

X-RAY DIFFRACTION STUDY OF $\text{Na}_2\text{O-GeO}_2$ MELTS

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The structure of $\text{Na}_2\text{O-GeO}_2$ melts in the temperature range from 1100 to 1150°C has been investigated with the high temperature X-ray diffraction technique. Comparing the radial distribution functions obtained for the melts with those for the corresponding glasses, the first peak due to the Ge–O interatomic distance is invariant upon melting, although it becomes broader due to thermal vibration. The second peak for the Ge–Ge interatomic distance for melts shifts toward the large distance, which is explained by broadening of the Ge–O–Ge bond angle, not by the thermal expansion of the Ge–O–Ge bond. The composition dependences of Ge–O distances and coordination numbers of the Ge^{4+} ion of the melts are found to be almost the same as the corresponding glasses, indicating that even in melts at such high temperatures 6-fold coordinated Ge^{4+} ions are present and their content changes with the Na_2O content as in the case of the corresponding glasses.

1. Introduction

The alkali germanate glasses have been known to display the so-called “anomaly”, which means the occurrence of a maximum or a minimum on the property–composition curve like alkali or alkaline earth borate glasses. This phenomenon was first noticed by Ivanov and Evstropiev [1] and was supposed to arise from the change in the coordination number of some of the Ge^{4+} ions from 4 to 6 on the addition of alkali oxides. So far, many investigations have been directed to finding the evidence of the occurrence of 6-fold coordinated Ge^{4+} ions in the alkali germanate glasses. Among them, there are X-ray diffraction studies [2–5], other spectroscopic analyses based on the infrared absorption [6,7], Raman scattering [8,9] and X-ray absorption [10–12] (EX-AFS). Recently, Ueno et al. [13] reported the short-range structure in $\text{Na}_2\text{O-GeO}_2$ glasses measured by the neutron scattering technique. The resolution of that method is so high that 4 and 6-fold Ge^{4+} ions in glasses can be unambiguously separated, enabling the estimation of the content of 6-fold Ge^{4+} ions with high accuracy.

According to the previous papers, it can be summarized that (1) some of Ge^{4+} ions of the GeO_2 glass which is constructed by three-dimensionally

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connected GeO₄ tetrahedra definitely change their coordination state from 4-fold to 6-fold on the addition of alkali oxides, and (2) the content of 6-fold coordinated Ge⁴⁺ ions, N_6 , is supposed to vary with the alkali oxide content x as follows,

$$N_6 = 100 \times \frac{x}{1-x} (\%). \quad (1)$$

In fact, the maximum N_6 of about 25% is attained at 20 mol% alkali oxide.

This scheme of coordination change of Ge⁴⁺ ions in alkali germanate glasses resembles that of B³⁺ ions of alkali or alkaline earth borate glasses from 3-fold to 4-fold, although a larger content of 4-fold coordinates B³⁺ ions is obtained at a larger alkali oxide content.

A glass can be regarded as a quenched melt, and in fact the structural similarity between the glass and the corresponding melt has been reported. In silicate systems [2], for instance, network forming cations, Si⁴⁺ ions are present in 4-fold coordination in the glassy state and even in melts.

On the contrary, when a cation can be present in two or more coordination states as in the case of Ge⁴⁺ ions, the situation may be somewhat complicated, because a low coordination state is generally believed to be preferred to a high one at high temperatures. Therefore, it is interesting to investigate whether 6-fold coordinated Ge⁴⁺ ions are formed in Na₂O–GeO₂ melts as in the corresponding glasses or not. With respect to that problem, Riebling [14] and Sekiya et al. [15] measured densities of alkali oxide–GeO₂ melts at 1300°C as a function of the alkali oxide content and found the appearance of a maximum in the curve relating the density to the composition. This implies that 6-fold Ge⁴⁺ ions are formed on adding alkali oxides to the GeO₂ melt as in the case of the corresponding glass.

No direct observation of the formation of 6-fold coordinated Ge⁴⁺ ions in the melts, however, has been made. In the present work, an X-ray diffraction study of Na₂O–GeO₂ melts was carried out. Then the resultant structure of the melts was compared with the corresponding glasses.

2. Experimental

2.1. Samples

The compositions and densities of the starting Na₂O–GeO₂ glasses are given in table 1. Reagent grade Na₂CO₃ and GeO₂ powders of extra purity were used as raw materials. The 20 g batches were melted in platinum crucibles in an electric furnace with SiC heating elements for 2 ~ 8 h at temperatures between 1200 and 1500°C depending on the composition. The densities of the melts were taken from the literature [14,15].

