Short- and medium-range order in Sb–Se glasses

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ABSTRACT

Neutron diffraction measurements were performed to investigate the structure of Sb_xSe_{100-x} bulk glasses with $x=5$, 10, 15, 20 and 25 at% Sb. The total pair distribution functions show two peaks at 2.36 Å and 2.64 Å, which are attributed to Se–Se and Sb–Se bonds, respectively. The coordination numbers calculated from these peaks indicate that Sb atoms are three-coordinated and Se atoms are two-coordinated for all the above compositions. However, the composition dependences of the first two peaks in the structure factors show an obvious change between 15 and 20 at% Sb, indicating that the medium-range structure is changed in this range of Sb content. In order to elucidate the medium-range structure, reverse Monte Carlo simulation was used with coordination number constraints. The structure models consisting of a mixture of the $SbSe_{3/2}$ network and Se_n chain clusters were in good agreement with neutron diffraction data for Se-rich glass (5, 10 and 15 at% Sb). On the other hand, a better fit was obtained for $Sb_{25}Se_{75}$ glass with a model based on the network structure formed by connected $SbSe_3$ units.

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1. Introduction

Antimony selenide glasses have attracted significant attention because of their electronic and optical properties [1–6]. Despite the continuing interest in these glasses, only a few studies have been conducted on their fundamental properties, especially for bulk glass samples, because of their low glass-forming ability. Tonchev and Kasap studied the thermal properties of Sb_xSe_{100-x} bulk glasses in a composition range from $x=0$ to 25 at% Sb using modulated temperature differential scanning calorimetry [7]. They reported that the composition dependence of the thermal properties shows extrema at $x=1$ and 15 at% Sb and the glass-forming ability is maximal at these compositions. Recently, Kostadinova and Yannopoulos studied the structure of Sb_xSe_{100-x} bulk glasses in a composition range from $x=0$ to 30 at% Sb using Raman scattering [8]. They concluded that a phase separation tendency does occur, namely, the structures consist of Sb_2Se_3-like domains and Se-rich ones. A structural study using a direct structural probe was reported in 1976 by Sagara *et al.* [9]. The authors used electron diffraction to investigate the structure of Sb_xSe_{100-x} glass films over a wide composition range, including their stoichiometric composition, i.e., $x=40$ at% Sb, Sb_2Se_3. However, the diffraction results reported in the literature are too limited to provide detailed information about the short-range structure because the structure

factors have a maximum momentum transfer $Q_{max} \sim 10 \, \text{Å}^{-1}$. In this work, pulsed neutron diffraction measurements were performed to investigate the structure of Sb_xSe_{100-x} bulk glasses ($x=0$, 5, 10, 15, 20 and 25 at%). Pulsed neutron diffraction technique provided the structure factor $S(Q)$ over a wide Q range and allowed us to obtain a highly resolved short-range structure in real space for a series of Sb_xSe_{100-x} glasses. Moreover, reverse Monte Carlo (RMC) simulation was used to investigate the medium-range structure. Previously proposed structural models were examined under the constraint of the short-range structure obtained from the neutron diffraction results.

2. Experimental procedure

2.1. Sample preparation

The Sb_xSe_{100-x} glass samples were prepared with $x=5$, 10, 15, 20 and 25 at% Se, including a pure-Se glass sample. Antimony (99.999%) and Selenium (99.999%) reacted for 24 h in a molten state in an evacuated quartz ampoule of 6 mm inner diameter and 0.5 mm wall thickness; then, they were quenched in an iced-water bath to prepare a homogenous Sb–Se alloy. The alloy sample was placed in an evacuated quartz ampoule of 2 mm inner diameter and 0.3 mm wall thickness and was quenched in an iced-water bath from the molten state. The vitrification of the samples was confirmed by X-ray diffraction with Mo-Kα radiation. No Bragg peaks were observed in the X-ray diffraction patterns of these samples.

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2.2. Neutron diffraction

Pulsed neutron diffraction measurements were performed using the high intensity total scattering spectrometer (HIT-II) installed at the pulsed neutron source of the High Energy Accelerator Research Organization (KEK, Japan). The structure factors, $S(Q)$, were obtained from the scattering intensity after correction for the background, absorption [10], and multiple scattering [11] and normalization with a vanadium rod.

The structure factors $S(Q)$ were derived using the Faber-Ziman definition [12]

$$S(Q) = \frac{I(Q) - \left\{ \langle b^2 \rangle - \langle b \rangle^2 \right\}}{\langle b \rangle^2},$$ (1)

and

$$\langle b^2 \rangle = \sum_i c_i b_i^2, \langle b \rangle = \sum_i c_i b_i,$$ (2)

where c_i and b_i are the concentration and the coherent scattering length for neutron diffraction, respectively, of atom i. The total correlation function, $T(r)$, can be derived from the Fourier transformation of $S(Q)$ as follows

$$T(r) = 4\pi r \rho + \frac{2}{\pi} \int_0^\infty Q(S(Q) - 1)\sin QrdQ,$$ (3)

where ρ is the average number density of the atoms, which was measured by a gas pycnometer (Quantachrome, Micro-Ultrapyc 1200e) with He gas (99.999%) at room temperature. The values of ρ for the Sb_xSe_{100-x} glasses are listed in Table 1. During the process of obtaining the structure factors and the total correlation functions for the Sb_xSe_{100-x} glass, no evidence of doubt about the validity of the sample composition was observed.

