

Pulsed Neutron Diffraction and X-ray Diffraction Study on the Short Range Structure of Na₂O-TeO₂ Glasses and Melts

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The short range structure of Na₂O-TeO₂ glasses and melts has been investigated by pulsed neutron diffraction (PND) and X-ray diffraction (XRD). In both glasses and melts, the existence of TeO₄ trigonal bipyramids and TeO₃ pyramids were confirmed and TeO₄ was converted to TeO₃ with increasing Na₂O or a rise of temperature.

KEYWORDS: diffraction, glass, melt, short range structure, sodium tellurite

§1. Introduction

There have been reported many studies of the tellurite glasses concerning low melting temperatures,^{1,2)} large thermal expansion,^{1,3)} high dielectric constants,⁴⁾ high refractive indexes, and good transmission for infrared lights with a wide range of wavelength⁵⁾ from scientific and technological points of view. Nowadays, these features of the tellurite glasses have been considered to promise for use as optical fibers or non-linear optical materials.⁶⁾ The structures of TeO₂-based glasses have frequently been examined by Raman and IR spectroscopy, reporting that there are two types of basic structural units such as TeO₄ trigonal bipyramid (tbp) with two equatorial and two axial Te-O bonds and a lone pair of electrons on Te atom, and TeO₃ trigonal pyramid (tp).⁷⁾ The coordination circumstance of Te changes from TeO₄ to TeO₃ with increasing alkali metal ions or a rise of temperature.⁸⁾ But these spectroscopic measurements were unfortunately insufficient for evaluation in the fractions of the structural units. On the contrary, Pulsed Neutron Diffraction (PND) and X-ray diffraction (XRD) provides one-dimensional interpretation of glass structures through the radial distribution function (RDF). Te-O and O-O distances and the coordination number of oxygen around tellurium are obtained with ease from RDF. The usage of PND and XRD enabled us to comprehend in some details what to happen in phase transition from glasses to melts.

§2. Experimental

Sodium tellurite glasses were prepared from the chemicals of reagent grade Na₂CO₃ and TeO₂ so as to mix in a prescribed ratio. The xNa₂O-(1-x)TeO₂ (x=0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30) glasses and melts were prepared using a conventional melt-quenching method. Mixtures of these materials with appropriate compositions were melted at 550-900 °C for 1 h in a platinum crucible. The resultant melt was poured into a stainless

steel vessel. The densities measured by the Archimedian method. The conventional X-ray diffraction technique was employed in the measurements of glassy powders.⁹⁾

Neutron diffraction measurement was carried out using the High Intensity Total scattering spectrometer (HIT-II) installed at a pulsed separation neutron source in High Energy Accelerator Research Organization in Tsukuba, Japan. Scattered neutrons were detected by the detectors located at the scattering angles of 150, 90, 50, 30, 25, 20 and 15°, respectively, and the data accumulation time was about 8 h. The structure factor $S(Q)$ was obtained from the scattered intensity after usual corrections such as subtraction of the cell intensity, absorption, and normalization with a vanadium standard. The details of the data acquisition procedure was described in the literature.¹⁰⁾

§3. Results and Discussion

3.1 X-ray diffraction

The definition of the interference function $Q \cdot i(Q)$ and the correlation function $G(r)$, are given in a previous paper.⁹⁾

It is necessary for the structural analysis of glass to understand what is the most basic short-range structure for the investigated glass. In case of alkali tellurite glasses, it has been proposed that two types of Te-O correlations are present, one is the long Te-O bond (0.2 nm) and the other the short Te-O bond (<0.2 nm).¹¹⁾

The correlation functions $G(r)$'s in glassy and molten Na₂O-TeO₂ systems obtained from XRD are depicted in Fig.1. There appeared two peaks at about $r=0.20$ nm and 0.36 nm. Another shoulder-like peak around $r=0.25$ nm was observed. The first peaks at around $r=0.20$ nm were thought to be due to the nearest neighbor Te-O correlations by taking into account the ionic radii of Te⁴⁺, Na⁺, and O²⁻ which were evaluated by Shannon.¹²⁾ However, some overlapping of the atomic pair correlations should be considered since the first peaks in $G(r)$ curve shown in Fig.1 were asymmetric on the tail

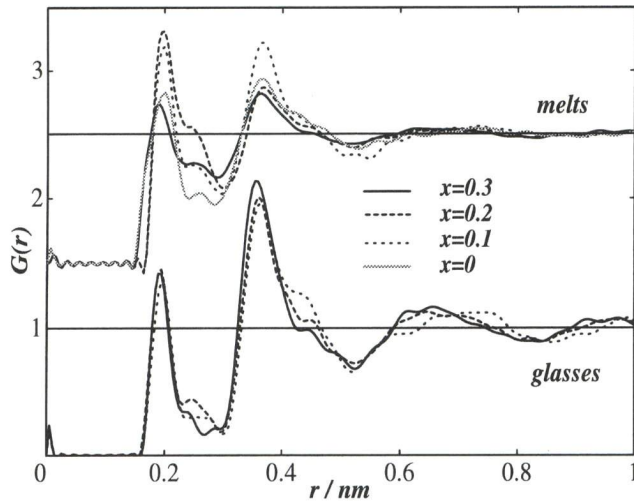


Fig. 1. Correlation function $G(r)$ of $x\text{Na}_2\text{O}-(1-x)\text{TeO}_2$.

