

X-ray diffraction measurement of liquid As_2Se_3 by using third-generation synchrotron radiation source

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Abstract

X-ray diffraction (XD) measurements of liquid As_2Se_3 were carried out in the temperature range up to 1600°C where the temperature is well beyond the semiconductor to metal (SC-M) transition temperature around 1000°C. The measurements were done by using third-generation synchrotron radiation source at SPring-8 and the obtained structure factors have much improvements over the previous XD measurements by using *in house* X-ray sources with regard to the momentum transfer range and the data statistics. The deduced pair distribution functions show that with increasing temperature, the the position of the first peak does not change within the errorbar and the coordination number gradually decreases up to 1600°C irrespective of the SC-M transition. These results contradict previous *in house* XD measurement but coincide with the first principle molecular dynamics simulation.

1. Introduction

As_2Se_3 is a typical liquid semiconductor and is well-known glass-forming material. At the low temperature near the melting point, liquid As_2Se_3 is believed to have a strong covalent bonded network structure, which is suggested originally in the glassy phase and subsequently supported in the liquid phase by the neutron diffraction [1], extended x-ray absorption fine structure (EXAFS) [6] and infrared absorption [3] measurements. The prepeak or the first-sharp diffraction peak (FSDP) in the total structure is one of the most important such evidence. On the other hand in the high temperature state, optical absorption [4] and electrical conductivity measurements [5] have revealed that the As_2Se_3 undergoes a temperature driven semiconductor-metal transition (SC-M) at about

1000°C at high pressure. In order to study how the structure changes in the SC-M transition, EXAFS and *in house* x-ray diffraction (XD) measurement [7] and first principle molecular dynamics (MD) simulation [8] have been done at the temperature from melting temperature to over the SC-M transition temperature. EXAFS result revealed the partial local structures: the coordination numbers for the As and Se edges are three and two respectively at around the melting temperature and both of them gradually decreases with increasing temperature up to 1400C irrespective of the SC-M transition; the nearest-neighbour distances for the edges are same values (0.24nm) and both of them slightly decrease at around 1000°C. The authors also discussed that the hetero-coordinated bond (As-Se) is dominant under 1000°C but the slight longer (0.26nm) additional As-As bond appears above the temperature. On the other hand, *in house* XD results deduced the total structures: the coordination number is about 2.4 around the melting temperature and

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with increasing temperature, it decreases up to around 1000°C and *increases* above the temperature; the nearest-neighbour distance (0.24nm) does not change up to 1000°C and it *increases* above the temperature. MD simulations obtained the total structure factors consistent with these from XD measurement and deduced the local structures: the nearest-neighbour distance of As-Se, Se-Se and As-As are 0.245, 0.245 and 0.255nm at around melting temperature and they do not change much up to 1400°C ; threefold coordinated As and twofold coordinated Se are dominant at around melting temperature but with increasing temperature, the fraction of twofold coordinated As and that of onefold coordinated Se increase; these smaller coordinated atoms generate many non-bonding electrons that do not occupy the p-like anti-bonding state which induces the metallic state.

The results of the previous XD measurements contradict that of the EXAFS and MD simulations as to the temperature variations of the nearest neighbour distance and the coordination number. To solve these contradiction and to investigate further structural information experimentally, we carried out XD measurements of liquid As₂Se₃ by using third-generation synchrotron radiation source at SPring-8 in Japan. The measurements were done in the temperature and pressure ranges up to 1600°C and 15 MPa and in the momentum transfer range between 10 and 150nm⁻¹ by the energy-dispersive method [9].

2. Experimental procedure

The As₂Se₃ sample of 99.999% purity with a thickness of 250μm was contained in a single-crystal sapphire cell. High temperature states up to 1600°C were achieved in an internally-heated high-pressure vessel; the pressurized states were needed to prevent the sample vaporization which were achieved with high purity He gas of 99.999% as a pressurizing material. The construction of the vessel and the sample cell are described in other paper [9]. The energy-dispersive X-ray diffraction (XD) measurements were performed at the white beam x-ray diffraction line (BL28B2) of SPring-8 in Japan. The energy range of the x-ray is up to 150keV and the scattering angles 2θ are fixed to seven values 4°, 7°, 11.5°, 15°, 20°, 25° and 33° due to the positions of the Be windows of the vessel. After several data corrections [9], we obtained the total structure

factors $S(Q)$ (Q:momentum transfer) with a good statistics in the momentum transfer range from 10 to 150 nm⁻¹ at the temperatures up to 1600°C .

