

Structural study of superionic conducting glasses $\text{AgI}-\text{AgPO}_3$ by X-ray diffraction

H. TAKAHASHI

Faculty of Engineering, Ibaragi University, 4-12-1 Nakanaursawa-cho, Hitachi-shi, Ibaragi-ken, 316, Japan

E. MATSUBARA, Y. WASEDA

Institute for Advanced Materials Processing, Tohoku University, Sendai, 980 Japan

Atomic structures of $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses for $x=0.0, 0.1, 0.2, 0.3$ and 0.5 have been investigated by X-ray diffraction. Coordination numbers and atomic distances in the near-neighbour region were determined by the least-squares variational method. The coordination numbers of P–O, P–P and O–O pairs are unchanged with x , which suggests no modification of the connectivity of the PO_4 tetrahedral chains by doping with AgI. The coordination number of I^- around Ag^+ linearly increases from 0 to 1.9 ± 0.2 with increase in x , while the coordination number of O^{2-} around Ag^+ linearly decreases from 5.1 ± 0.2 to 2.5 ± 0.2 . This also suggests that the AgI gets into the PO_4 chains while keeping the local environment of the AgI itself.

1. Introduction

Recently, vitrified superionic conductors have been intensively studied by many workers because of their unusually high ionic conductivity at temperatures rather close to room temperature. These types of glass are usually found in a system composed of superionic and glass-forming compounds such as $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ [1], $(\text{Ag}_2\text{S})_x(\text{AgPO}_3)_{1-x}$ [1] and $(\text{AgI})_x(\text{Ag}_2\text{O} + 2\text{B}_2\text{O}_3)_{1-x}$ [2, 3]. Several structural studies on these glasses have now become available for understanding the conduction mechanism.

Tachez *et al.* [4] investigated the atomic structures of $(\text{AgI})_{0.5}(\text{AgPO}_3)_{0.5}$ and AgPO_3 glasses by neutron diffraction. They concluded that AgPO_3 glass consists of long chains of PO_4 tetrahedra joined together by Ag^+ ions, and that added AgI does not modify these tetrahedral chains but forms microclusters in $(\text{AgI})_{0.5}(\text{AgPO}_3)_{0.5}$ glass. A pre-peak observed in $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses of $x = 0.3, 0.5$ and 0.55 is attributed to the AgI clusters. The radial distribution function (RDF) obtained by X-ray diffraction by Musinu *et al.* [5], however, could not be explained satisfactorily by this AgI cluster model. They maintain the view that the pre-peak is rather attributable to the relatively distinct correlation between Ag and I ions. Börjesson *et al.* [6] constructed a structural model of $\text{AgI}-\text{AgPO}_3$ glass using the reverse Monte Carlo simulation method and found that the pre-peak is caused by density fluctuation of the PO_3 chains. Although some other experimental information is reported from using different methods such as nuclear magnetic resonance, infrared and Raman measurements, no conclusive conclusions about the atomic

structure have been reached. A further structural study is necessary for a better understanding of the mechanism of ionic conductivity in this glass system.

In the present paper, our systematic X-ray diffraction study on the structure of $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses for $x = 0.1, 0.2, 0.3, 0.5$ will be described in comparison with the result for AgPO_3 glass.

2. Experimental procedure

Samples of AgPO_3 and $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses for $x = 0.1, 0.2, 0.3$ and 0.5 were prepared from the high-grade chemical reagents of AgNO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ and AgI. Calculated amounts of the materials were weighed, thoroughly mixed and then placed in a Pyrex beaker, followed by melting at 650 K until no gas evolution was observed. These samples were re-melted between 800 and 850 K and cast into a 20 mm wide, 20 mm high and 2 mm thick window of an Al sample holder for X-ray diffraction measurements. The sample surface was smoothly polished by emery paper.

