The structures of $(\text{Na}_{0.5}\text{Ca}_{0.5})\text{Ga}_{1.5}\text{Ge}_{2.5}\text{O}_8$ and $\text{CaGa}_2\text{Ge}_2\text{O}_8$ glasses

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Abstract

The short-range structures of $(\text{Na}_{0.5}\text{Ca}_{0.5})\text{Ga}_{1.5}\text{Ge}_{2.5}\text{O}_8$ and $\text{CaGa}_2\text{Ge}_2\text{O}_8$ glasses have been analysed by X-ray diffraction and EXAFS spectroscopy techniques. Structural differences have been found between these two glasses. The structure of $(\text{Na}_{0.5}\text{Ca}_{0.5})\text{Ga}_{1.5}\text{Ge}_{2.5}\text{O}_8$ glass is similar to that of $\text{NaGaGe}_3\text{O}_8$ glass, and seems to be made of GaO_4 and GeO_4 tetrahedra. On the other hand, the coordination number of T (Ga and Ge atoms) of $\text{CaGa}_2\text{Ge}_2\text{O}_8$ glass is larger than 4 (and about 5) and the T-O distance ($= 1.83 \text{ \AA}$) is longer than that of $\text{NaGaGe}_3\text{O}_8$ glass.

Therefore, on $\text{CaGa}_2\text{Ge}_2\text{O}_8$ glass, it is supposed that the coordination number of Ga atom is larger than 4 because of its larger Ga-O distance obtained by EXAFS analysis.

Introduction

The knowledges on the structures of plagioclase melts are important to understand the physical properties and crystallization processes of magmas in the crust.

The structures of anorthite and albite melts were analysed by X-ray diffraction method (Okuno and Marumo, 1982). It was found that there was a difference between these two melts, i.e., the structure of anorthite melt is based on the 4 membered ring of TO_4 (T: Al and Si) tetrahedra but that of albite 6 membered ring.

Furthermore, the structures of $\text{NaGaSi}_3\text{O}_8$, $\text{NaAlGe}_3\text{O}_8$, $\text{NaGaGe}_3\text{O}_8$, KAlGe_3O_8 and KGaGe_3O_8 glasses have been analysed by X-ray diffraction and EXAFS measurements (Okuno *et al.*, 1984; Okuno *et al.*, 1986). They reported that the basic structures of these glasses were composed of three dimensional networks of TO_4 tetrahedra.

As mentioned above, the structures of the glasses with feldspar components have been studied. However, detail structures have many unknown parts. Therefore, it is important to accumulate structural data of feldspar glasses. In this paper we analyse the structures of $(\text{Na}_{0.5}\text{Ca}_{0.5})\text{Ga}_{1.5}\text{Ge}_{2.5}\text{O}_8$ and $\text{CaGa}_2\text{Ge}_2\text{O}_8$ glasses by X-ray diffraction method and EXAFS analysis from the standing point of finding changes in the structures of these glasses by adding $\text{CaGa}_2\text{Ge}_2\text{O}_8$ component to $\text{NaGaGe}_3\text{O}_8$ glass.

Experimental

Sample preparation

The $(\text{Na}_{0.5}\text{Ca}_{0.5})\text{Ga}_{1.5}\text{Ge}_{2.5}\text{O}_8$ and $\text{CaGa}_2\text{Ge}_2\text{O}_8$ glasses (henceforth these compositions are symbolized as NCGG and CGG, respectively) were prepared by melting mixtures of Na_2CO_3 , CaO , Ga_2O_3 and GeO_2 in the molar ratios to obtain compounds with the respective compositions. The mixtures were melted in Pt crucible and quenched to the room temperature in the air. These glasses were crushed for experiments.

The densities of glasses were measured by pycnometer method, which are given in Table 1. Table 1 shows that the NCGG and CGG glasses have similar densities to each other and which are larger than that of NGG glass.

X-ray diffraction measurement

The X-ray diffraction intensity data were obtained by a Phillips powder diffractometer (PW1050/25) of Tokyo Institute of Technology with $\text{Mo K}\alpha$ radiation monochromated with a Zr foil placed in the incident beam path and with a pyrolytic graphite on the path of the diffracted beam. Slit systems of $1/2^\circ$ (divergence) $-1/2^\circ$ (scattering) and $1^\circ-1^\circ$ were adopted in the lower ($5^\circ \leq 2\theta \leq 30^\circ$) and the higher angle ($20^\circ \leq 2\theta \leq 130^\circ$) ranges, respectively. The ω - 2θ step scanning technique was employed with a fixed time method and a step interval of 0.5° in 2θ . Scanning was repeated until the minimum of the total counts per a datum point exceeded 10000.