3. Results

Figure 1 shows the temperature variations of $S(Q)$. The pressures are from 13 to 15 MPa at these temperatures. $S(Q)$ at 600 and 1600°C by the previous *in house* XD measurement are also indicated in the figure by the crosses. At 500°C , substantial oscillation is observed in the Q-range up to 150nm⁻¹. The prepeak or FSDP, which thought to be the reflection of the intermediate range order, at around 12nm⁻¹ is also clearly observed. With increasing temperature, the oscillation in $S(Q)$ gradually dampen; the height of the first (~ 22 nm⁻¹) and the second peak (~ 36 nm⁻¹) gradually decreases and the dip between them almost disappears and merges each other at the highest temperature 1600°C . The height of the FSDP also decreases. It changes to a shoulder at around 1100°C , but still remains at 1600°C .

Figure 2 shows the pair distribution function, $g(r)$, obtained from the Fourier transformation of $S(Q)$ shown in Fig.1. The first (~ 0.24 nm), second (~ 0.37 nm) and third (~ 0.56 nm) peaks are observed at the low temperatures and the height of them decreases with increasing temperature; the third peaks almost disappear at high temperatures; the positions of these peaks are almost unchanged; the depth of dip at 0.28nm which is between the first and second peaks gradually decreases.

Fig.3(a) shows the temperature variation of the total nearest-neighbour distance r_1 estimated from the position of the first peak of $g(r)$. It does not change within the errorbar in the whole temperature region. Fig.3(b) is the temperature dependence of the total coordination numbers calculated by two different method as shown in the inset of Fig.3(a) schematically: (method A) To integrate $4\pi r^2 \rho_0 g(r)$ up to r_1 and twice the integrated value; ρ_0 denotes the average number density of As₂Se₃ which is estimated from the measured temperature and pressure according to the literature [10]. (method B) To integrate $4\pi r^2 \rho_0 g(r)$ up to the minimum point of $g(r)$, r_{min} . With increasing the temperature, N_A shows substantial decrease but N_B does not change much.

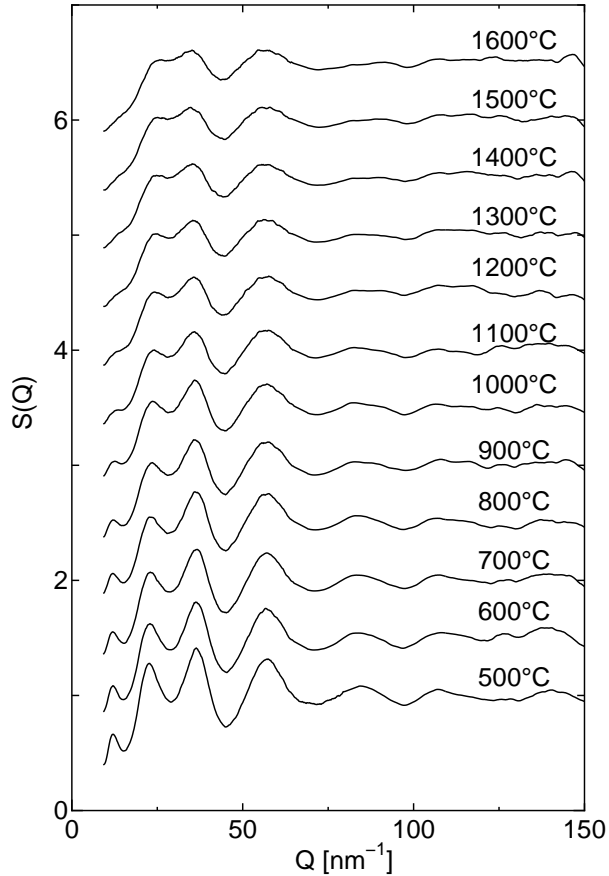


Fig. 1. Structure factors $S(Q)$ at the temperatures in the figure. $S(Q)$ at different temperatures are shifted against one another by 0.5 for clarity.

4. Discussion

The present measurements serve the new $S(Q)$ in wider Q -ranges and better statistics than that from the previous *in-house* XD measurements [7]. The major features of $S(Q)$ under 100nm^{-1} such that the oscillation gradually dampen with increasing temperature and the FSDP changes to shoulder at around 1100°C are consistent with the previous one. Strong oscillations in $S(Q)$ are compared with the previous XD results.

