on the assumption that the ionic refractivities of the cations remain constant with the variation of composition. Table 2 shows the ionic refractivities of the cations quoted from Fajans¹⁹⁾ and Kordes²⁰⁾ works. The ionic refractivity of Ge⁴⁺ was also shown in this table, which was calculated by Verweij and Buster⁴⁾ for the hypothetical case that the germanium glass is structurally equivalent to silica glass and the refractivity of the oxygen ion in the germanate glass is

Table 2. Ionic Refractivities of the Cations Quoted from the Works of Fajans and Kreidl,¹⁹⁾ Kordes²⁰⁾ and Verweij and Buster⁴⁾

Na ⁺	Ba ²⁺	B ³⁺	Si ⁴⁺	Ge ⁴⁺
0.47	4.73	0.05	0.12	2.6

same as that in silica glass.

The number of the ion in a unit volume for each component in a glass was calculated from the density and the average molecular weight of a glass.

3. Results

3.1 Refractive index and its dispersion

Figure 1 shows the variation of refractive index with wavelength for Na₂O–GeO₂ glasses. Table 3 shows the refractive indexes relative to the air of Na₂O–GeO₂ glasses at representative wavelengths and their densities. Figure 2 compares (a) refractive index n_d and (b) density results of the present work

Fig. 1. Refractive index versus wavelength for sodium germanate glasses.

Table 3. Refractive Index Results Relative to the Air of Sodium Germanate Glasses at Representative Wavelengths and Their Densities

Wavelength (μm)	Spectral source	Nominal glass composition (mol%)					
		5Na ₂ O·95GeO ₂	10Na ₂ O·90GeO ₂	15Na ₂ O·85GeO ₂	20Na ₂ O·80GeO ₂	25Na ₂ O·75GeO ₂	30Na ₂ O·70GeO ₂
0.3650 (i)	Hg	1.6924	1.7220	1.7344	1.7292	1.7126	1.6898
0.4047 (h)	Hg	1.6790	1.7077	1.7196	1.7139	1.6976	1.6751
0.4358 (g)	Hg	1.6713	1.6995	1.7111	1.7053	1.6891	1.6669
0.4800 (F')	Cd	1.6632	1.6909	1.7023	1.6964	1.6802	1.6579
0.4861 (F)	H ₂	1.6623	1.6899	1.7012	1.6954	1.6791	1.6567
0.5461 (e)	Hg	1.6549	1.6821	1.6931	1.6872	1.6711	1.6489
0.5876 (d)	He	1.6512	1.6781	1.6891	1.6831	1.6670	1.6448
0.6439 (C')	Cd	1.6475	1.6739	1.6847	1.6787	1.6626	1.6405
0.6563 (C)	H ₂	1.6465	1.6731	1.6839	1.6780	1.6618	1.6397
0.7065 (r)	He	1.6445	1.6704	1.6812	1.6752	1.6593	1.6370
1.0140 (t)	Hg	1.6344	1.6610	1.6712	1.6658	1.6495	1.6277
Density / 10 ³ kg·m ⁻³		3.89	4.03	4.07	4.01	3.89	3.72

Fig. 2. (a) Refractive index n_d and (b) density versus Na₂O content for sodium germanate glasses. ○ Present work, ● Murthy and Ip,¹⁾ ▲ Efimov et al.²⁾

Fig. 3. Refractive index n_d versus Abbe number v_d for sodium germanate, barium borate,¹⁶⁾ and sodium silicate glasses¹⁷⁾: ○ Na₂O-GeO₂, △ BaO-B₂O₃¹⁶⁾ and ■ Na₂O-SiO₂¹⁷⁾ glasses.

with those of Murthy and Ip¹⁾ and Efimov et al.²⁾ All the results show a maximum at about 15–16 mol% Na₂O in each figure.

Figure 3 shows the relationship between the refractive index n_d and Abbe number v_d for Na₂O-GeO₂ glasses. The results of BaO-B₂O₃ and Na₂O-SiO₂ glasses are also shown in this figure to compare with those of Na₂O-GeO₂ glasses. For Na₂O-SiO₂ glasses the refractive index n_d increases monotonically with the addition of Na₂O and Abbe number v_d decreases largely.