Table 1
Compositions and densities of Na₂O–GeO₂ glasses and melts

Na ₂ O (mol%)	Density (g/cm ³)	
	Glass	Melt (at 1100°C) ^{a)}
0	3.661	3.46
10	4.013	3.58
20	4.010	3.45
30	3.680	3.13

^{a)} After Riebling (ref. [14]).

2.2. X-ray diffraction at high temperatures

The measurements were conducted with the X-ray machine, Geigerflex RAD type of Rigaku Denki Mfg. Co. which is schematically shown in fig. 1. In this machine, both the detector system (a scintillation counter) and an X-ray target tube are scanned at the same rate, the specimen being kept on the level. The powdered glass specimen was melted in a platinum pan horizontally positioned at the goniometer head at 1150°C in the case of the GeO₂ composition and others at 1100°C. The temperature of a melt was measured by a thermocouple adhering to the platinum pan.

The CuK α and MoK α radiation were monochromatized by balanced filters (a combination of Ni and Co for CuK α radiation, and Zr and Y for MoK α

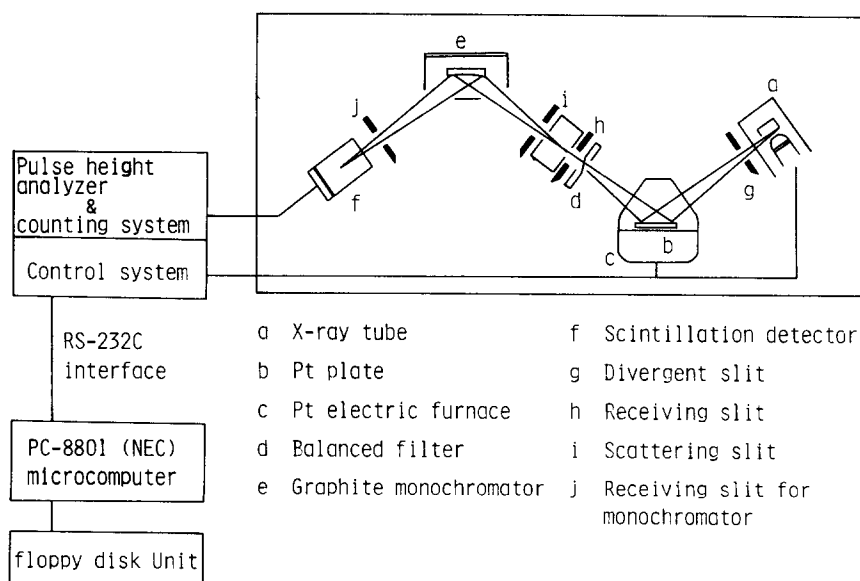


Fig. 1. A schematic diagram of the apparatus used for measuring the radial distribution function (RDF).

radiation respectively) and a graphite monochromator. Filters were placed in the scattered beam to eliminate the interference of the fluorescence from the glass specimen, especially when the Mo target tube was used. The scattering intensity was measured stepwise at intervals of 0.5° in 2θ (θ is the diffraction angle) by a scintillation counter equipped with a pulse height analyzer. In order to minimize the counting error, the intensity measurement for 100 s was repeated. The scattering intensity at each diffraction angle was accumulated up to at least 10 000 counts. The CuK α radiation covered the range of $4\pi \sin \theta/\lambda$ from 0.7 to 6.0, and the MoK α radiation from 3.0 to 12.6. After the measured intensities were corrected for the polarization, background and residual Compton scattering [16], two partial scattering curves obtained by CuK α and MoK α radiation were combined to form a single scattering curve between $4\pi \sin \theta/\lambda$ values of 3.5 and 5.5. The difference between the two curves was small and they were easily combined.

The measurements at high temperatures lasted for about 20 h for one specimen. The change in the composition of a melt during the measurement was scarcely observed. This was confirmed by measuring the density of the cooled melt (the corresponding glass) before and after measurement. For instance the density of 20Na₂O·80GeO₂ glass was 4.01₃ g/cm³ after 2 h-heating, and 4.00₉ g/cm³ after 44 h-heating at 1100°C.

For comparison, X-ray diffraction measurements of Na₂O–GeO₂ glasses were carried out at room temperature in a similar manner.

