Small-angle x-ray scattering and density measurements of liquid $\text{Se}_{50}-\text{Te}_{50}$ mixture at high temperatures and high pressures using synchrotron radiation

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Abstract. We have carried out small-angle x-ray scattering and x-ray transmission measurements of liquid $\text{Se}_{50}-\text{Te}_{50}$ mixture at SPring-8 in Japan and obtained the structure factor $S(Q)$ at small-$Q$ region ($0.6 < Q < 3.5 \text{ nm}^{-1}$) and the density at high temperatures and high pressures up to 1000 °C and 180 MPa. We report preliminary results in this paper.

With increasing temperature, the density shows a minimum at around 500 °C and a maximum at around 700 °C. On the other hand, $S(0)$ becomes maximum and $S(Q)$ strongly depends on $Q$ at around 600 °C, which is about the middle temperature where the density shows the minimum and maximum. The temperatures shift to lower side when the pressure increases. These results prove that, with increasing temperature, the sample exhibits gradual transition from low-density structure to high-density structure, which causes mesoscopic density fluctuations in the intermediate temperature region.

1. Introduction

Liquid Se-Te mixtures are known to exhibit gradual change from 2-fold coordinated Se-like structure to 3-fold coordinated Te-like one when the composition and/or the temperature of sample change [1, 2]. This structural change accompanies gradual change of the electronic properties [3, 4] and liquid Se-Te mixtures exhibit semiconductor-metal transition. It also accompanies anomalous thermodynamic features: density minimum [5], sound velocity minimum [6] and heat capacity maximum [7]. These properties are also observed in the high-pressure region [8, 9, 10]. In $\text{Se}_{50}\text{Te}_{50}$, as the pressure increases, the transition temperature gradually decreases from about 650 °C at ambient pressure to about 450 °C at 500 MPa [8]. To explain these features, existence of large fluctuations [6] (inhomogeneity [11]) are probable, but there have been no clear direct experimental observations of such density fluctuations. Recent small-angle neutron scattering measurement [12] indicated such density fluctuations and now more experimental evidences are expected. We have carried out small-angle x-ray scattering and density measurements using synchrotron radiation to detect such fluctuations in density.
2. Experiment

The experiments were carried out at the High Energy X-ray Diffraction beamline BL04B2 of SPring-8 in Japan. The energy of incident x-ray was 37.8 keV and the beamsize was 0.3 × 0.3 mm². The scattered x-ray was detected and accumulated for 20 min with an imaging plate of 300 × 300 mm² located at 2.96 m distance from the sample position. In order to determine the sample density and to make absorption corrections, the intensity of transmitted x-ray was also detected with an ionization chamber. Se₅₀–Te₅₀ sample with a thickness of about 180 μm was contained in a poly-crystalline sapphire cell, which was located in a high-pressure vessel equipped with single-crystalline diamond windows for both incident and scattered x-rays. The vessel was pressurized by He gas and the sample was heated by tungsten heaters. Further details of the experiment were shown in Ref. [13].

3. Results and Discussion

The measurements were carried out from 500 to 1000 °C at 6 MPa and from 400 to 1000 °C at 100 and 150 MPa. At 175 MPa, only transmission measurement was carried out from 400 to 1000 °C. In Fig. 1, (a) temperature- and (b) pressure- dependence of the transmitted x-ray intensities are plotted by marks. These values are normalized by the transmitted x-ray intensity of empty cell measurement under vacuum condition. As shown in Fig. 1 (a) at each pressure, with increasing temperature, the intensity first increases at lower temperature, decreases at intermediate temperature and increase again at higher temperature. Temperature variation of the intensity at a constant pressure is within 5%. With increasing pressure, the intensity decreases and the intensity curve shifts to lower temperature side. In the present measurement, the observed x-ray intensity $I$ is affected by both the transmission of the sample and that of He gas as follows:

$$I = \exp[-a \, l \, \rho(P, T)] \times \exp[-a_{\text{He}} \, l_{\text{He}} \, \rho_{\text{He}}(P)]$$

(1)

$a = 15.54, a_{\text{He}} = 0.188$ [cm²/g] are the absorption coefficients at 37.8 keV, $l=180\mu\text{m}, l_{\text{He}}=144\text{mm}$ are the thicknesses and $\rho \simeq 4.6 - 5.0, \rho_{\text{He}} = 0 - 0.2$ [g/cm³] are the densities, of Se–Te sample and He gas, respectively. Pressure variation of the transmission of He gas is calculated as shown.
in Fig. 1 (b) by the solid curve. The effect of He gas is very large and thus, the estimation of the absolute value of the sample density, especially of the pressure variation (difference between marks and solid curve in Fig. 1 (b)), is less accurate.