Scattering intensity was measured with monochromatic MoK_α radiation obtained with a pyrolytic graphite monochromator in the diffracted beam. A diffraction profile was observed from 5 to 120 nm^{-1} in Q , where $Q = 4\pi\sin\theta/\lambda$, θ is half the scattering angle between incident and diffracted beams and λ the X-ray wavelength. After corrections for air scattering, absorption and polarization, the coherent scattering intensity I_{co} in electron units per atom is estimated from the measured intensity using the Krogh-Moe-Norman method [7] with X-ray atomic scattering

factors [8] including the anomalous dispersion terms [9] and the Compton scattering intensity [10, 11] corrected for Breit-Dirac recoil factors. The interference function $Q_i(Q)$ is obtained from

$$Q_i(Q) = \frac{I_{\text{cu}}(Q) - \langle f^2 \rangle}{\langle f \rangle^2} \quad (1)$$

$$\langle f^2 \rangle = \sum_{j=1}^N c_j f_j^2 \quad \langle f \rangle = \sum_{j=1}^N c_j f_j \quad (2)$$

where c_j and f_j are the atomic concentration and atomic scattering factor of the j th element. N is the total number of elements. The Fourier transformation of the interference function gives the reduced radial distribution function (RDF)

$$2\pi^2 r \rho(r) = 2\pi^2 r \rho_0 + \int_0^\infty Q_i(Q) \sin(Qr) dQ \quad (3)$$

where $\rho(r)$ is the radial number-density function and ρ_0 the average number density.

3. Results and discussion

The coherent scattering intensity profiles of AgPO_3 and $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses of $x = 0.1, 0.2, 0.3$ and 0.5 are shown in Fig. 1 in the lower- Q region for better illustrating the variation with x . The pre-peaks indicated with arrows are observed in all samples. Tachez *et al.* [4] also observed the pre-peaks in AgI-AgPO_3 glasses and stressed their interpretation of the AgI cluster formation in this glass system. The distinct pre-peak is, however, observed even in the AgPO_3 glass as shown in Fig. 1. At this position, Tachez *et al.* [4] observed a shoulder of the first peak in the intensity profile of AgPO_3 glass which was measured by neutron diffraction, although they said nothing about this shoulder. The positions of these

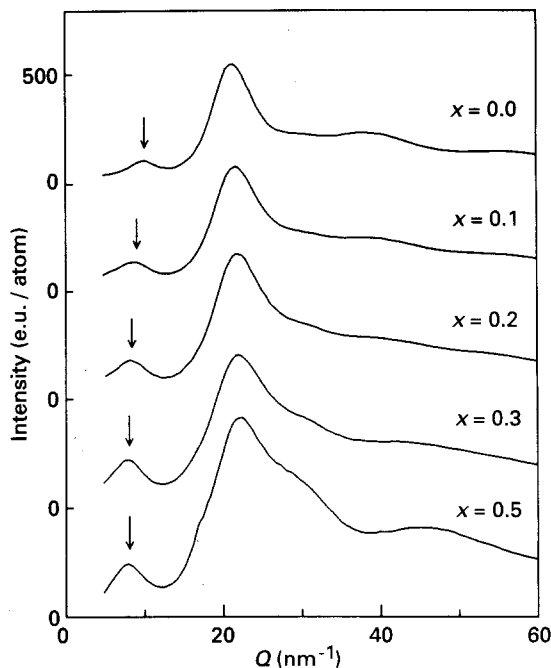


Figure 1 Scattering intensity profiles of the low- Q region in $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses for $x = 0.0, 0.1, 0.2, 0.3$ and 0.5 .

peaks gradually increase and their intensities slightly decrease with decrease in the AgI concentration x . As far as the pre-peak profiles in Fig. 1 are concerned, this tendency seems to be extended even to the AgPO_3 glass of $x = 0$. In general, the presence of a pre-peak is attributed to a certain chemical short-range order in a sample [12-14].

The atomic distances and coordination numbers of the glasses were determined using the least-squares variational method originally proposed by Narten and Levy [15] on the basis of its successful application to determining the local unit structure in SiO_2 and BeF_2 glasses. According to Narten and Levy, the interference function $Q_i(Q)$ may be given by

$$Q_i(Q) = \sum_{j=1}^N \sum_k c_j \frac{f_j f_k}{\langle f \rangle^2} \frac{N_{jk}}{r_{jk}} \exp(-b_{jk} Q^2) \sin(Qr_{jk}) + \sum_{\alpha=1}^N \sum_{\beta=1}^N \frac{c_\alpha c_\beta f_\alpha f_\beta}{\langle f \rangle^2} 4\pi \rho_0 \exp(-b_{\alpha\beta} Q^2) \times \frac{QR_{\alpha\beta} \cos(QR_{\alpha\beta}) - \sin(QR_{\alpha\beta})}{Q^2} \quad (4)$$

where N_{jk} is the number of type- k atoms around any type- j atom at the average distance of r_{jk} and the value of b_{jk} is the mean square variation. The quantities $R_{\alpha\beta}$ and $b_{\alpha\beta}$ correspond respectively to the mean and variance of the boundary region which need not be sharp [15, 16]. In practice, the distances and coordination numbers of near-neighbour correlations are obtained by the least-squares calculation of Equation 4 so as to reproduce the experimental interference function. The non-linear least-squares program developed by Levy *et al.* [17] was slightly modified and used in the present analysis.