ends. The second shoulder-like peak at about $r=0.25$ nm was expected to be assigned to the Na-O and O-O correlations. The third peaks at about $r=0.36$ nm in the correlation function $G(r)$ were thought to be attributed mainly to the Te-Te pairs and there were many other correlations after this distance because of the broad profiles in the peaks. But it should be noted that the contributions of O-O and Na-O pairs to the $G(r)$ curve were rather difficult to be estimated since the compositional ratios of Na to O or Te were very small and the atomic scattering factor of Te was rather greater than those of O and Na. Consequently, the peaks of O-O and Na-O pairs were in effect undetectable and only Te-O and Te-Te pairs appeared clearly in the $G(r)$ curve. Accordingly, it is necessary to estimate the contributions of Na-O and O-O pairs using PND.

3.2 Neutron diffraction

In the total structure factor $S(Q)$ for the $(1-x)\text{Na}_2\text{O}-\text{TeO}_2$ glasses at ambient temperature, the shoulder-like peak called "prepeak" was noticeable at about $Q=15$ nm^{-1} , which is often observed in amorphous materials.¹³⁾ The reduced intensity function $Q \cdot i(Q)$ was defined by $Q \cdot i(Q) = Q \cdot [S(Q) - 1]$.

Fourier transformation of the original $Q \cdot i(Q)$ produces ghost peaks in $G(r)$ in front of the first peaks corresponding to the Te-O pair in this work. Hence the so-called cut value, $r=0.165$ nm for $\text{Na}_2\text{O}-\text{TeO}_2$ glasses, was introduced in an iteration process of Fourier and Fourier inverse transformation to remove ghost peaks resulting from truncation of the Fourier integral. The multiplot of $G(r)$ curves are illustrated in Fig. 2.

As discussed above, the first peak appearing at about $r=0.20$ nm in the $G(r)$ was thought to be due to the first nearest neighbour Te-O pairs in TeO_2 based glasses. The second peak at about $r=0.24$ nm might be assignable to the Na-O correlation because the intensities of the first peaks at around $r=0.20$ nm decreased and those of the second peaks at about $r=0.24$ nm increased with increasing Na_2O content. The third peak at about $r=0.28$ nm was attributable to the O-O pairs. Only information of

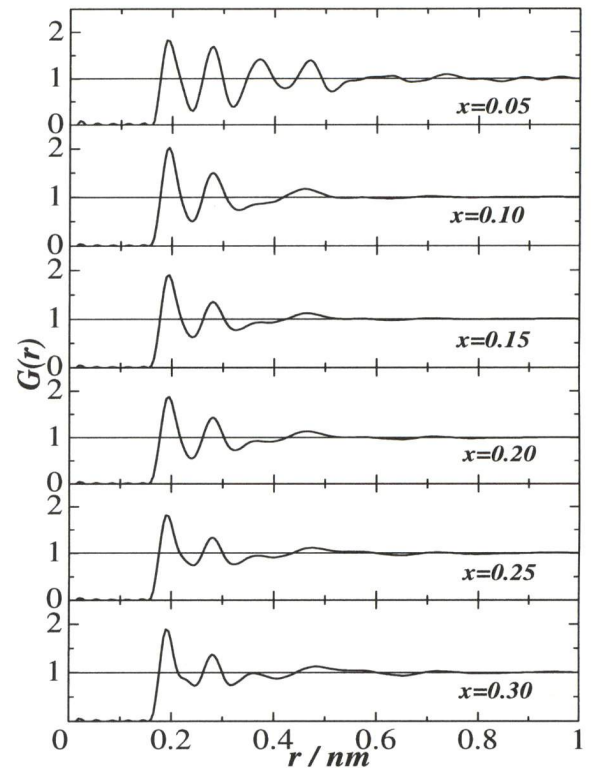


Fig. 2. Correlation function $G(r)$ of $x\text{Na}_2\text{O}-(1-x)\text{TeO}_2$ glasses.

the nearest neighbor can easily be obtained from $G(r)$ analysis, as was not the case with the other correlations.

In order to refine the short-range structure of the glass because of the difficulty of analysis in r -space, the structural parameters for each atomic pair need to be optimized in Q -space by the correlation method,^{14,15)} using the nonlinear least-squares fitting of eq.(3.1),

$$Q \cdot i(Q) = \left[\sum_i \sum_j n_{ij} b_i b_j \exp(-B_{ij} Q^2) \sin(Q r_{ij}) / r_{ij} \right] / \left(\sum_i b_i^2 \right) \quad (3.1)$$

where n_{ij} , b_i , B_{ij} and r_{ij} are the average coordination number, the scattering length, the temperature factor and the average interatomic distance for the atomic pair ij , respectively. Each atomic pair was assumed to be Gaussian distributed and centered at r_{ij} with a mean square displacement $2B_{ij}$ and the initial value of the structural parameters were predetermined to be equal to those obtained in $G(r)$ analysis taking into account the ionic radius¹²⁾ and the crystallographic data.¹⁶⁾ The calculated $Q \cdot i(Q)_{\text{calc}}$ reproduced from Debye scattering eq.(3.1) was fitted to the observed $Q \cdot i(Q)_{\text{obs}}$ in Q -space. The calculated $Q \cdot i(Q)_{\text{calc}}$ revealed the good agreement with the observed $Q \cdot i(Q)_{\text{obs}}$ in the Q -range of more than 10 nm^{-1} , indicating that the obtained structural parameters reproduced the real structure of glasses with a fairly accuracy.

