

Neutron Diffraction Study of Amorphous $(\text{As}_{0.5}\text{Te}_{0.5})_{1-x}\text{I}_x$ System

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Neutron and X-ray diffraction measurements have been carried out on amorphous $(\text{As}_{0.5}\text{Te}_{0.5})_{1-x}\text{I}_x$ alloys with $x = 0 \sim 0.2$ to elucidate details of structural and bonding features in the amorphous As-chalcogenide system. The first sharp diffraction peak is clearly found at around $Q = 1.2 \text{ \AA}^{-1}$ in the structure factor of the neutron diffraction measurement. The position of the first peak at $r = 2.57 \text{ \AA}$ in the pair distribution function of amorphous $\text{As}_{0.5}\text{Te}_{0.5}$ shifts to a larger r side with increasing x . Interatomic distances in the first coordination shell, $r_{\text{As-As}}$, $r_{\text{As-Te}}$ and $r_{\text{Te-I}}$, determined by the least squares fitting analysis to the observed structure factor, are 2.51, 2.64 and 2.75 \AA , respectively, which are in good agreement with those reported in our previous EXAFS study. It has become apparent by the present result that I atoms in the system are preferentially bonded to Te atoms in the $\text{AsTe}_{3/2}$ -unit network structure.

KEYWORDS: neutron scattering, X-ray diffraction, short-range order, chalcogenide glass

§1. Introduction

Structural studies on amorphous As-chalcogenide systems have extensively been performed, and it has been made clear that halogen atoms in the system are preferentially bonded to cation (As) atoms to form molecular As-halide units.¹⁾ On the other hand, the authors have obtained the result that I atoms in the amorphous As-Te-I alloys combine rather with chalcogen (Te) atoms, through the X-ray diffraction measurement, together with Raman spectroscopic and EXAFS ones.^{2,3)} However, structural information of the short-range order from a single X-ray diffraction measurement have been severely restricted because of the limiting Q_{max} (the upper limit of scattering vector magnitude, Q , on the Fourier integration of observed diffraction intensities). Moreover, the first sharp diffraction peak (FSDP) in the structure factor, $S(Q)$, which evidences the presence of medium-range order, can not be clearly detected.^{2,3)} The high resolution diffraction measurements with the wider Q range, such as the time of flight (TOF) neutron diffraction, are highly desired to know the further structural information on covalent disordered systems like the present amorphous alloys.

The purpose of the present study is to carry out the TOF-neutron diffraction measurement for amorphous $(\text{As}_{0.5}\text{Te}_{0.5})_{1-x}\text{I}_x$ alloys, together with the X-ray diffraction one, and to elucidate details of structural and bonding features in the amorphous As-chalcogenide system.

§2. Experimental Procedures

Amorphous $(\text{As}_{0.5}\text{Te}_{0.5})_{1-x}\text{I}_x$ alloys ($x = 0, 0.1$ and 0.2 , respectively) were prepared by mixing the required amounts of the elemental materials (purity: 99.99% for Te and I, 99.95% for As, respectively) in an evacuated quartz ampoule and subsequently quenching the ampoule containing the melt into a liquid N_2 bath.

TOF-neutron diffraction measurements were carried

out using the HIT-II apparatus installed at the pulsed spallation neutron source (KENS) of High Energy Acceleration Research Organization (KEK), Tsukuba, Japan. Scattered neutrons were detected by 104 pieces of ^3He counters, which covered the scattering angle region of $10^\circ \leq 2\theta \leq 157^\circ$. The procedure of corrections for scattering intensities has already been described elsewhere.⁴⁾

The apparatus, experimental procedure and data-corrections for X-ray diffraction measurements are all identical to those in our previous papers.^{2,3)}

§3. Results and Discussions

Figures 1 and 2 show X-ray and neutron diffraction structure factors, $S_X(Q)$ and $S_N(Q)$, respectively, in amorphous $(\text{As}_{0.5}\text{Te}_{0.5})_{1-x}\text{I}_x$ alloys with $x = 0, 0.1$ and 0.2 . $S_X(Q)$ is observed to oscillate clearly even at a considerably larger Q region beyond 17 \AA^{-1} which is the upper limit of Q in the present X-ray diffraction measurement. The oscillation in $S_N(Q)$ seems to be smoothly damped in the range of $Q > 25 \text{ \AA}^{-1}$.