The basic structural units for several binary phosphate glasses including NaPO_3 glass have been successfully determined by this least-squares variational method [18] using starting parameters computed from the appropriate crystalline phase. Thus, the AgPO_3 glass was first analysed by this method with starting parameters estimated from the crystalline structure [19]. In Fig. 2 the experimental interference function for the AgPO_3 glass is compared with that obtained by the least-squares variational method. The final result and starting parameters for the AgPO_3

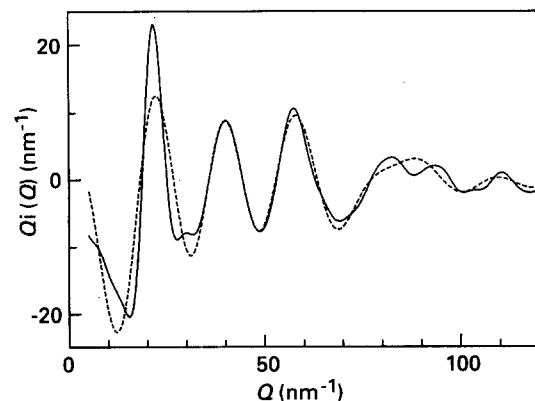


Figure 2 (—) Experimental and (---) calculated interference functions of AgPO_3 glass.

TABLE I Atomic distances r and coordination numbers N of $(\text{AgPO}_3)_x(\text{AgI})_{1-x}$ glasses for $x = 0.0, 0.1, 0.2, 0.3$, and 0.5 ; values for crystalline AgPO_3 are used as starting parameters for the least-squares method

Pair	Present work $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glass		$x = 0.0$		$x = 0.1$		$x = 0.2$		$x = 0.3$		$x = 0.5$	
	r (nm)	N	r (nm)	N	r (nm)	N	r (nm)	N	r (nm)	N	r (nm)	N
Ag-O	0.243	5	0.245 ± 0.002	5.1 ± 0.2	0.243 ± 0.002	4.6 ± 0.2	0.242 ± 0.002	4.1 ± 0.2	0.240 ± 0.002	3.6 ± 0.2	0.239 ± 0.002	2.5 ± 0.2
Ag-I					0.285 ± 0.002	0.6 ± 0.1	0.285 ± 0.002	0.9 ± 0.2	0.284 ± 0.002	1.2 ± 0.2	0.283 ± 0.002	1.9 ± 0.2
Ag-O	0.305	1.5	0.297 ± 0.002	1.6 ± 0.3	0.315 ± 0.003	2.0 ± 0.2	0.319 ± 0.003	2.2 ± 0.2	0.311 ± 0.002	2.3 ± 0.2	0.312 ± 0.002	2.5 ± 0.2
Ag-P	0.339	5	0.325 ± 0.002	4.6 ± 0.2	0.327 ± 0.002	3.5 ± 0.2	0.327 ± 0.002	3.7 ± 0.2	0.326 ± 0.002	3.5 ± 0.2	0.325 ± 0.002	3.6 ± 0.2
Ag-Ag	0.361	4	0.360 ± 0.007	3.3 ± 0.2	0.362 ± 0.007	3.2 ± 0.2	0.362 ± 0.002	3.2 ± 0.2	0.361 ± 0.007	3.1 ± 0.3	0.360 ± 0.007	3.0 ± 0.2
Ag-O	0.360	4.5	0.361 ± 0.002	4.1 ± 0.3	0.362 ± 0.002	4.0 ± 0.3	0.362 ± 0.002	4.1 ± 0.3	0.361 ± 0.002	3.9 ± 0.3	0.361 ± 0.002	3.9 ± 0.3
P-O	0.155	4	0.157 ± 0.002	4.3 ± 0.3	0.156 ± 0.002	4.3 ± 0.3	0.156 ± 0.002	4.2 ± 0.3	0.157 ± 0.002	4.3 ± 0.3	0.157 ± 0.002	4.3 ± 0.3
P-P	0.293	2	0.292 ± 0.012	2.0 ± 0.8	0.303 ± 0.012	2.0 ± 0.8	0.313 ± 0.012	1.9 ± 0.8	0.298 ± 0.012	1.8 ± 0.8	0.297 ± 0.012	1.8 ± 0.8
P-O	0.345	5.5	0.342 ± 0.005	5.4 ± 0.9	0.342 ± 0.005	5.4 ± 0.9	0.342 ± 0.005	5.3 ± 0.9	0.342 ± 0.005	5.3 ± 0.9	0.335 ± 0.005	5.9 ± 0.9
O-O	0.252	4	0.245 ± 0.008	3.6 ± 0.8	0.243 ± 0.008	4.2 ± 0.8	0.248 ± 0.007	4.4 ± 0.9	0.253 ± 0.007	4.4 ± 0.9	0.253 ± 0.008	4.4 ± 0.9
O-O	0.331	5	0.334 ± 0.008	5.1 ± 1.2	0.332 ± 0.008	4.8 ± 1.2	0.332 ± 0.008	4.8 ± 1.2	0.332 ± 0.008	4.8 ± 1.2	0.334 ± 0.008	5.4 ± 1.2