As to the local structure deduced from the $g(r)$, the present results such that r_1 keeps a constant value and N_A gradually decreases against the temperature are consistent with that from the MD simulations except for the absolute value of N_A . The present values $N_A = 3.0$ at 500°C is 0.3 times larger than the previous XD results ($N=0.24$) and about 0.1 times larger than that (0.27) estimated from

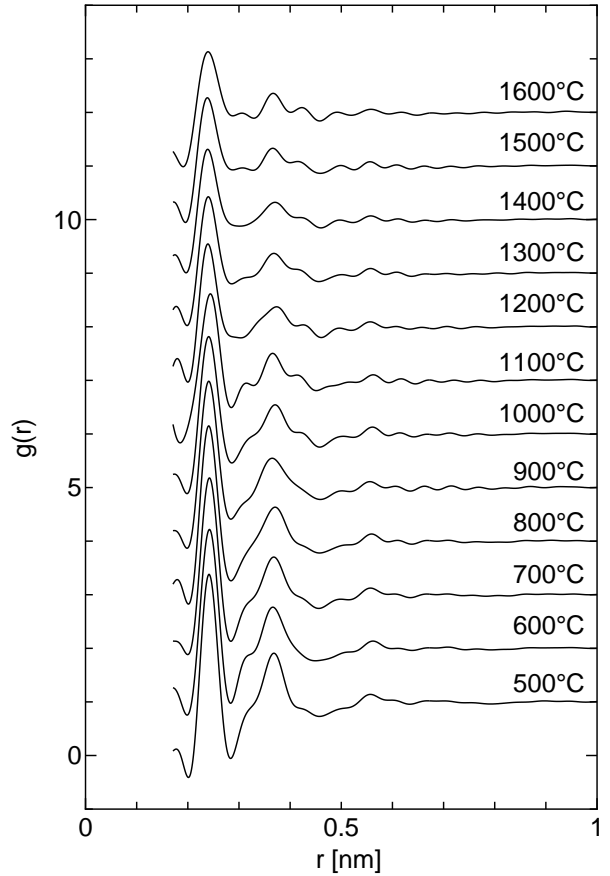


Fig. 2. Pair distribution functions $g(r)$ corresponding to the structure factors in Fig.1. $g(r)$ at different temperatures are shifted against one another by unity.

the neutron diffraction measurements [1]. We can not identify the reason of this overestimation at the present stage but the decreasing behaviour against the temperature is consistent with the MD simulations and EXAFS results. Furthermore, N_B keeps a constant value against the temperature in spite of the decreasing behaviour of N_A : this means that the number of the atoms with a long bond of the distance from $r_1=2.42$ to $r_2 \sim 0.28\text{nm}$ increase with increasing temperature. This is also consistent with the MD simulations and EXAFS results that the fraction of As-As bonds with about $0.255\text{-}0.26\text{nm}$ bond-length increase at higher temperature.

In this way, the present results support the MD simulation and EXAFS results but differ from the previous XD results. We suppose this apparent contradiction derived from the shortage of the data statistics at high- Q region in the previous measurements. In order to prove this hypothesis, we calculated another pair distribution functions whose Q -

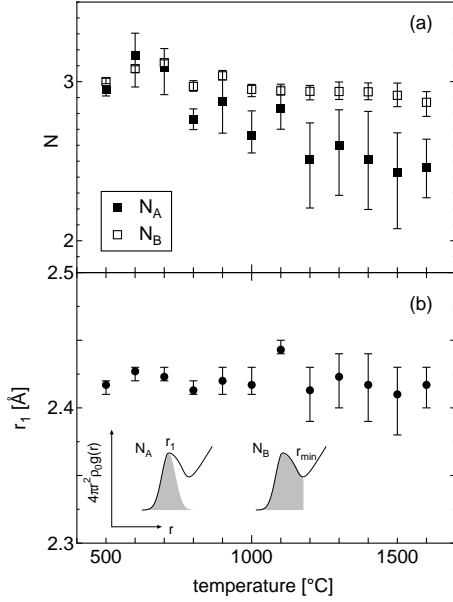


Fig. 3. Temperature dependence of (a) the average nearest-neighbour distance r_1 . and (b) the average coordination numbers N_A and N_B estimated by the two different methods that are schematically shown in the inset.