2.3. Analysis

The corrected scattering intensities were normalized to electron units per unit of composition by Krogh–Moe and Norman's method. Then, intensities were transformed into atomic radial distribution curves (RDF) according to the eq. (2).

$$\sum_m K_m 4\pi r^2 \rho_m(r) = \sum_m K_m 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{s_{\max}} s \cdot i(s) \cdot \exp(-\alpha^2 s^2) \cdot \sin rs \cdot ds, \quad (2)$$

where $s = 4\pi \sin \theta/\lambda$, K_m is the effective number of electrons in the glass specimen, r the interatomic distance in Å and $\exp(-\alpha^2 s^2)$ the damping factor, and

$$i(s) = \left\{ I_{\text{obs}} - \left[\sum_m f_m^2 + \sum_m \left(Z_m - \sum_j f_{mj}^2 \right) \right] \right\} / f_e^2$$

in which $\sum_m (Z_m - \sum_j f_{mj}^2)$ is a term for compton scattering and f_e is the average scattering factor of an electron.

The small ripples overlapping on the resultant RDF curve which came from the termination error were eliminated by applying the inversed Fourier trans-

formation technique. All the data accumulation and calculations were performed with a PC8801 microcomputer of NEC Co.

3. Results

Fig. 2 shows X-ray scattering intensity curves of Na₂O-GeO₂ melts measured at 1100 ~ 1150°C. The $s \cdot i(s) \cdot \exp(-\alpha^2 s^2)$ curves of the melts are shown in fig. 3. In both figures, data for glasses of corresponding compositions are superimposed by broken lines for comparison. It can be seen in figs. 2 and 3 that peaks in the scattering intensity curve or the $s \cdot i(s) \cdot \exp(-\alpha^2 s^2)$ curve of a melt are weaker and broader than those of the corresponding glass, and are positioned at smaller s 's (or lower diffraction angle 2θ) than the glass.

The atomic radial distribution (RDF) curves of Na₂O-GeO₂ melts and glasses are represented by solid and broken lines, respectively, in fig. 4. The peak at 1.7 ~ 1.8 Å of RDF curves corresponds to the shortest Ge-O interatomic distance of melts or glasses. The second intensive peak at 3.1 ~ 3.3 Å is assigned mainly to the Ge-Ge interatomic distance. The peaks in RDF curves of melts are lower and broader than glasses due to the thermal vibration.

The numerical values of the shortest Ge-O and Ge-Ge distances obtained in the present work for Na₂O-GeO₂ melts and glasses are given in table 2 together with those previously obtained for the glasses. Good agreement between the shortest Ge-O distance of the present work and others can be seen. The trend of the change in the shortest Ge-O and Ge-Ge distances on melting the glass of the GeO₂ composition corresponds with that reported by

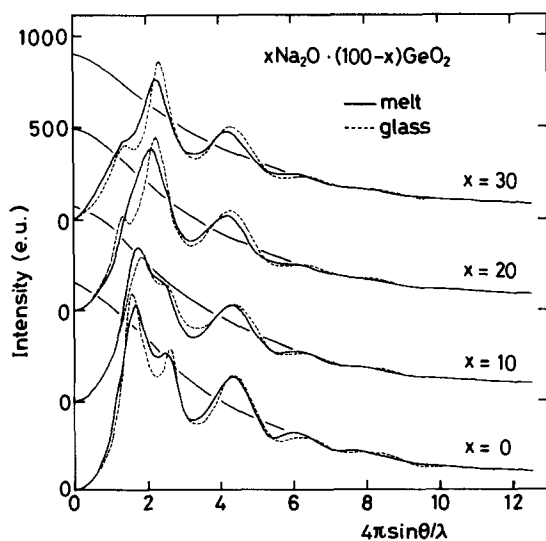


Fig. 2. X-ray scattering intensity curves of Na₂O-GeO₂ melts (—) and glasses (---).

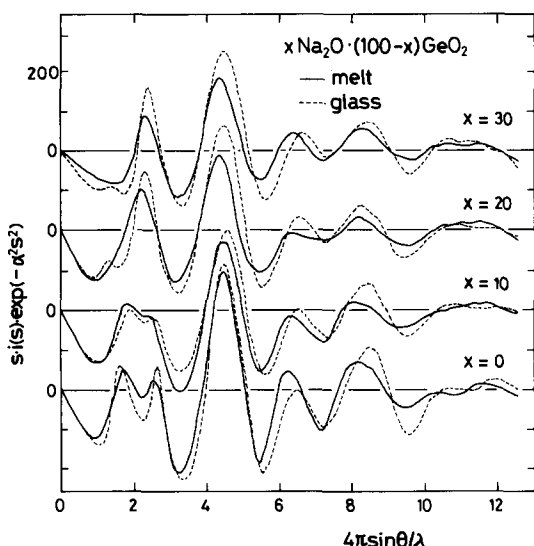


Fig. 3. The $s \cdot i(s) \cdot \exp(-\alpha^2 s^2)$ curves of Na₂O-GeO₂ melts (—) and glasses (----).