glass are summarized in Table I. The errors were estimated from the variance-covariance matrix in the least-squares variational analysis. It is found from the results of Table I that the structural parameters for the AgPO_3 glass are quite similar to those for the crystal in which the PO_4 tetrahedron is the basic structural unit and these tetrahedra form spiral chains by sharing oxygen atoms at their vertices. For example, the average coordination numbers of oxygen and phosphate atoms around a phosphate atom are 4.3 ± 0.3 at 0.157 ± 0.002 nm and 2.0 ± 0.8 at 0.292 ± 0.012 nm, respectively, which suggests that the local-order structure in the glass is similar to that in the crystal, i.e. the PO_4 tetrahedron and the tetrahedral chains. On the other hand, on the average, Ag^+ ions are coordinated by 5.1 ± 0.2 oxygen atoms at 0.245 ± 0.002 nm and 1.6 ± 0.3 oxygen atoms at 0.297 ± 0.002 nm in the glass. These values are comparable to the average oxygen coordination numbers in the crystal, i.e. 5 oxygen atoms at 0.243 nm and 1.5 oxygen atoms at 0.305 nm. This suggests that the average local environmental structure around Ag^+ ions also appears very similar to the crystal case. The same structural analysis was applied to the interference functions of the AgI-AgPO_3 glasses. The structural parameters obtained for the AgPO_3 glass are used as the starting parameters for the AgI-AgPO_3 glasses. The experimental and calculated interference functions for $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses are compared in Fig. 3. The results are summarized in Table I together with those for the AgPO_3 glass. The coordination numbers and atomic distances for P-O, P-P and O-O pairs show no significant change with the value of x , which implies that the PO_4 tetrahedral chains are not affected by AgI doping. This is consistent with the results of Tachez *et al.* [4] and Börjesson *et al.* [6].

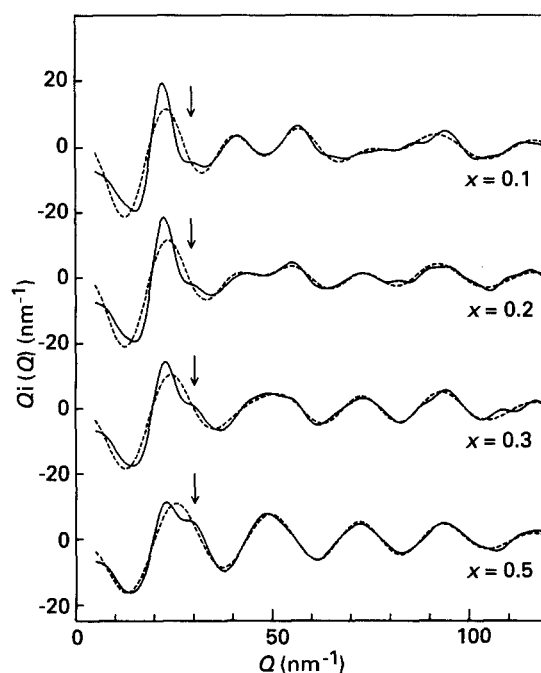


Figure 3 (—) Experimental and (---) calculated interference functions of $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses for $x = 0.1, 0.2, 0.3$ and 0.5 .