The least squares fitted structural parameters are listed in Table I. As described before, there were two types of near neighbor Te-O distances, i.e., one was at about $r=0.18$ nm and the other around 0.20 nm. This trend

Table I. Least squares fitted structural parameters of xNa₂O-(1-x)TeO₂ glasses.

i-j		n _{ij}	r _{ij} / nm		n _{ij}	r _{ij} / nm
Te-O	x=0.05	1.35	0.186	x=0.10	1.37	0.191
		1.35	0.200		1.37	0.212
		1.20	0.217		1.07	0.245
	x=0.15	1.38	0.189	x=0.20	1.40	0.189
		1.38	0.212		1.40	0.211
		0.93	0.243		0.79	0.241
	x=0.25	1.42	0.189	x=0.30	1.44	0.188
		1.42	0.213		1.44	0.214
		0.65	0.239		0.52	0.241
Na-O	x=0.05	1.53	0.274	x=0.10	2.07	0.274
	x=0.15	2.24	0.270	x=0.20	1.72	0.268
	x=0.25	1.17	0.260	x=0.30	1.17	0.247
O-O	x=0.05	2.51	0.279	x=0.10	1.82	0.275
		2.92	0.385		2.82	0.293
	x=0.15	1.55	0.275	x=0.20	1.13	0.279
		2.26	0.291		1.71	0.290
	x=0.25	1.18	0.280	x=0.30	0.80	0.280
		1.45	0.286		1.43	0.281
Te-Te	x=0.05	14.50	0.376	x=0.10	9.26	0.355
		13.74	0.472		26.81	0.449
	x=0.15	9.11	0.350	x=0.20	6.24	0.357
		24.51	0.452		22.70	0.477
	x=0.25	6.87	0.357	x=0.30	9.65	0.352
		21.75	0.485		21.95	0.495

was consistent with those of the other alkali tellurite glasses having two sorts of Te-O pairs in the TeO₄ trigonal bipyramids (tbp).³⁾ As can be seen in Table I, the third Te-O pair was observed at about $r=0.24$ nm. This would be due to that the Te-O bonds in the TeO₄ trigonal bipyramids (tbp) were broken partly into TeO₃ trigonal pyramids with increasing Na₂O. The total coordination number of O around Te (in the first coordination shell) decreased with increasing Na₂O content. The results suggest that the alkali tellurite glasses having lower Na₂O content had networks composed of mainly TeO₄ trigonal bipyramids (tbp).

As can be seen from the Na-O correlations in Table I, the Na-O distance was calculated to be 0.274 to 0.247 nm by the addition of Na₂O content. Taking into account the crystal structure of Na₂O, it was caused by only the dense distribution of Na⁺ ions with increasing Na₂O content. This finding might indicate that the bond nature between Na and O was not covalent but ionic and thus the sodium atoms distributed easily and unrestrictedly as Na⁺ ions in the gaps of network formed by TeO₃ or TeO₄ structural units. The coordination number of O-O decreased with increasing Na₂O content. This may be caused by breaking Te-O and O-O connections by Na⁺. However, it should be noted that the contributions of Na-O and O-O correlations were rather difficult to be estimated since the compositional ratios and the atomic

scattering factor of Te was rather greater than those of Na and O. Consequently, the peaks of Na-O were in effect undetectable in $G(r)$ curves. The coordination number of Te-Te changed more drastically than other correlations, but the parameters of Te-Te pair tend to contain some unavoidable errors and the peaks corresponding to Te-Te correlations were broad after $r=0.35$ nm in $G(r)$ curves.

§4. Conclusion

According to X-ray diffraction (XRD) and pulsed neutron diffraction (PND), the short range structure of Na₂O-TeO₂ glasses and melts has been investigated. The results obtained in the present work are that the structure of sodium tellurite glass consisted of the TeO₄ trigonal bipyramids (tbp) and the TeO₃ trigonal pyramids (tp), and the TeO₄ trigonal bipyramids convert to the TeO₃ trigonal pyramids with increasing modifier Na₂O content and a rise of temperature. In the TeO₄ trigonal bipyramids (tbp), there are two sorts of near neighbor Te-O distances.

Acknowledgements

The present work has been carried out as a part of the JAERI-University Research Cooperation financially and technically supported by the Inter-University Program for the Joint Use of JAERI Facilities and owing to the Regulations for Acceptance of Guest Research by AIST Institutes.

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