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Structural analysis of a high-pressure amorphous phase of SnI₄

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Abstract

We have performed a high-pressure synchrotron x-ray diffraction study of a metallic amorphous state in SnI₄ induced by pressure. The Faber–Ziman structure factor $S(Q)$ was obtained from diffraction intensities measured at pressures between 25 and 65 GPa. The first peak in $S(Q)$ is relatively intense and sharp and the second peak is overlapped with the third one. Such features are also found in $S(Q)$ for pure metallic glasses of Ni and Fe at 1 atm but not in molecular liquids. The obtained reduced radial distribution function $g(r)$ shows no evidence for the presence of the SnI₄ molecules in the metallic amorphous state.

1. Introduction

A structural characteristic of molecular crystals is the significant difference in strength between the strong intramolecular chemical bonding and the weak intermolecular bonding. This distinction brings about a variety of novel phenomena when molecular crystals are compressed to high pressures. The molecular crystal SnI₄ exhibits several of such effects of pressure: an insulator–metal transition, amorphization, a structural transition in the amorphous state, molecular dissociation and a superconductive transition [1].

In SnI₄ the pressure-induced, metallic amorphous state appears between 20 and 61 GPa at room temperature. This non-crystalline state plays a key role in determining its high-pressure properties. The molecular dissociation is recognized in a crystalline phase which emerges directly from the amorphous state at 61 GPa. The superconductive transition first appears at 30 GPa. Thus, it is crucial to study the structure of the amorphous state to understand structural and electronic properties of SnI₄ at high pressure. Although some models for amorphous structure of SnI₄ have been proposed [2–4], no direct determination based on diffraction measurement has been conducted with the only exception of the work by Kruger and Meade [5] for high-pressure amorphous GeI₄. In the present work, we study the structure of the amorphous state in SnI₄ by means of synchrotron x-ray diffraction measurements.

2. Experimental details

Polycrystalline SnI₄ of 99.9% purity purchased from Kojundo Chem. Co. was ground for an hour to obtain fine powder. A lightly pre-compressed sample was placed in a 100 μm diameter hole drilled in a rhenium gasket with a thickness of 50 μm with ruby chips and loaded in a modified Mao–Bell-type diamond anvil cell (DAC). All the sample preparation was carried out in an argon atmosphere. No pressure transmitting medium was used. The pressure was determined from the fluorescence of ruby chips. The pressure variation in the sample was measured as less than 1.5 GPa at 55 GPa. A thickness of the sample recovered from 65 GPa to 1 atm was typically 14 μm.

Synchrotron x-ray diffraction measurements were carried out at beamline BL04B2 at SPring-8. High-energy x-rays tuned to 61.08 keV ($\lambda = 0.203 \text{ \AA}$) with the single-bounce Si(220) crystal monochromator were used to cover a wide range of wavenumber, Q , up to $\sim 16 \text{ \AA}^{-1}$. The incident x-rays were collimated to $40 \times 40 \text{ \mu m}^2$. An imaging plate was used as a detector. The exposure time was set to either 50 or 100 min and four or two exposures, respectively, were repeated to obtain good counting statistics.

In three separate runs, diffraction from amorphous SnI₄ was measured at 35, 45, 54, and 55 GPa on compression and at 25 GPa on decompression. We also measured diffraction from the non-molecular crystalline phase with the fcc structure at 65 GPa. This spectrum was used to estimate the ‘background’ intensity arising from air scattering, stray x-rays around the diffractometer, and the incoherent scattering from both the diamonds and the sample. In order to convert measured raw data into electron units, the spectrum was first normalized to the intensity of the incident x-rays and then corrected for the polarization and the absorption due to the diamonds and the sample. After subtracting the estimated ‘background’ intensity from the spectrum and employing the normalization factor calculated by the Krogh–Moe–Norman method, we obtain the coherent scattering intensity per atom, $I(Q)$.

3. Results and discussion

The Faber–Ziman structure factor $S(Q)$ is given by

$$S(Q) = \frac{I(Q) - (\langle f^2(Q) \rangle - \langle f(Q) \rangle^2)}{\langle f(Q) \rangle^2}, \quad (1)$$

where $\langle f^2(Q) \rangle$ and $\langle f(Q) \rangle^2$ are the square of the average and average of the squared atomic scattering factors for SnI₄. Figure 1 shows $S(Q)$ for the amorphous state of SnI₄ at various pressures. The general features of $S(Q)$ shown in figure 1 are that the first peak is markedly sharper and higher than other peaks and that the second peak is overlapped with the third peak. The amplitude of oscillation in $S(Q)$ at large Q appears to develop with increasing pressure.

Three structure models of the amorphous SnI₄ [2–4] all involve the SnI₄ molecule as a structure unit. In order to see whether the molecular amorphous model can reproduce the experimental $S(Q)$ shown in figure 1, we calculated $S(Q)$ for the model proposed by Sugai [2], in which dimerized SnI₄ molecules are randomly oriented. The configuration of the model structure was constructed by following the procedures developed by Misawa [6] for tetrahedral molecular liquids. The density of the amorphous state was estimated by extrapolating the density of the fcc crystalline phase to low pressures provided that they do not differ significantly. We found that the large- Q oscillations mainly arising from the atomic correlation within the molecule differ completely between the calculated $S(Q)$ and the experimental one at $Q > 6 \text{ \AA}^{-1}$. Even in the low- Q range, the measured $S(Q)$ was not reproduced by the calculated $S(Q)$. We therefore conclude that the SnI₄ molecule is no longer the fundamental structural unit in the high-pressure amorphous state.