With AgI doping, the intensity of the shoulder indicated by the arrows in Fig. 3 increases. Simultaneously, the oscillations present in the AgPO_3 glass are gradually reduced and finally taken over by new oscillations with a different period observed in the $(\text{AgI})_{0.5}(\text{AgPO}_3)_{0.5}$ glass. It is worth noting that the position of the peak at about 30 nm^{-1} in the $(\text{AgI})_{0.5}(\text{AgPO}_3)_{0.5}$ glass coincides with that of the first peak of molten AgI [20]. Furthermore, the peak positions of the new oscillations at about $50, 70 \text{ nm}^{-1}$ etc. also give good coincidence with those of molten AgI. This suggests that the local atomic order of the added AgI is similar to that of molten AgI. In the molten AgI, about 4I^- ions are tetrahedrally coordinated around Ag^+ ions with an average distance of about 0.290 nm at 933 K [20].

Fig. 4 shows the RDFs obtained from the experimental and calculated interference functions in Figs 2 and 3 using the Fourier transformation of Equation 3. The atomic distances given in Table I determined by the least-squares variational method are also indicated in Fig. 4. With increase in x , the height of the peak for the nearest neighbouring Ag–O pair at about 0.24 nm decreases and contrarily that for the Ag–I pair at about 0.28 nm increases. This is more clearly seen in the coordination numbers for the corresponding pairs in Table I. The coordination numbers of O^{2-} ions around Ag^+ ions almost linearly decrease from 5.1 ± 0.2 for $x = 0.0$ to 2.5 ± 0.2 for $x = 0.5$ and the coordination numbers of I^- ions around Ag^+ ions almost linearly increase from 0.6 ± 0.1 for $x = 0.1$ to 1.9 ± 0.2 for $x = 0.5$. Taking account of the local structures for Ag^+ ions in the AgPO_3 glass and in the molten AgI discussed above, the linear variations in the coordination numbers for the nearest neighbouring Ag–O and Ag–I pairs with x strongly suggest that

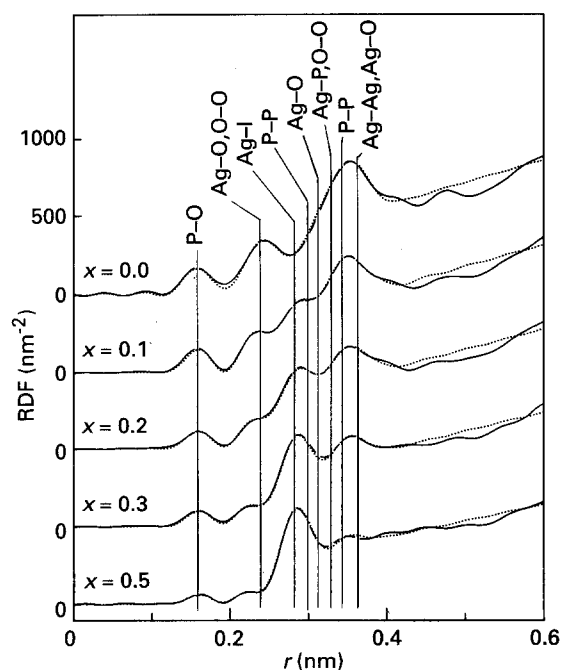


Figure 4 (—) Experimental and (· · ·) calculated reduced radial distribution functions (RDFs) of the $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses for $x = 0.0, 0.1, 0.2, 0.3$ and 0.5 .

AgI does not modify the connectivity of the PO_4 tetrahedral chains and simply gets into the PO_4 network while keeping the local structure similar to that in the molten AgI.