There is a distinct difference between the results of Na₂O-SiO₂ glasses and those of BaO-B₂O₃ and Na₂O-GeO₂ glasses. For Na₂O-GeO₂ glasses the maximum, which means relatively high refractive index and low dispersion, appears around 15 mol% Na₂O. In 5 < Na₂O < 15 mol% in which the oxygen coordination number of Ge ions varies from 4 to 6 with the addition of Na₂O,⁸⁾⁻¹²⁾ the refractive index n_d increases with a slight decrease of v_d . This behavior is similar to the result of BaO-B₂O₃ glasses in 20 < BaO < 32.5 mol%, in which the oxygen coordination number of B ions varies from 3 to 4 with the addition of BaO.²¹⁾ At Na₂O > 15 mol%, the refractive index n_d decreases with a slight decrease of v_d in Na₂O-GeO₂ glasses. On the other hand, for Na₂O-SiO₂ glasses, n_d increases with a larger decrease of v_d ,

i.e., a characteristic of high refractive index and high dispersion.

3.2 Number of the ion in a unit volume for each glass component

Figure 4 shows the variations of (a) the number of O²⁻, (b) the numbers of Na⁺ and Ba²⁺, and (c) the numbers of Ge⁴⁺, B³⁺ and Si⁴⁺ with modifier content in Na₂O-GeO₂, BaO-B₂O₃ and Na₂O-SiO₂ glasses. For Na₂O-GeO₂ glasses the number of O²⁻ in a unit volume increases in 5 < Na₂O < 15 mol%, exhibits a maximum around 15 mol% Na₂O, and then decreases at Na₂O > 15 mol% (see Fig. 4(a)). Although this anomaly is also shown around 32.5 mol% BaO for BaO-B₂O₃ glasses in this figure, the number of O²⁻ in a unit volume decreases monotonically for Na₂O-SiO₂ glasses. The numbers of Na⁺ and Ba²⁺ in a unit volume increase largely in proportion to Na₂O or BaO contents in all the glass systems (see Fig. 4(b)). The number of Ge⁴⁺ in a unit volume increase slightly with the addition of Na₂O in the range of 5 to 10 mol% Na₂O, but as a whole the numbers of Ge⁴⁺, B³⁺ and Si⁴⁺ in a unit volume decrease with the additions of Na₂O or BaO in all the glass systems (see Fig. 4(c)).

3.3 Apparent refractivity of the oxygen ion

Figure 5 shows the variations of the apparent refractivity of O²⁻ with modifier content in Na₂O-

Fig. 5. Apparent refractivity of the oxygen ion versus modifier content for germanate, borate and silicate glasses: ○ Na₂O-GeO₂, △ BaO-B₂O₃¹⁶⁾ and ■ Na₂O-SiO₂¹⁷⁾ glasses. Solid lines are guides to the eye.

Fig. 4. The numbers of (a) O²⁻, (b) Na⁺ and Ba²⁺, and (c) Ge⁴⁺, B³⁺ and Si⁴⁺ in a unit volume versus modifier content for germanate, borate and silicate glasses: ○ Na₂O-GeO₂, △ BaO-B₂O₃¹⁶⁾ and ■ Na₂O-SiO₂¹⁷⁾ glasses.

GeO₂, BaO–B₂O₃ and Na₂O–SiO₂ glasses. For Na₂O–GeO₂ glasses, the results of the apparent refractivity of O²⁻ can be plotted as the combination of two lines intersecting around 15 mol% Na₂O, and in 5 < Na₂O < 15 mol% the slope of the line is smaller than that in 15 < Na₂O < 30 mol%. A similar phenomenon is also shown around 32.5 mol% BaO for BaO–B₂O₃ glasses. However, for Na₂O–SiO₂ glasses the apparent refractivity of O²⁻ increases largely in proportion to Na₂O content.

4. Discussion

The numbers of Ge⁴⁺, B³⁺ and Si⁴⁺ in a unit volume decrease with the additions of Na₂O or BaO, and the ionic refractivities of them are smaller than that of the oxygen ion. The numbers of Na⁺ and Ba²⁺ in a unit volume increase monotonically in proportion to Na₂O or BaO contents for all the glass systems. However, the number of O²⁻ in a unit volume shows different variation with composition for each glass system in Figs. 4 and 5. These results suggest that the difference of the relationship between the refractive index n_d and Abbe number ν_d for each glass system is due to the difference of the role of the oxygen ion. We argue that the oxygen ion has a large ionic refractivity and show different variation for each glass system.

