Phase Transition in SnI_4 at High Pressure

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Synchrotron x-ray diffraction study of SnI_4 establishes a rich sequence of high-pressure structural transitions; 1st crystalline phase - 2nd crystalline phase - amorphous state - 3rd crystalline phase. Both metallization and amorphization proceed in the newly found 2nd phase stable above 7.2 GPa. The 3rd crystalline phase exhibits a simple diffraction pattern that can be indexed only with the fcc lattice with the nearest interatomic distance of 3.003 ± 0.001 Å at 61 GPa. This short distance is taken as evidence for pressure-induced dissociation of the SnI_4 molecules.

[synchrotron x-ray diffraction, Rietveld analysis, phase transition, amorphous, molecular dissociation]

1. Introduction

Tin tetraiodide is a molecular crystal with a cubic structure ($P\bar{a}3$) composed of tetrahedral SnI_4 molecules loosely bound to each other. Early high-pressure experiments on this compound demonstrated that SnI_4 underwent a gradual insulator-to-metal transition above 7 GPa [1] and exhibited an unusually large compressibility [2]. A new aspect of structural stability of a molecular crystal was disclosed by an x-ray diffraction study on SnI_4 by Fujii *et al.* [3]; they reported a reversible crystalline-to-amorphous transition between 10 and 20 GPa. A subsequent Raman study [4] showed that this transition is indeed accompanied by a disappearance of intermolecular modes. Since then high-pressure metallic amorphous SnI_4 has been the subject of extensive studies [5-7]. A similar reversible crystal-to-amorphous transition was also observed in SnBr_4 [8] and GeI_4 [9].

In this high-pressure study of SnI_4 we focus our attention on the following two points. One is the disordering process of the crystalline phase. Despite of extensive high-pressure works on SnI_4 , a structure model of the amorphous state is not unified yet. Sugai [4] proposed a formation of $(\text{SnI}_4)_2$ dimers based on his Raman study, Pasternak and Taylor [5] proposed the model of randomly oriented SnI_4 chains based on Mössbauer study, and from their XAFS measurement Wang and Ingalls [7] suggested a structure in which distorted and rotated SnI_4 molecules were arranged so as to form smaller tetrahedral units of I atoms. In this context, it would be worth re-examining whether or not SnI_4 molecules are dimmerized, distorted or rotated in the crystalline phase and how the long-range order disappears with increasing pressure.

The other interest is in stability of the amorphous state. SnI_4 is known to keep the amorphous state to the maximum pressure reached in the previous studies, 33 GPa, at room temperature [3]. In the same paper, Fujii *et al.* pointed out that, analogous to iodine, further compression of SnI_4 would destroy the molecule and result in a crystalline form with a simple lattice. In order to search for a post-amorphous phase and the possibility of molecular dissociation, the structure of SnI_4 has been studied up to 153 GPa.

Here we report the results of synchrotron x-ray powder diffraction measurement on SnI_4 at high pressures. We document the presence of a new crystalline phase prior to the amorphization and a phase transition from the amorphous state to a molecular-dissociated crystalline phase.

2. Experiment

A commercial polycrystalline SnI_4 of 99.9% purity was sublimated at 105°C in vacuum. Resulting crystals were ground into fine powder, placed in a cavity drilled in a T-301 stainless steel gasket and loaded into a diamond anvil cell in an argon atmosphere. Four separate experiments were carried out at room temperature. In one experiment dedicated to precise determination of atomic displacements in the cubic phase, a mixture of normalpentane-isopentane was used as a pressure medium. No pressure medium was used in the other three experiments, in one of which gold powder was mixed with the sample as an internal pressure marker in a pressure range from 70 to 153 GPa. We employed the ruby fluorescence technique below 70 GPa [10]. At higher pressures the lattice constant of gold was used to determine pressure with the aid of the equation of state given by Anderson *et al.* [11]. Synchrotron x-ray diffraction measurements were carried out at BL6B and BL18C of the Photon Factory at KEK. The white x-ray beam was monochromatized with Si(111) double crystals to an energy of 18, 20 or 24 keV. Diffraction patterns were collected with an imaging plate detector. Details of the experimental apparatus and techniques were described elsewhere [12].

3. Results and Discussion

All of diffraction patterns of the $P\bar{a}3$ phase analyzed with the Rietveld technique using the program RIETAN [13] were measured in the experiment with the pressure transmitting fluid. Figure 1 shows a Rietveld refinement profile for the data obtained at 6.6 GPa, the maximum pressure to which the $P\bar{a}3$ phase was observed. Although the normalpentane-isopentane mixture froze at 6.2 GPa, diffraction peaks remained very sharp at 6.6 GPa,

Fig. 1. Rietveld refinement plot for the $P\bar{a}3$ structure measured at 6.6 GPa.

Fig. 2. Pressure dependence of the *intramolecular* and *intermolecular* distances between iodine ions. In the $Pa\bar{3}$ structure, the I ions occupy two independent atomic sites with different site symmetries, I(1):8c and I(2):24d. Solid triangles and open squares denote the intramolecular I(2)-I(2) and I(1)-I(2) distances respectively. Other symbols denote three, nearest *intermolecular* I-I distances.

indicating good homogeneity of pressure applied to the sample. Resulting values of the goodness-of-fit parameter, R_{wp}/R_c , are in a range of 0.82 to 1.8. From least-squares fitting of the volume data to the Vinet equation of state, we obtained a bulk modulus of $K_0 = 6.1 \pm 0.2$ GPa and its pressure derivative of 7.6 ± 0.3 at a fixed V_0 of $1847 \text{ Å}^3/\text{unit cell}$. Those values indicate that SnI_4 is as compressive as I_2 .