A small hump at around $Q = 1.2 \text{ \AA}^{-1}$ is detected in $S_X(Q)$ for amorphous $\text{As}_{0.5}\text{Te}_{0.5}$ ($x = 0$). On the other hand, a well-resolved peak is clearly observed at around $Q = 1.2 \text{ \AA}^{-1}$ at any composition in $S_N(Q)$ as the FSDP. The total $S(Q)$ in a poly-component system can be expressed by the following equations, using the Faber-Ziman form;

$$S_{\text{total}}(Q) = \sum_{i,j} W_{i-j} S_{i-j}(Q), \quad (3.1)$$

where

$$W_{i-j} = \frac{c_i c_j b_i b_j}{\langle b \rangle^2}, \quad \langle b \rangle = \sum_i c_i b_i, \quad (3.2)$$

for the neutron diffraction and

$$W_{i-j} = \frac{c_i c_j f_i(Q) f_j(Q)}{\langle f \rangle^2}, \quad \langle f \rangle = \sum_i c_i f_i(Q), \quad (3.3)$$

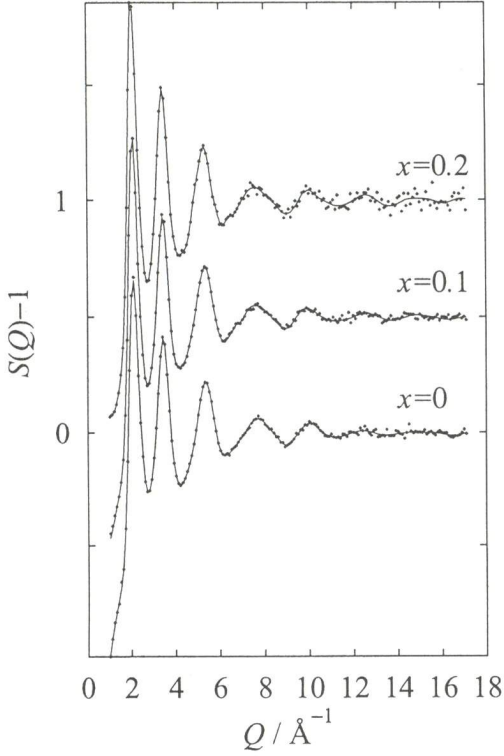


Fig.1. X-ray diffraction structure factors, $S_X(Q)$, in amorphous $(\text{As}_{0.5}\text{Te}_{0.5})_{1-x}\text{I}_x$ alloys.

for the X-ray diffraction. Symbols, c_i , b_i and $f_i(Q)$, are the atomic fraction, scattering length of neutron and atomic scattering factor of X-ray for i -type atoms, respectively. Weighting factors, W_{i-j} , calculated at $Q = 1.2 \text{ \AA}^{-1}$ for both diffractions are given in Table I.

Structural information relating to the environmental structure around As atoms is emphasized in $S_N(Q)$ compared with $S_X(Q)$, because $b_{\text{As}} > b_{\text{Te}} \simeq b_{\text{I}}$ and $f_{\text{As}} < f_{\text{Te}} \simeq f_{\text{I}}$. Especially, the fact that $W_{\text{As-As}}^N$ is 2 ~ 3 times greater than $W_{\text{As-As}}^X$ in Table I may suggest that the FSDP in $S_N(Q)$ and the hump in $S_X(Q)$ are related to the As-As correlation. This is supported by the result that the partial structure factor of the As-As correlation obtained by the anomalous X-ray diffraction technique for amorphous As_2Te_3 has a clear peak at around 1.2 \AA^{-1} .⁵⁾ Therefore, the FSDP in $S_N(Q)$ for the present alloys is expected to be a clear evidence of the formation of medium-range order, that is, the ordered sequence of

Table I. Weighting factors for neutron and X-ray diffractions, W_{i-j}^N and W_{i-j}^X , calculated at $Q = 1.2 \text{ \AA}^{-1}$.

$i-j$	x					
	0	0.1	0.2	0	0.1	0.2
As-As	0.300	0.149	0.249	0.115	0.201	0.087
As-Te	0.495	0.474	0.411	0.365	0.333	0.275
As-I	—	—	0.089	0.083	0.162	0.140
Te-Te	0.204	0.376	0.170	0.290	0.137	0.218
Te-I	—	—	0.073	0.131	0.134	0.223
I-I	—	—	0.008	0.015	0.032	0.057