The intensities were corrected for polarization and absorption factors, and for

TABLE 1. The compositions and densities of glasses and crystals.

symbol	composition	density (g/cm^3)
NCGG glass	$(\text{Na}_{0.5}\text{Ca}_{0.5})\text{Ga}_{1.5}\text{Ge}_{2.5}\text{O}_8$	4.07
CGG glass	$\text{CaGa}_2\text{Ge}_2\text{O}_8$	4.05
NGG glass ¹⁾	$\text{NaGaGe}_3\text{O}_8$	3.84
KGG glass ²⁾	KGaGe_3O_8	3.64
NGG crystal ³⁾	$\text{NaGaGe}_3\text{O}_8$	3.90
Cristobalite ⁴⁾ type GeO_2	GeO_2	3.93
Low-Quartz ⁵⁾ type GeO_2	GeO_2	4.36

1) Okuno *et al.* (1984)

2) Okuno *et al.* (1986)

3) Bruno and Pentinghaus (1984)

4) Seifert *et al.* (1971)

5) Smith and Issacs (1964)

Compton scattering with the usual method (Levy, Danford and Narten, 1966). Normalization was carried out by the Krogh-Moe and Norman method (Krough-Moe, 1956; Norman, 1957).

EXAFS measurements

The EXAFs measurement system with two proportional counters at the Institute of Physical and Chemical Research (Ito and Iwasaki, 1983) was used in this study. The energy resolution of the system is about 5 eV at 10keV X-ray energy. The EXAFS measurements of Ga and Ge K absorption edges were carried out by a fixed count method for the incident beam. We measured the spectra of Ga K edge on NCGG and CGG glasses, and NGG crystal, and the spectra of Ge K edge on NCGG and CGG glasses, low-quartz type GeO_2 and NGG crystals.

Results

RDF analyses

The RDF analyses of the glass structures were carried out with the procedures described in the previous paper (Marumo and Okuno, 1984). The $S \cdot i(S)$ curves of NCGG and CGG glasses are shown in Fig. 1 together with the curve of NGG glass (Okuno *et al.*, 1984). The radial distribution functions $D(r)$'s and correlation functions $G(r)$'s

FIG. 1. Observed $S \cdot i(S)$ curves of glasses.

FIG. 2. The radial distribution functions $D(r)$ and the correlation functions $G(r)$.

of NCGG and CGG glasses were calculated from $S_i(S)$ curves in the range $S \leq 16.3$ and $14.0 \text{ \AA}^{-1}$, respectively, and shown in Fig. 2 as well as the curves of NGG glass.

As seen in Fig. 1, two maxima around $2 \text{ \AA}^{-1}$ in the NGG glass become a single peak at $2.2 \text{ \AA}^{-1}$ in CGG glass and the amplitudes of some peaks diminish in the order of NGG, NCGG and CGG glasses. These facts suggest that there is a structural change from NGG glass to CGG glass by increasing CGG component.

In the $D(r)$ curve of NCGG glass, peaks are observed at $r = 1.82, 2.28, 2.65, 3.16$ and $3.87 \text{ \AA}$ etc.. For CGG glass, peaks are at $r = 1.83, 2.40, 3.25$ and $3.87 \text{ \AA}$, but no peak is found at around $r = 2.65 \text{ \AA}$. The first peaks at $r = 1.82 \text{ \AA}$ (NCGG glass) and $1.83 \text{ \AA}$ (CGG glass) can be assigned to the nearest T-O (T:Ga,Ge) pairs. The numbers of oxygen atoms around a T atom were estimated to be 4.6 and 5.0 for NCGG and CGG glasses, respectively, from the first peak of $D(r)$ curve. The peaks at $r = 2.28$ and $2.40 \text{ \AA}$ are considered respectively to be Na-O and Ca-O pairs, and those at 3.16 and $3.25 \text{ \AA}$ are assigned to the nearest T-T pairs. The peak at $r = 2.65 \text{ \AA}$ of NCGG glass is supposed to be due to O-O pairs in TO_4 tetrahedra. On CGG glass, a peak due to O-O pairs might be hidden in the peak of T-T pairs.

EXAFS analyses

The EXAFS analyses of the glasses were carried out with the procedures described in the previous paper (Okuno *et al.*, 1984). The observed $\chi(k)$ curves are shown in Fig. 3. The Fourier transforms of $k^3 \cdot \chi(k)$ (in the range $2.7 \leq k \leq 13.0$ for Ga atom and $2.8 \leq k \leq 14.3$ for Ge atom) were calculated to obtain the radial distribution $|F(r)|$ curves around the absorbing atom. Fig. 4 shows the $|F(r)|$ curves for Ga and Ge atoms.