Zarzycki [2], although the Ge-Ge interatomic distance obtained in the present work is slightly lower than that of Zarzycki, probably because of the higher temperature used in the latter case.

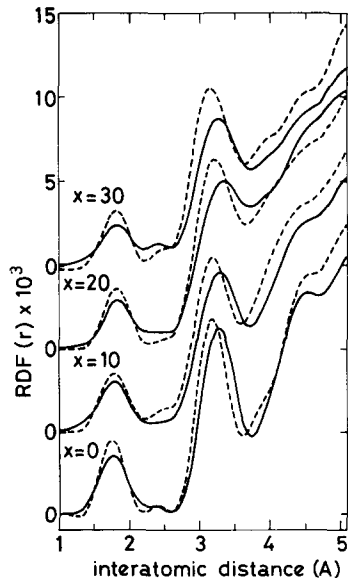


Fig. 4. Atomic radial distribution (RDF) curves of Na₂O-GeO₂ melts (—) and glasses (----).

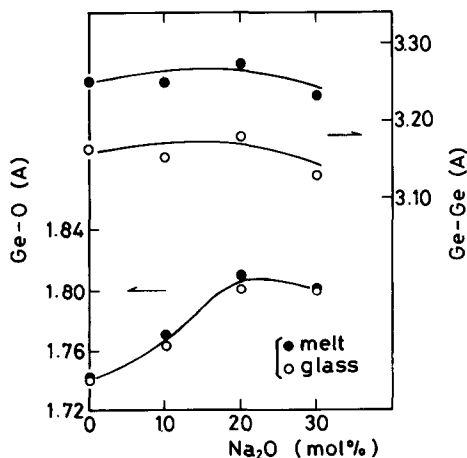


Fig. 5. Variation of Ge-O and Ge-Ge interatomic distances of Na₂O-GeO₂ melts (closed circle) and glasses (open circle) with Na₂O content.

Table 2

The shortest Ge–O and Ge–Ge interatomic distances of $x\text{Na}_2\text{O} \cdot (100-x)\text{GeO}_2$ glasses and melts obtained in the present work and by other authors

Authors	Distance	Temperature (°C)	Na ₂ O (mol%)			
			0	10	20	30
Present work	Ge–O	30	1.74	1.76	1.80	1.80
		1100	1.74 ^{a)}	1.77	1.81	1.80
	Ge–Ge	30	3.16	3.15	3.18	3.13
		1100	3.25 ^{a)}	3.25	3.28	3.23
Iwamoto and Umesaki [5]	Ge–O	r.t. ^{b)}	1.74	1.77	1.80	–
Kamiya and Sakka [3]	Ge–O	r.t.	1.73	1.77	1.80	1.80
Ueno et al. [13]	Ge–O	r.t.	1.74	1.77	1.79	1.79
Zarzycki [2]	Ge–O	r.t.	1.70	–	–	–
		1200	1.70	–	–	–
	Ge–Ge	r.t.	3.15			
		1200	3.30			

^{a)} At 1150°C.

^{b)} Room temperature.

The shortest Ge–O and Ge–Ge interatomic distances of the melts and glasses obtained in the present work are plotted against the Na₂O content in fig. 5. It can be seen that the shortest Ge–O distance is scarcely varied even if the glass is melted, while larger Ge–Ge interatomic distances of melts than glasses can be seen.

As for the composition dependence of interatomic distances, it can be seen in fig. 5 that the shortest Ge–O interatomic distance of the Na₂O–GeO₂ melt increases with increasing Na₂O content and reaches the ceiling at 20 mol% Na₂O followed by levelling off on further increase, just like in the glasses. On the other hand, the Ge–Ge interatomic distances of melts and glasses show only a slight composition dependence.

4. Discussion

The structure of Na₂O–GeO₂ melts will be discussed mainly on the basis of interatomic distances obtained by the X-ray diffraction technique and compared with the corresponding glasses. The coordination number of Ge⁴⁺ ions tentatively calculated from the area of peaks in radial distribution curves is used to develop the discussion. First, the relation between the overall thermal expansion of melts or glasses and the thermal expansion of the essential Ge–O, Ge–Ge interatomic distances themselves is discussed.