There are two types of the oxygen ion in a glass, that is, bridging oxygen (BO) and non-bridging oxygen (NBO). Generally, the resonance absorption related to NBO exists at longer wavelengths in the ultraviolet region than that of BO.²²⁾ It was also reported that a glass shows a high dispersion characteristic as the average resonance absorption of a glass shifts to longer wavelengths.^{23),24)} From these studies, glasses with larger numbers of NBO show higher dispersion characteristics.

In the results of Na₂O–SiO₂ glasses shown in Figs. 4(a) and 5, the number of the oxygen ion in a unit volume decreases and the apparent refractivity of the oxygen ion increases monotonically with the addition of Na₂O. These variations are due to the decrease of the polymerization degree of silicate networks and the formation of NBO.²⁵⁾ Therefore, it can be argued that the increase in the refractive index n_d of Na₂O–SiO₂ glasses is mainly caused by an increase in the apparent refractivity of the oxygen ion with the formation of NBO; the increase of the refractive index n_d accompanies with the large decrease of ν_d (relatively high dispersion) (see Fig. 3).

On the other hand, in 5 < Na₂O < 15 mol% of Na₂O–GeO₂ glasses, in which the oxygen coordination number of Ge ions varies from 4 to 6,⁸⁾⁻¹²⁾ the apparent refractivity of the oxygen ion increases slightly and the number of the oxygen ion in a unit volume increases largely with the addition of Na₂O, as shown in Figs. 4(a) and 5. In this region, n_d increases largely with the slight decrease of ν_d (relatively

low dispersion) to compare with the Na₂O–SiO₂ glasses. The increase of n_d is likely to be caused by an increase of the number of the oxygen ion in a unit volume, that is, the packing of BO. This phenomenon is also shown in 20 < BaO < 32.5 mol% of BaO–B₂O₃ glasses.¹⁶⁾ In this region of the borate glasses, the refractive index is mainly affected by the number of Ba²⁺ in a unit volume, because the Ba²⁺ ion has a larger ionic refractivity of 4.74 compared with the results of apparent refractivity of the oxygen ion, and the number of the oxygen ion in a unit volume and the apparent refractivity of the oxygen ion are almost constant.

For Na₂O–GeO₂ glasses, while the n_d shows a maximum around 15 mol% Na₂O and then decreases with the addition of Na₂O, ν_d decreases monotonically (see Fig. 3). In 15 < Na₂O < 30 mol%, the decrease in the refractive index n_d is due to a large decrease in the number of the oxygen ion in a unit volume, in spite of an increase in the apparent refractivity of the oxygen ion; the monotonic decrease in Abbe number ν_d is due to an increase in the apparent refractivity of the oxygen ion, that is, the formation of NBO.^{8),9),13)}

5. Conclusions

The influence of change in glass structure on the refractive index and its dispersion for Na₂O–GeO₂ glasses is discussed in terms of the number of the oxygen ion in a unit volume and the apparent refractivity of the oxygen ion. The apparent refractivity of the oxygen ion is calculated on the assumption that the ionic refractivities of the cations remain constant with composition variation.

(1) In 5 < Na₂O < 15 mol% of Na₂O–GeO₂ glasses, the increase of n_d is likely to be caused by an increase in the number of the oxygen ion in a unit volume, that is the packing of the bridging oxygen, which is related to the variation of oxygen coordination number of Ge ions from 4 to 6 with the addition of Na₂O. The refractive index n_d increases with a slight decrease of ν_d , the result shows relatively high refractive index and low dispersion characteristics around 15 mol% Na₂O.

(2) In 15 < Na₂O < 30 mol% of Na₂O–GeO₂ glasses, n_d decreases with a slight decrease of ν_d . In this region, the decrease of n_d is mainly caused by an decrease in the number of the oxygen ion in a unit volume. On the other hand, the slight decrease of ν_d is mainly caused by an increase in the apparent refractivity of the oxygen ion, in other words, the formation of the non-bridging oxygen.

Acknowledgement One of the authors (H. Takebe) acknowledges the Nippon Sheet Glass Foundation 1994 for Materials Science.

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