Temperature variation of the estimated density is shown in Fig. 2 (a). The absolute value is, however, hard to estimate, so the vertical axis is arbitrary one at the present stage. At 100 MPa, with increasing temperature, the density decreases below about 500 °C, anomalously increases up to 760 °C and again normally decreases at higher temperature region. As a result, the density shows a minimum at 500 °C and a maximum at 760 °C. This result is similar to that at ambient pressure which was already observed for over thirty years ago [5]. With increasing pressure, the curve shifts to lower temperature side. The temperature variation of the density at each pressure indicates that in Se-Te mixture there are two (meta-)stable states, low-density and high-density structure that are similar to liquid Se and liquid Te, respectively, and with increasing temperature, the fraction of high-density one gradually increases from almost negligible below 500 °C to almost dominant above 800 °C. The slope of the density curve (thermal expansion) at low-temperature side is steeper than that at high-temperature side, which is consistent that liquid Se has larger thermal expansion coefficient than that of liquid Te.

From the observed scattered x-ray intensity, the structure factor $S(Q)$ is calculated through some corrections [14] (background subtraction, correction for atomic formfactor, etc.). Figure 3 shows $S(Q)$ at small-$Q$ region at 100 MPa. In our method, the absolute value of $S(Q)$ can be determined by comparing the scattering intensity of pressurized He gas [14] and its reliability is checked by the consistency between the scattering measurement and the pressure

![Figure 2](image1.jpg)

**Figure 2.** Temperature dependence of (a) density and $S(Q)$ fitting parameters (b) $a_q$ and (c) $S(0)$ at the pressures in the figure. Solid curves are guides for the eyes.

![Figure 3](image2.jpg)

**Figure 3.** $S(Q)$ at 400, 600 and 1000 °C at 100 MPa. Solid lines indicate linear fitting results with $Q < 2.5$nm$^{-1}$.
variation of density with the equation \( S(0) = k_B T (\partial \rho / \partial P)_T / M \) \( (k_B: \text{Boltzmann constant}, \ M: \text{atomic weight}) \) [15]. But in the present measurement, not only the scattered x-ray but also great amount of the fluorescence x-ray was detected because the energy of incident x-ray (37.8 keV) is near K-edge of Te (31.8 keV), the estimated \( S(Q) \) is much shifted upward and the real value should be much smaller. Thus the vertical axis is arbitrary one at the present stage. At 400 °C, \( S(Q) \) hardly changes with \( Q \). But at 600 °C, where the temperature dependence of the density is positive, the small-angle scattering intensity becomes larger and \( S(Q) \) exhibits strong \( Q \)-dependence. At 1000 °C, the intensity decreases and the slope becomes flat. We fitted \( S(Q) \) in the small \( Q \) range \((0.6 < Q < 2.5 \ \text{nm}^{-1})\) with a linear function, \( S(Q) = S(0)(1 - a_Q Q) \), and plot these fitting parameters in Fig. 2 (b) and (c). At 100 MPa, with increasing temperature, \( a_Q \) and \( S(0) \) increase at lower temperature but decrease at higher temperature. They exhibit maximum at around 620 °C, which is the middle temperature where the density shows anomalous temperature dependence.

At other pressures, similar temperature dependencies are observed, but the temperature where the fitting parameters show maximum shifts to lower temperature with increasing pressure. It proves that the density fluctuations increase in the intermediate temperature region due to the gradual structural transition and the sample becomes inhomogeneous structure which consists of low-density and high-density structures. With increasing pressure, the transition region shifts to lower temperature side. Furthermore, the present result also clarifies another important point: the intensity of these density fluctuations is not so large. Usually, slowing down of the sound velocity due to the density fluctuations, for example, near the liquid-gas critical point, becomes distinct only when \( S(0) \) is the order of \( 10^1 \) or larger, but in this case \( S(0) \) is only about 0.5 or much smaller which does not seem to explain the sound velocity minimum of Se-Te mixtures [6, 11]. Other contribution such like internal-energy fluctuations [16] should be also considered.

To determine the absolute value of density and \( S(Q) \) and make further discussion, we will carry out next experiments and improve the accuracy of the data in near future.

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