ranges of the Fourier transformations are limited: in the previous measurements, effective $S(Q)$ with a good statistics are limited only in the Q -range up to 80nm^{-1} at higher temperatures. Thus we calculated another pair distribution function $g_{\text{Ltd}Q}(r)$ by Fourier-transforming $S(Q)$ in the Q -region between 10 to 80nm^{-1} . $g_{\text{Ltd}Q}(r)$ at 600 and 1500°C are shown in Fig.4 by the dashed lines and corresponding non-limited $g(r)$ are also plotted by the solid lines. Compared with $g(r)$, $g_{\text{Ltd}Q}(r)$ have broad peaks at around 0.25 and 0.37 nm because limitation of Q -range in $S(Q)$ leads to the bad spacial resolution in $g(r)$. At 600°C , the broadening of the peaks do no effect on the position of the peaks: $g(r)$ and $g_{\text{Ltd}Q}(r)$ have the same r_1 and r_2 (second neighbour distance) values. But at 1600°C , the first and the second peaks overlap due to the broadening of the peaks and show apparent increases of r_1 and decreases of r_2 . We show the temperature variations of r_1 estimated from $g_{\text{Ltd}Q}(r)$ in Fig.5(a) by the open symbols. r_1 by the previous *in house* XD measurements are also shown in the same figure by the crosses. Apparent increase of r_1 against the temperature is almost explained by this process. We also estimated the N_A from $g_{\text{Ltd}Q}(r)$ and show the results in Fig.5 (b). The decreasing behaviour of N_A ceases at around 1100°C , which does not contradict with the previous *in house* XD results. These consis-

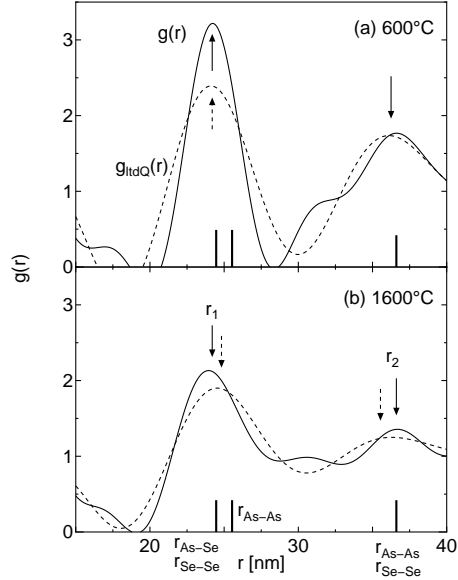


Fig. 4. Changes of the pair distribution functions $g(r)$ when the Q -range of the Fourier transformation is limited: non-limited $g(r)$ are plotted by the solid lines and Q -limited $g_{\text{Ltd}Q}(R)$ by the dashed lines at (a) 600°C and (b) 1600°C , respectively. See details in the text. Bond lengths estimated by the MD simulations are also shown by the bars.

tency between the behaviour of r_1 and N_A from the present Q -limited $g_{\text{Ltd}Q}(r)$ and that from the previous *in house* measurements prove that our hypothesis, that the previous *in house* measurements have a problem of the shortage of the data statistics in high- Q region, is true.

As to FSDP, to quantify the changes are interesting, but it is difficult to estimate that at the present stage because the absolute value of $S(Q)$ in the low- Q region is much affected by the data correction in the energy-dispersive method.

5. Summary

We have carried out the XD measurements of liquid As_2Se_3 in the temperature range up to 1600°C at SPring-8. $S(Q)$ with better statistics and wider momentum transfer range than that from the previous *in-house* XD measurements have been obtained. Major features of the present $S(Q)$ are qualitatively consistent with the previous one. But as to $g(r)$, there are some differences: the nearest-neighbour distance does not change within the errorbar in this temperature range; the coordination number decreases with increasing temperature. These features are almost consistent with the MD simulations.

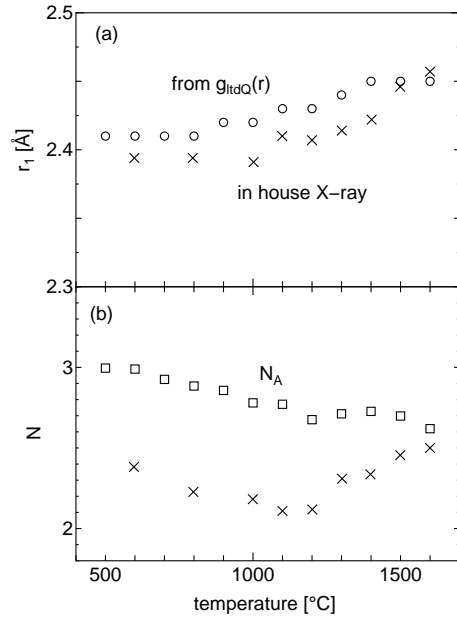


Fig. 5. (a) Nearest-neighbour distance r_1 and (b) coordination number N_A : open symbols denote the deduced values from the present Q-range limited $g_{tidQ}(r)$ and crosses are the values from the previous *in house* XD measurements.

The contradiction between the previous *in house* XD results and the present XD study (or the MD results) can be explained by the shortage of the data statistics at high-Q region of the *in house* XD measurements.

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