Figure 2 shows a pressure variation of *intramolecular* and *intermolecular* I-I distances calculated from measured atomic positions. As seen in Fig. 2, the *intramolecular* I-I distance decreases only slightly with increasing pressure. Similarly, the Sn-I distance was observed to change a little from $2.65 \pm 0.01 \text{ Å}$ at 1 atm to $2.63 \pm 0.05 \text{ Å}$ at 6.6 GPa, being consistent with the XAFS result [7]. The covalent bonded SnI_4 molecules are rigid and not distorted in the $Pa\bar{3}$ structure. On the other hand, the *intermolecular* I-I distance decreases remarkably but monotonically from $4.317 \pm 0.008 \text{ Å}$ at 1 atm to $3.69 \pm 0.05 \text{ Å}$ at 6.6 GPa. Such a large contraction due to weak van der Waals bonding is a common feature to molecular crystals. Consequently, in the $Pa\bar{3}$ structure we find no line broadening of diffraction peaks, no indication of distortion nor dimerization of molecules and hence no precursor of the structural disordering.

When the pressure was raised above 7.2 GPa, there appeared several new diffraction peaks, as shown in Fig. 3, which can not be indexed with the $Pa\bar{3}$ structure. Two dominant new peaks are located at $2\theta \sim 14^\circ$. They grew with increasing pressure, while the original 222 reflection became weaker. The reverse transition was observed at 5.4 GPa upon decompression from 9.3 GPa. Clearly, this is a phase transition to another crystalline phase. It should be noted that Sugai [4] already reported this crystalline-to-crystalline transition. He observed the growth of a new A_g peak with a frequency lower than that of the original

Fig. 3. Diffraction patterns showing a phase transition from the $Pa\bar{3}$ phase (a) to a new crystalline form (b). Two phases coexist at 8.3 GPa.

A_g mode above 9 GPa and the coexistence of them until the original mode disappeared at 13 GPa. The lack of observation of this transition in the previous x-ray study [3] seems to be due to the unresolvable overlap of many diffraction peaks broadened by inhomogeneous pressure distribution in a sample cavity. Although we are yet unable to interpret the results of Mössbauer and XAFS measurements consistently with the present result, the agreement of the transition pressure of 7.2 GPa with the onset pressure of the decrease in electrical resistivity, 7 GPa [1,3], strongly suggests that this structural transition is an insulator-to-metal transition.

The compression of SnI_4 above 10 GPa was carried out in the experiments without a pressure medium. In this non-hydrostatic condition, the crystalline-to-crystalline transition took place between 7.6 and 9.7 GPa. A broad halo scattering appeared around $2\theta \sim 14^\circ$ at 15 GPa, where two crystalline phases still coexisted. Above 24 GPa, only the halo scattering typical of amorphous materials was observed. The amorphous state transformed into the third crystalline phase at 61 GPa, as shown in Fig. 4. Observed reflections can be indexed only with the fcc lattice with a lattice constant of $4.248 \pm 0.002 \text{ Å}$. Assuming the fcc structure, the nearest interatomic distance is calculated

Fig. 4. Diffraction patterns showing a phase transformation from the amorphous state (a) to the third crystalline phase (b). Diffraction lines are indexed with the fcc structure.

to be 3.003 ± 0.001 Å, which is considerably shorter than the intramolecular I-I distance of 4.32 Å at 6.6 GPa. This fact can be taken as evidence for the occurrence of pressure-induced molecular dissociation in SnI_4 .

The third crystalline phase persists to the maximum pressure reached in this study, 153 GPa. No extra reflections from the sample were observed throughout the compression. When the pressure was reduced, this phase transformed to the amorphous state at 30 GPa with a large pressure hysteresis. Finally, the original crystalline phase recovered at 0.3 GPa. The second crystalline phase was not observed upon decompression.

The observed fcc-like diffraction pattern of the third phase can be interpreted by the following three structure models; (a) phase separation into I_2 and amorphous Sn or into I_2 and amorphous SnI_4 , (b) full-disorder structure in which both the I and Sn atoms randomly occupy the fcc-lattice sites, and (c) partial-disorder structure, in which the I atoms are located at the fcc-lattice sites and the Sn atoms are randomly distributed at interstitial sites of the fcc lattice. We found that the P-V relation of the third phase coincides with that of the pure iodine [14] with the fcc structure over a pressure range of 60 to 153 GPa within a precision of $\Delta V/V \sim 0.025$. This similarity gives negative support to model (c) because the partial-disorder structure having the density much larger than the fcc iodine must be less compressible. It seems quite difficult to distinguish models (a) and (b) by an x-ray diffraction measurement. Observation of the local structure around the Sn atoms is crucial to determine the crystal structure of the third phase.

In summary, the present high-pressure x-ray diffraction study shows a rich sequence of structural transitions in SnI_4 . A newly found crystalline phase is responsible for metallization and amorphization. Determination of this new structure is important in understanding a mechanism of the disordering process. Also shown is a phase transition from the amorphous state to a molecular-dissociated crystalline phase. Although this structure appears to be simple, further experimental studies are required to clarify atomic arrangement in it.

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