Pre-peaks are observed in all glasses including the AgPO_3 glass as clearly seen in Fig. 1. These pre-peaks are usually ascribed to a particular correlation of the short-range ordering in disordered system. An empirical relation between the correlation length r in real space and the peak position Q in an intensity profile, $Qr = 2.5\pi$, is noted in various liquid alloys [12]. Based upon the fact that the general structural features of the glassy state are similar to those of the liquid state, it is plausible that the above relation still holds even in the glass. The pre-peak positions of Q in Fig. 1 are $10.0, 8.8, 8.2, 7.9$ and 7.9 nm^{-1} for the glasses of $x = 0.0, 0.1, 0.2, 0.3$ and 0.5 , respectively. The corresponding correlation distance r is calculated to be $0.785, 0.893, 0.958$ and 0.994 and 0.994 nm . The pre-peak at 1.0 nm observed in the AgPO_3 glass is also observed in NaPO_3 and LiPO_3 glasses [18]. It is found in the atomic structure of the AgPO_3 crystal that the correlation distance of 0.785 nm corresponds to P–P distances along the spiral PO_4 tetrahedral chain and between the next neighbouring PO_4 tetrahedral chains, and also to the distances between Ag^+ ions across the chains. As discussed above in relation to Fig. 2, the local atomic structure of the AgPO_3 glass appears to be similar to that of the crystal, and the pre-peaks for AgPO_3 glass may then be explained by the density fluctuation of atoms located along the PO_4 tetrahedral chains. It therefore appears that an increase in the correlation distance with x may indicate expansion of the PO_4 chains. Although there remains much work to be done in understanding all aspects of ionic conductivity of AgI– AgPO_3 glasses, the present result may support the model proposed by Börjesson *et al.* [6] rather than the cluster model [4]: namely, the added AgI contributes to the expansion of PO_4 chains while keeping its connectivity and the large volume introduced by this expansion is filled with the salt.

References

1. A. MAGISTRIS, G. CHIODELLI and M. DUCLOT, *Solid State Ionics* **9–10** (1983) 611.
2. H. L. TULLER, D. P. BUTTON and D. R. UHLMANN, *J. Non-Cryst. Solids* **40** (1980) 93.
3. L. BÖRJESSON, L. M. TORELL, U. DAHLBORG and W. S. HOWELLS, *Phys. Rev. B* **39** (1989) 3404.
4. M. TACHEZ, R. MERCIER, J. P. MALUGANI and P. CHIEUX, *Solid State Ionics* **25** (1987) 263.
5. A. MUSINU, G. PASCHINA, G. PICCALUGA and M. MAGINI, *J. Chem. Phys.* **80** (1984) 2772.
6. L. BÖRJESSON, R. L. MCGREEVY and W. S. HOWELLS, *Phil. Mag. B* **65** (1992) 261.
7. C. N. J. WAGNER, H. OCKEN and M. L. JOSHI, *Z. Naturforsch.* **20a** (1965) 325.
8. J. A. IBERS and W. C. HAMILTON (eds), "International Tables for X-ray Crystallography", Vol. IV (Kynoch, Birmingham, 1974) p. 99.
9. *ibid.* p. 149.
10. D. T. CROMER and J. B. MANN, *J. Chem. Phys.* **47** (1967) 1892.
11. D. T. CROMER, *ibid.* **50** (1969) 4857.
12. Y. WASEDA, "The Structure of Non-Crystalline Materials" (McGraw-Hill, New York, 1980) p. 60.

13. H. F. BUHNER and S. STEEB, *Z. Naturforsch.* **24a** (1969) 428.
14. S. STEEB and R. HEZEL, *Z. Metallkde* **57** (1963) 374.
15. A. H. NARTEN and H. A. LEVY, *Science* **160** (1969) 447.
16. A. H. NARTEN, *J. Chem. Phys.* **56** (1972) 1905.
17. H. A. LEVY, M. D. DANFORD and A. H. NARTEN, Report No. ORNL-3960 (ORNL, 1966).
18. Y. WASEDA, E. MATSUBARA, K. SUGIYAMA, I. K. SUH, T. KAWAZOE, O. KASU, M. ASHIZUKA and E. ISHIDA, *Sci. Rep. Res. Inst. Tohoku Univ. A* **35** (1990) 19.
19. Von K. H. JOST, *Acta Crystallogr.* **16** (1963) 640.
20. M. INUI, S. TAKEDA, Y. SHIRAKAWA, S. TAMAKI, Y. WASEDA and Y. YAMAGUCHI, *J. Phys. Soc. Jpn* **60** (1991) 3025.

*Received 21 July 1992
and accepted 26 August 1993*