FIG. 3. Normalized EXAFS $\chi(k)$ curves for Ga and Ge K edges. FIG. 4. The $|F(r)|$'s curves.
(a) Ga atoms, (b) Ge atoms.

The first peaks on the $|F(r)|$ curves for Ga atoms in the NGG crystal and in the NCGG and CGG glasses are located at about $r = 1.45 \text{ \AA}$. These peaks can be assigned Ga-O pairs. As the phase shift correction was not made, the distance is shorter than the real ones by about $0.4 \text{ \AA}$. However, their profiles are different a little each other.

The $|F(r)|$ curve of low-quartz type GeO_2 crystal is already reported and explained (Okuno *et al.*, 1984). The first peaks on the $|F(r)|$ curves for Ge atoms in the NGG

TABLE 2. Results of least-squares parameter fitting for EXAFS.

sample	N	$r_{\text{Ga-O}}(\text{\AA})$	$\sigma_{\text{Ga-O}}(\text{\AA})$
NGG crystal	4.0*	1.830*	0.0994***
NCGG glass	4.5	1.830(1)	0.0973
CGG glass	4.0	1.845(1)	0.0984
sample	N	$r_{\text{Ge-O}}(\text{\AA})$	$\sigma_{\text{Ge-O}}(\text{\AA})$
Low-quartz type GeO_2	4.0**	1.739**	0.0756***
NGG crystal	4.0*	1.746(1)***	0.0616***
NCGG glass	4.5	1.755(1)	0.0715
CGG glass	4.0	1.761(1)	0.0728

* Bruno and Pentinghaus (1974)

** Smith and Issacs (1964)

*** Okuno *et al.* (1984)

crystal and in the NCGG and CGG glasses are located at about $r = 1.35 \text{ \AA}$, having similar shapes. From comparison of the peaks in NCGG and CGG glasses with that in low-quartz type GeO_2 crystal, these peaks are assigned to tetrahedral Ge-O pairs.

The parameter fitting method was applied to obtain more detailed structural information of glasses. The first peak of $|F(r)|$ was inversely transformed in order to obtain the $k^2 \cdot \chi(k)$ curves. The mean bond distance $r_{\text{Ga-O}}$ and $r_{\text{Ge-O}}$, coordination number N and Debye-Waller type factor σ were varied to get the best fit between the calculated and observed $k^2 \cdot \chi(k)$ curves, using the values of back scattering amplitude and phase shift factors derived from reference compounds, low-quartz type GeO_2 and NGG crystals. The Ga-O distance of NGG crystal was fixed at $1.83 \text{ \AA}$, and the Ge-O distance of low-quartz type GeO_2 was fixed at $1.739 \text{ \AA}$. The coordination numbers of Ga and Ge atoms in crystals were also fixed at 4.0. The obtained N , $r_{\text{Ga-O}}$ and $r_{\text{Ge-O}}(\text{\AA})$ and $\sigma(\text{\AA})$ are given in Table 2. The Ga-O and Ge-O distances in the glasses are larger than those in crystals without the Ga-O distance of the NCGG glass. The Ga-O distance of NCGG glass is equal to that in the crystal.

Discussion

RDF

Comparing $G(r)$ curves of NGG, NCGG and CGG glasses, the peaks at $r = 1.8 \text{ \AA}$ and $3.2 \text{ \AA}$ diminish their height in the order of NGG, NCGG and CGG glasses. There

are two possible reasons for the diminish of these peak heights, the Ga/Ge atomic ratio and the number of Ca^{2+} ions. It is supposed that the change in Ga/Ge atomic ratio from 1:3 (NGG) to 1:1 (CGG) has a relation to this peak height change, because the contributions of Ga-O, Ge-O, Ga-Ge, Ga-Ga and Ge-Ge pairs to these peaks change according to the compositional change from NGG to CGG. On the other hand, it is considered that Ca^{2+} ions give larger influence on distortion of TO_4 tetrahedra because of its larger electric charge than that of Na^+ ions. This change in peak heights from NCGG to CGG glasses is larger than that from NGG to NCGG glasses.

The T-O distance and coordination number of these glasses are obviously larger than those of NGG glass (Table 3). This fact suggests the following possibilities. As Ca^{2+} ion increases in these glasses, TO_4 tetrahedra have larger influences from Ca^{2+} , and the T-O distance and its coordination number increase. It is expected that the large Ga/(Ga + Ge) ratio and large number of Ca^{2+} ions give large distortions in the structure of the glass.