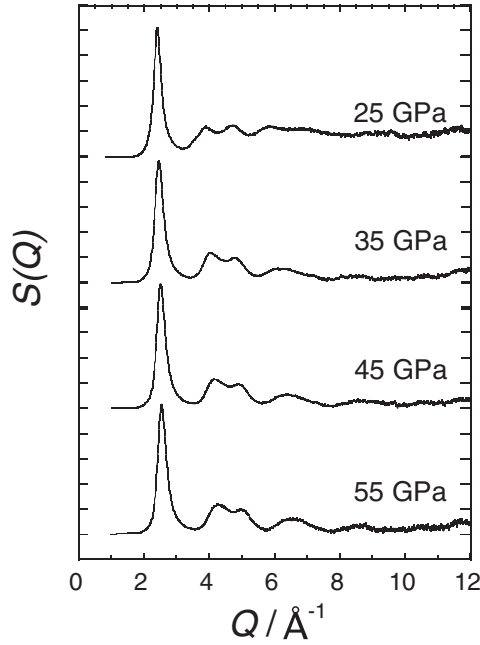


Figure 1. Faber-Ziman structure factor, $S(Q)$, for SnI₄ at 35, 45, and 55 GPa on compression and at 25 GPa on decompression.

More direct and detailed information about atomic correlation in non-crystalline systems can be obtained from the radial distribution function (RDF). Using the Fourier transformation, we obtain

$$g(r) = \frac{2}{\pi} \int_0^{Q_{\max}} Q(S(Q) - 1)M(Q) \sin(Qr) dQ, \quad (2)$$

where $g(r)$ is the reduced RDF and $M(Q)$ is a high-frequency filter that removes the finite truncation effects in the transform. Because SnI₄ contains two types of atom, $g(r)$ is a convolution of the Sn-Sn, I-I, and Sn-I correlations. It is difficult to distinguish those contributions in x-ray diffraction data, since these atoms have nearly the same numbers of electrons. Figure 2 shows the experimental $g(r)$ calculated from $S(Q)$ presented in figure 1. The arrow at 2.65 Å indicates the Sn-I spacing and that at 4.33 Å the I-I spacing within the SnI₄ molecule. It is again evident that the molecules are absent in the amorphous state. The strong oscillations in $g(r)$ extending to distances larger than 15 Å are indicative of medium-range ordering in the structure.

The first maximum in $g(r)$ at 55 GPa appears at 3.0 Å and the three subsequent peaks are located at 5.2 Å $\sim \sqrt{3}r_1$, 6.0 Å $\sim 2r_1$, and 7.9 Å $\sim \sqrt{7}r_1$. Interestingly, the nearest-neighbour distance in the fcc crystalline structure at 61 GPa is also 3.0 Å. This coincidence, together with the presence of medium-range ordering, seems to support the microcrystalline model for amorphous SnI₄. However, this possibility is ruled out by the fact that there is no singularity in $g(r)$ at $\sqrt{2}r_1$ which is the atomic spacing inherently present in the fcc structure. The absence of this maximum in any of $g(r)$ shown in figure 2 is evidence for the non-microcrystalline character of amorphous SnI₄.

We were aware of remarkable similarities in $S(Q)$ and $g(r)$ between the pressure-induced amorphous state in SnI₄ and pure metallic glasses of Ni and Fe [8]. It is worth noting that amorphous SnI₄ is metallic and that the metallic crystalline phase stable above 61 GPa has fcc structure of the substitutionally disordered binary alloy type [9]. A structure model of pure metallic glass is a dense random packing of hard spheres (DRPHS) in which slightly deformed

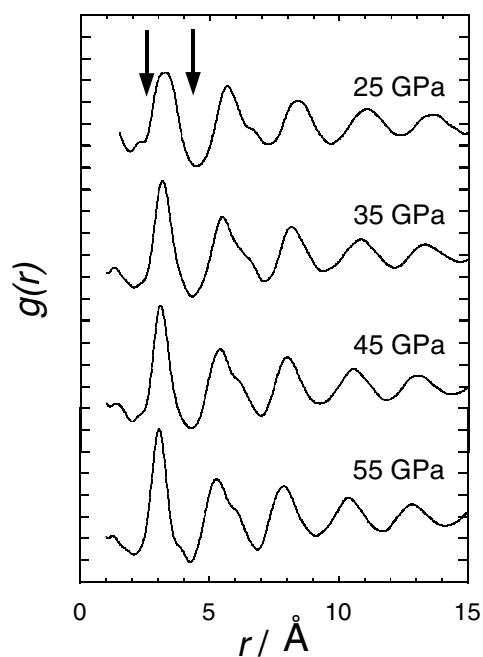


Figure 2. Reduced RDF $g(r)$ for the amorphous SnI_4 at various pressures. The arrow at 2.65 Å indicates the Sn–I spacing and that at 4.33 Å the I–I spacing within the SnI_4 molecule.

tetrahedra are dominant structural units and their packing is relatively rigid. In the case of SnI_4 at high pressures, it is likely that the amorphous state consists of the tetrahedra, with an edge length of 3.0–3.2 Å, as the fundamental units of a close-packed disordered atomic distribution.

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