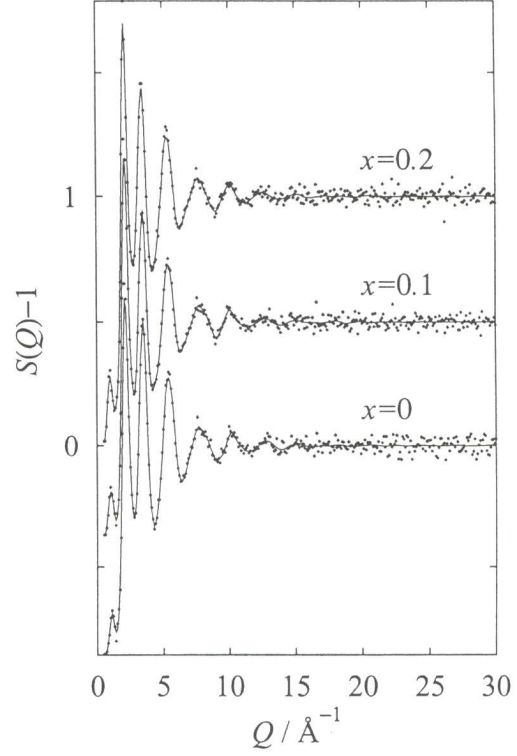


Fig.2. Neutron diffraction structure factors, $S_N(Q)$, in amorphous $(\text{As}_{0.5}\text{Te}_{0.5})_{1-x}\text{I}_x$ alloys.

neighboring $\text{AsTe}_{3/2}$ units.

Figure 3 denotes pair distribution functions, $g_N(r)$ and $g_X(r)$, in the present alloys. Since it was already appeared that there are no indications for the As-I bonding in Raman spectra for As-Te-I alloys,^{2,3)} it may easily be supposed that I atoms incorporated into amorphous $\text{As}_{0.5}\text{Te}_{0.5}$ are bonded to Te atoms in the network matrix. Therefore, the larger r shift and broadening of the first peak in both $g_N(r)$ and $g_X(r)$ with increasing x seem to be caused by the formation of Te-I bonds in the nearest neighbor shell, because they are longer than As-As and As-Te bonds.

We determine structural parameters of As-As, As-Te and Te-I correlations contained in the nearest neighbor shell in the present alloys, through the least squares fit to the observed $S_N(Q)$ at $8 \leq Q \leq 30 \text{ \AA}^{-1}$. The range of Q is much wide compared with the corresponding range for the X-ray diffraction. The below model function was prepared for the present fit;

$$S_{\text{model}}(Q) = 1 + \sum_{i,j} \frac{c_i b_i b_j n_{i-j}}{(\sum_i c_i b_i)^2} \times \exp\left(-\frac{1}{2} l_{i-j}^2 Q^2\right) \frac{\sin(Q r_{i-j})}{Q r_{i-j}}, \quad (3.4)$$

where, n_{i-j} , l_{i-j} and r_{i-j} denote number of atoms j around a given atom i , the root mean square displacement and interatomic distance for $i-j$ pairs, respectively. The fitting result for $S_N(Q)$ is summarized in Table II. The corresponding result for $S_X(Q)$, which was similar to that reported elsewhere,³⁾ was abbreviated for want of space.

Values of three interatomic distances, which are almost

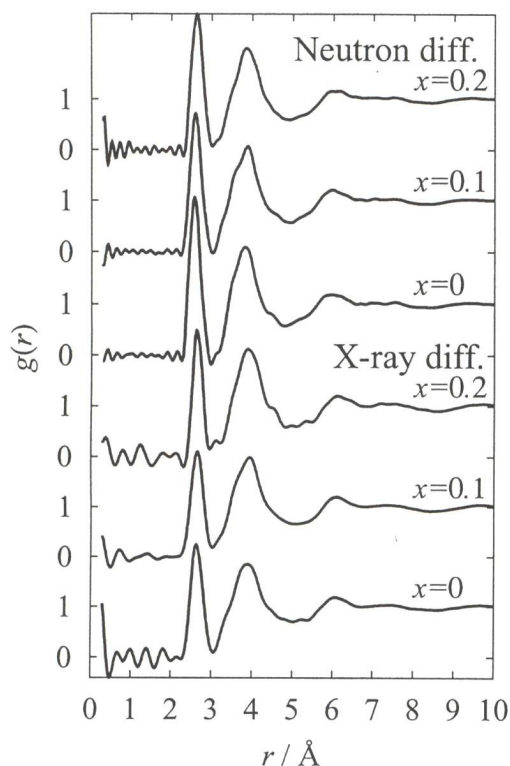


Fig. 3. Neutron and X-ray diffraction pair distribution functions, $g_N(r)$ and $g_X(r)$, at $x = 0, 0.1$ and 0.2 , respectively, in amorphous $(\text{As}_{0.5}\text{Te}_{0.5})_{1-x}\text{I}_x$ alloys.

similar to those from $S_X(Q)$, are in good agreement with those reported in our previous EXAFS study.³⁾ These values are slightly longer than the corresponding covalent distances.