The average linear thermal expansion coefficients of Na₂O–GeO₂ glasses in the temperature range of 25°C to their glass transition temperatures fall between 80 and $120 \times 10^{-7}/^{\circ}\text{C}$ [17], and those of melts at 1300°C are in the range of 80 to $300 \times 10^{-7}/^{\circ}\text{C}$ [15], giving the overall elongation of at most 3% for germanate glasses on heating to 1100°C. If the overall thermal expansion of germanate glasses or melts is uniquely brought about by the expansion of interatomic distances themselves, the Ge–O and Ge–Ge distances of the melts should be increased by as much as 0.05 Å and 0.09 Å, respectively, relative to the glasses at 25°C. However, in SiO₂ crystals, it has been reported that the Si–O bond length itself is practically not increased on heating but the increase of the bonding angle between SiO₄ tetrahedra, i.e. the Si–O–Si bond angle contributes to the overall thermal expansion [18]. This is also true for the vitreous state. Actually, the Si–O interatomic distance of the SiO₂ melt is 1.60 Å at 1600°C [2], being almost the same as that at room temperature. In the case of pure GeO₂, no significant difference in the Ge–O distance between the melt and glass was observed by Zarzycki [2] and in the present work. Therefore, the essential elongation of the shortest Ge–O interatomic distance of Na₂O–GeO₂ melts relative to the corresponding glasses due to thermal expansion is considered to be much smaller than that assumed above and may be within the experimental error. Accordingly, it can be said that in discussing the structure of Na₂O–GeO₂ melts on the basis of the interatomic distances given in table 2 and fig. 5, the influence of thermal expansion is ignored and the difference in interatomic distances, if any, between melts and glasses is regarded purely as a reflection of the difference in structure or configuration of the polyhedron including Ge⁴⁺ ions.

According to the published papers [3,13] on the structure of alkali germanate glasses, the content of 6-fold coordinated Ge⁴⁺ ions increases with the increase of the content of alkali oxide following eq. (1). The simultaneous increase in the shortest Ge–O distances of the glasses with increasing alkali oxide content has been closely related to the formation of 6-fold Ge⁴⁺ ions, since the Ge–O distance in GeO₆ octahedral groups is larger than in GeO₄ tetrahedral groups. The shortest Ge–O distances of Na₂O–GeO₂ melts agreed with those of the corresponding glasses, increasing with the Na₂O content up to 20 mol%. This fact indicates that 6-fold coordinated Ge⁴⁺ ions are also formed in the melts and the content of 6-fold Ge⁴⁺ ions of the melt is supposed to coincide with the corresponding glass.

The occurrence of 6-fold coordinated Ge⁴⁺ ions in Na₂O–GeO₂ melts could be also detected by measuring the area under the first peak of RDF curves. For that purpose the line on the large r side of the first peak was extrapolated so smoothly that a symmetrical peak due to the Na–O distance will remain at about 2.5 Å. The resultant first peak was asymmetrical probably due to the coexistence of 4-fold and 6-fold Ge⁴⁺ ions for glasses containing 10 or 20 mol% Na₂O. The separation of the asymmetrical peak into two symmetrical component peaks would be possible, but would give rise to uncertainties in the results. Therefore, in the present work, the average coordination number

Table 3

Coordination number of Ge⁴⁺ ions of $x\text{Na}_2\text{O} \cdot (100 - x)\text{GeO}_2$ glasses and melts

	Na ₂ O (mol%)			
	0	10	20	30
Glass (30°C)	4.25	4.50	4.68	4.29
Melt (1100°C)	4.20	4.34	4.46	4.15

of Ge⁴⁺ ions with respect to oxygen ions, n , was estimated from the area $A_{\text{Ge-O}}$ of the first peak even if it was asymmetrical by using eq. (3)

$$n = A_{\text{Ge-O}} / (2a \cdot \overline{K}_{\text{Ge}} \cdot \overline{K}_{\text{O}}), \quad (3)$$

where a is the mole fraction of the constituent GeO₂, \overline{K}_{Ge} and \overline{K}_{O} are the effective average electron numbers of Ge and oxygen in the melts, respectively, which were referred to in the previous paper [3]. Although such a K -approximation method for estimating n does not give accurate value, it has been conveniently used to obtain information on the relative change in the coordination number of cations of Na₂O–GeO₂ melts and glasses with respect to GeO₂.