The total correlation function $T(r)$ of a Sb–Se binary mixture is described as the weighted sum of three partial correlation functions, $t_{i-j}(r)$:

$$T(r) = \frac{c_{Sb}^2 b_{Sb}^2}{\langle b \rangle^2} t_{Sb-Sb}(r) + \frac{2c_{Sb}c_{Se}b_{Sb}b_{Se}}{\langle b \rangle^2} t_{Sb-Se}(r) + \frac{c_{Se}^2 b_{Se}^2}{\langle b \rangle^2} t_{Se-Se}(r).$$ (4)

2.3. RMC simulation

In the RMC simulation, atoms were randomly moved in a simulation box with periodic boundary conditions so as to minimize χ^2, which is the difference between the experimentally obtained structure factor, $S_e(Q)$, and that calculated from the model, $S_m(Q)$:

$$\chi^2 = \sum_{i=1} [S_e(Q_i) - S_m(Q_i)]^2 / \sigma^2(Q_i),$$ (5)

where $\sigma(Q_i)$ is the experimental error [13]. The value of σ used in this work was 0.005.

The starting configuration comprised approximately 5000 atoms with appropriate concentrations, randomly distributed in a cube box. To ensure a physically realistic configuration, the closest distances for Sb–Sb, Sb–Se and Se–Se pairs that they were allowed to approach were determined from the experimental data to be 3.00, 2.45 and 2.20 Å, respectively. The r-spacing of the partial correlation functions was set to 0.05 Å.

The RMC models were constrained to the short-range structure obtained from the neutron diffraction results. Namely coordination number constraints were used. The formation of a triangular three-atom unit was prevented in the RMC simulation.

3. Results

Fig. 1 shows the experimental structure factors, $S(Q)$, for the Sb_xSe_{100-x} glasses. The total correlation functions, $T(r)$, which were obtained from the Fourier transformation of the structure factors according to Eq. (3) with $Q_{max}=30$ Å^{-1}, are displayed in Fig. 2. The total correlation function for pure Se glass shows a well-resolved first peak at $r=2.36$ Å, which corresponds to the Se–Se bond. As Sb is added to the pure Se glass, the Se–Se peak remains at the same position but decreases in intensity. On the other hand, a new peak appears at $r=2.64$ Å and increases in intensity with increasing Sb content. Its distance is similar to the average Sb–Se bond length, $r=2.69$ Å, in crystal Sb_2Se_3 [14]. Considering this similarity, as well as the composition dependence of the peak position and intensity, the peak at $r=2.64$ Å in the total correlation function was attributed to the Sb–Se bond.

The Se–Se and Sb–Se peaks in the total correlation functions overlap. Gaussian fits were applied to these peaks to calculate the coordination numbers of the Sb and Se atoms. The fitting results for five glass samples ($x=5, 10, 15, 20$ and 25 at% Sb) are shown in Fig. 3, together with the residual. The coordination numbers, calculated from the areas of the Gaussian peaks, are listed in Table 2,
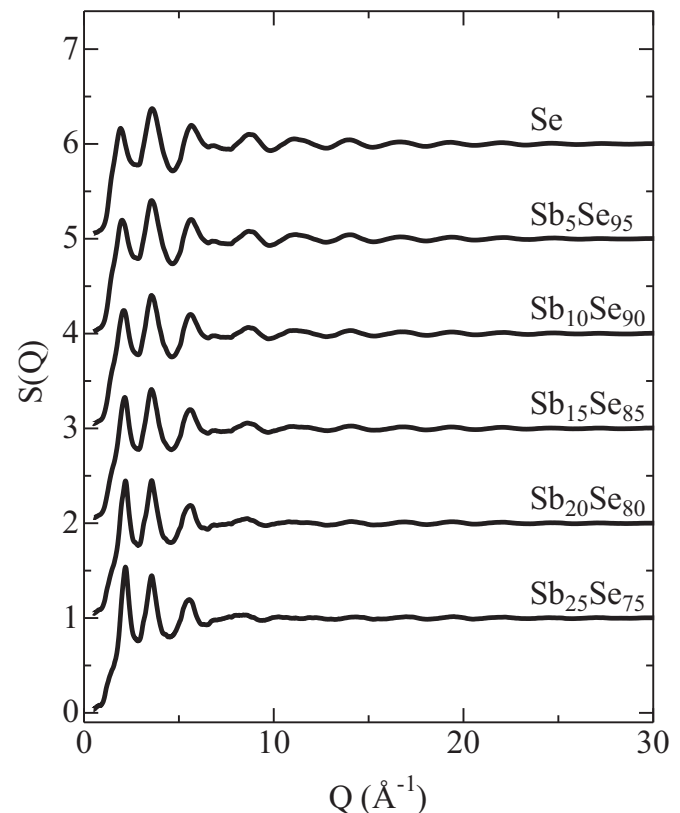
Table 1
Average number density, ρ, for the Sb_xSe_{100-x} glasses, measured by a gas pycnometer using 99.999% He gas at room temperature.

Sample	ρ (Å^{-3})
Se	0.03267(5)
Sb_5Se_{95}	0.03279(5)
$Sb_{10}Se_{90}$	0.03298(5)
$Sb_{15}Se_{85}$	0.03324(5)
$Sb_{20}Se_{80}$	0.03348(5)
$Sb_{25}Se_{75}$	0.03385(5)

Fig. 1. Experimental structure factors, $S(Q)$, for the Sb_xSe_{100-x} glasses obtained from neutron diffraction measurements. The data are shifted vertically for clarity.