Coordination numbers, $n_{\text{As-As}}$, $n_{\text{As-Te}}$, and $n_{\text{Te-I}}$ obtained by the present fit are plotted against x in Fig. 4, together with the theoretical lines calculated under the following assumptions; (1) All I atoms participate in the formation of Te-I bonds, (2) Extra Te atoms coordinate to As atoms, (3) The remaining As atoms form As-As bonds, and (4) As, Te and I atoms are trivalent, divalent and monovalent, respectively, at all compositions. The theoretical n_{i-j} can be expressed as a function of x , as follows;

$$n_{\text{As-As}} = \frac{1+x}{1-x}, \quad n_{\text{As-Te}} = \frac{2-4x}{1-x}, \quad n_{\text{Te-I}} = \frac{2x}{1-x}, \quad (3.5)$$

respectively. We find in Fig. 4 that each n_{i-j} obtained by the present neutron diffraction measurement satisfactorily falls on the corresponding theoretical line, in the other word, the above structural assumptions may be considered to be reasonable as the structural model for the present alloys. The bonding between halogen and chalcogen atoms may occur in the alloys where the atomic size of both atoms is extremely similar.

§4. Conclusion

The following has been made apparent after TOF-neutron and X-ray diffraction measurements for amor-

Table II. Structural parameters, r_{i-j} , l_{i-j} and n_{i-j} for amorphous $(\text{As}_{0.5}\text{Te}_{0.5})_{1-x}\text{I}_x$ alloys.

	interatomic distance $r_{i-j} / \text{\AA}$		
	x		
	0	0.1	0.2
$r_{\text{As-As}}$	2.49(1)	2.50(1)	2.53(2)
$r_{\text{As-Te}}$	2.62(3)	2.64(1)	2.66(3)
$r_{\text{Te-I}}$	—	2.75(1)	2.75(1)
	root mean square displacement $l_{i-j} / \text{\AA}$		
	0	0.1	0.2
$l_{\text{As-As}}$	0.096(1)	0.097(1)	0.096(2)
$l_{\text{As-Te}}$	0.11(2)	0.11(3)	0.10(2)
$l_{\text{Te-I}}$	—	0.12(3)	0.11(2)
	coordination number n_{i-j}		
	0	0.1	0.2
$n_{\text{As-As}}$	1.0(1)	1.2(1)	1.5(2)
$n_{\text{As-Te}}$	1.9(1)	1.7(2)	1.6(2)
$n_{\text{Te-I}}$	—	0.2(1)	0.6(2)

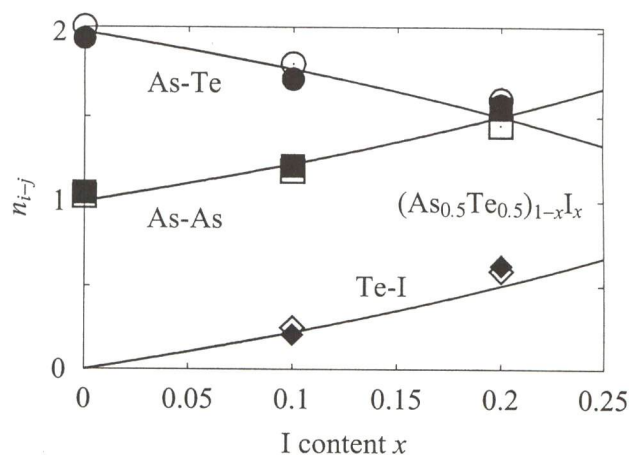


Fig. 4. $n_{\text{As-As}}$ (squares), $n_{\text{As-Te}}$ (circles) and $n_{\text{Te-I}}$ (diamonds) obtained by neutron diffraction (solid marks) and X-ray diffraction (open marks), together with the corresponding theoretical values (lines).

phous $(\text{As}_{0.5}\text{Te}_{0.5})_{1-x}\text{I}_x$ alloys with $x = 0, 0.1$ and 0.2 ;

(1) The first sharp diffraction peak is clearly observed in $S_N(Q)$ at any composition, which evidences the presence of the ordered sequence of neighboring $\text{AsTe}_{3/2}$ units formed in the alloy.

(2) I atoms incorporated into amorphous $\text{As}_{0.5}\text{Te}_{0.5}$ are preferentially bonded to Te atoms.

(3) The present result differs from that in most of amorphous As-chalcogenide alloys, in which halogen atoms strongly combine with As atoms to form molecular As-halide units.

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