Further, the mean T-O-T angles were estimated from the T-O and T-T distances on the $D(r)$ curves. The T-O and T-T distances and the estimated T-O-T angles in the glasses are compared with the corresponding values in feldspar, cristobalite type GeO_2 and low-quartz type GeO_2 crystals in Table 3 together with the coordination numbers of T atom and the densities. In Table 3, T-O-T angle is minimum at NCGG glass, the

TABLE 3. Coordination numbers (N), T-O and T-T distances ($\text{\AA}$), T-O-T angles ($^\circ$) and densities (g/cm^3).

specimen	N	T-O ($\text{\AA}$)	T-T ($\text{\AA}$)	$\angle\text{T-O-T} (^\circ)^*$	density (g/cm^3)
NCGG glass	4.6	1.82	3.16	120.5	4.07
CGG glass	5.0	1.83	3.25	125.2	4.05
NGG glass ¹⁾	4.6	1.78	3.16	124.5	3.84
KGG glass ²⁾	4.6	1.78	3.17	125.9	3.64
NGG crystal ³⁾	4.0	1.76	3.25	135.0	3.90
Cristobalite ⁴⁾ type GeO_2	4.0	1.750	3.146	128.0	3.93
Low-quartz ⁵⁾ type GeO_2	4.0	1.739	3.153	130.1	4.36

$$* \angle\text{T-O-T} = 2\sin^{-1} [(T-T)/2(T-O)]$$

1) Okuno *et al.* (1984)

2) Okuno *et al.* (1986)

3) Bruno and Pentinghaus (1974)

4) Seifert *et al.* (1971)

5) Smith and Isaacs (1964)

coordination number of NCGG glass is nearly equal to that of NGG glass and the density of NCGG glass is equal to CGG glass. No change in coordination number from NGG glass to NCGG glass suggests that the structural change from NGG to NCGG is based on the change of the linkages of TO_4 tetrahedra. The large coordination number of CGG glass ($=5.0$) suggests that the structural change from NCGG to CGG glass is based on the change in the coordination number of T atom and polyhedra packing.

NGG, NCGG and KGG (Okuno *et al.*, 1986) glasses have similar $G(r)$ curves and coordination numbers of T atoms. Therefore, it is supposed that these glasses have similar structures. However, comparing $G(r)$ curves and coordination numbers of these glasses with those of CGG glass, we see that the structures of these glasses are very different from that of CGG glass.

EXAFS

Comparing the $\chi(k)$ curves of NCGG and CGG glasses with that of the low-quartz type GeO_2 and NGG crystals and NGG glass (Fig. 3), it is found that the amplitude of $\chi(k)$ curve of CGG glass is smaller than the others in the range of $9.0 \leq k$. In the $|F(r)|$ curve of CGG glass (Fig. 4), the first peak of Ga K edge is smaller and broader than those of the others. In Table 2, $r_{\text{Ga-O}}$ of CGG glass is larger than that of NCGG glass. These results suggest that the observed structural change accompanied by the change in the coordination number of NCGG glass from that of CGG glass on $D(r)$ curves is mainly related with the structural change around Ga atom.

The average T-O distances calculated from $r_{\text{Ge-O}}$ and $r_{\text{Ga-O}}$ obtained by EXAFS analyses are 1.79 Å for NCGG glass and 1.81 Å for CGG glass. These values are in approximately agreement with those obtained by X-ray diffraction analyses (Table 4).

Now, as to the coordination number of CGG glass, the results by X-ray diffraction analysis give larger value than that obtained by EXAFS analysis (The standard deviations of coordination number for experimental conditions and calculation procedures in this study are roughly estimated about ± 0.5 for EXAFS and ± 0.2 for RDF analyses).

TABLE 4. Comparison between the results of EXAFS analyses and X-ray diffraction analyses.

	EXAFS				RDF	
	$r_{\text{Ga-O}}(\text{\AA})$	$r_{\text{Ge-O}}(\text{\AA})$	$\text{T-O}(\text{\AA})$	N	$\text{T-O}(\text{\AA})$	N
NCGG glass	1.83	1.76	1.79	4.5 4.5	1.82	4.6
CGG glass	1.85	1.76	1.81	4.0 4.0	1.83	5.0

T: Ga and Ge atoms

N: estimated coordination number

We suppose that the strong correlation between coordination number N and the Debye-Waller type factor σ is one of the possible factors of this discrepancy.

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