The coordination number of Ge⁴⁺ ions in Na₂O–GeO₂ melts and glasses, tentatively calculated, are given in table 3. It can be noticed that even in melts, n increases with the Na₂O content, reaches a maximum at 20 mol% Na₂O and then decreases on further addition of Na₂O. The smaller coordination number of Ge⁴⁺ ions in melts than in glasses may not necessarily be a reflection of the difference in structure between the two states, but is considered to be rather due to the ambiguity in measuring the area of the peak of the Ge–O distance which is broadened in melts as seen in fig. 4.

As for the Ge–Ge interatomic distances, Zarzycki [2] reported the larger value for the GeO₂ melt than for the glass. He attributed the change of the Ge–O–Ge bond angle from 125 ~ 152° to 137 ~ 180° to the increase in the Ge–Ge distance on melting at 1200°C. In the present work, the large Ge–Ge interatomic distance of Na₂O–GeO₂ melts relative to the glasses was also observed in the GeO₂. The larger Ge–Ge distance in a melt than in the corresponding glass may also be attributed to a widening of the average Ge–O–Ge bond angle. The average bond angle, however, could not be evaluated in the case of the binary system, because of the coexistence of GeO₆ groups with GeO₄ groups.

In conclusion, it is interesting that even in the case of the Ge⁴⁺ ions which can be present in the two coordination states, the structure of the melt is successfully quenched without conversion of 4-fold coordinated Ge⁴⁺ ions into more stable 6-fold coordinated Ge⁴⁺ ions during cooling.

5. Summary

The X-ray diffraction measurements were carried out on Na₂O–GeO₂ melts. The structure of the melts, especially the coordination state of Ge⁴⁺ ions was investigated and compared with the corresponding glasses. The following results were obtained:

- (1) The formation of 6-fold coordinated Ge⁴⁺ ions in Na₂O–GeO₂ melts is ascertained from the increase in the shortest Ge–O interatomic distance with the Na₂O content and the average coordination number of Ge⁴⁺ ions with respect to oxygen atoms evaluated based on the *K*-approximation method.
- (2) The content of 6-fold coordinated Ge⁴⁺ ions in Na₂O–GeO₂ melts is supposed to change with the Na₂O content in a similar manner to the corresponding glasses, showing a maximum at about 20 mol% Na₂O.
- (3) The essential difference in the structure between Na₂O–GeO₂ melts and glasses lies in Ge–O–Ge interpolyhedron angle. The average Ge–O–Ge bond angle is larger in melts than in glasses.

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References

- [1] A.O. Ivanov and K.S. Evstropiev, Dokl. Akad. Nauk SSSR 145 (1960) 797.
- [2] J. Zarzycki, Verres Refract. 11 (1957) 3.
- [3] K. Kamiya and S. Sakka, Phys. Chem. Glasses 20 (1979) 60.
- [4] S. Sakka and K. Kamiya, J. Non-Cryst. Solids 49 (1982) 103.
- [5] N. Iwamoto and N. Umesaki, Nippon-Kinzoku-Gakkai-Shi 42 (1978) 857.
- [6] M.K. Murthy and E.M. Kirby, Phys. Chem. Glasses 5 (1964) 144.
- [7] S. Sakka and K. Kamiya, Rev. Chim. Min. 16 (1979) 293.
- [8] T. Furukawa and W.B. White, J. Mat. Sci. 15 (1980) 1648.
- [9] H. Verweij and J.H.J.M. Buster, J. Non-Cryst. Solids 34 (1981) 81.
- [10] S. Sakka, K. Kamiya and M. Hayashi, Bull. Inst. Chem. Res. (Kyoto Univ.) 59 (1981) 172.
- [11] M. Tada, F. Marumo, H. Oyanagi and S. Hosoya, Yogyo-Kyokai-Shi 90 (1982) 247.
- [12] A.D. Cox and P.W. McMillan, J. Non-Cryst. Solids 44 (1981) 257.
- [13] M. Ueno, M. Misawa and K. Suzuki, Physica 120B (1983) 347.
- [14] E.F. Riebling, J. Chem. Phys. 39 (1963) 3022.
- [15] K. Sekiya, K. Morinaga and T. Yanagase, Yogyo-Kyokai-Shi 88 (1980) 367.
- [16] B.E. Warren, X-ray Diffraction (Addison–Wesley, New York, 1969) p. 374.
- [17] J.E. Shelby, J. Appl. Phys. 45 (1975) 193.
- [18] D. Taylor, Min. Mag. 38 (1972) 593.