Structural change in liquid SnI$_4$ under high pressure

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Abstract. Structure of the liquid forms of tin tetraiodide, SnI$_4$, has been studied at high pressure and high temperature by synchrotron x-ray diffraction experiment. Using a new sample container, we managed to collect diffract data with much better quality than before. The presence of two different liquid forms was verified. The structural change between these two liquid forms is expected to take place in a very narrow pressure range between 1.35 GPa at 850K and 2.03 GPa at 1000K.

1. Introduction

The discovery of the phase transition between the low and the high density amorphous forms in ice established the presence of polymorphism in a disordered state[1]. Since then, polyamorphism in solids and liquids has been subjected to extensive theoretical and experimental studies[2]. A pressure-induced first order phase transition in a one-component liquid system was discovered in black phosphorus[3,4]. It has been considered that a maximum of the melting temperature with increased pressure is originated from the occurrence of distinct two liquid forms[5]. In black P, the melting curve having a positive and steep initial slope breaks sharply at $\sim$1 GPa and exhibits a gentle ascent at higher pressures.

Tin tetraiodide is a crystal consisting of tetrahedral SnI$_4$ molecules. This compound has the melting curve with a break point at $\sim$ 1.5 GPa and $\sim$920 K and its overall shape is very similar to that of black P[6]. This motivated us to search for structural change in the liquid form under pressure and lead us to the finding of different structures existing below 0.7 GPa and above 1.8 GPa[7]. We also observed that, unlike black P, the profile of structure factor measured for the low pressure liquid(LPL) form does not change drastically after transformation to the high pressure liquid(HPL) form. To discuss such subtle changes in the liquid structure of SnI$_4$ quantitatively in further detail, obtaining diffraction data with much better quality than those shown in Ref.[7] is crucial.

In this paper we report the results of synchrotron x-ray diffraction study of liquid SnI$_4$ at high pressure and high temperature using a newly developed sample container. The new container allowed us to collect good diffraction data including only scattering from the sample. We show that the transformation from the LPL to the HPL forms occurs in a very narrow pressure range.
2. Experiment

We carried out synchrotron x-ray diffraction measurements at AR NE5C at the Photon Factory, KEK using an energy-dispersive technique and MAX80, a cubic anvil press. A sample was placed in the center of a 9 mm-edge cubic cell made of a mixture of boron and epoxy resin. A graphite tube heater and a thermocouple were also assembled. We chose a sleeve made of single crystal diamond with 2.0 mm outer diameter, 0.5 mm inner diameter and 1.0 mm height as a sample container, as shown in figure 1. The diamond sleeve was sandwiched by a diamond disk at the bottom and a pyrolytic boron nitride disk at the top. Both disks were 2.0 mm diameter and 0.2 mm thick in size. A cylindrical bore in the sleeve was half filled with a pulverized sample of SnI₄ first. Then a movable diamond piston with 0.5 mm diameter and 0.2 mm thick was put into the bore to prevent the sample from mixing with a pressure marker of NaCl, which was loaded last. All the sample preparation was made in an argon atmosphere to avoid the reaction of the sample with water in air.

Because diamond remains practically rigid in a pressure range covered in this study, compressive force can be transmitted to the sample by only deformation of pyrolytic boron nitride disk. Although this yields pressure gradient inside the hole upon compression, the internal pressure was observed to become uniform at high temperatures above 600K. This was confirmed by a preliminary in-situ measurement in which a small amount of NaCl was also loaded in the sample side. The diamond container was successfully used in this study and often allowed us to continue measurements more than a couple of ten hours.

Typical size of the incident x-ray beam was 0.05 mm in height and 0.2 mm in width. X-ray diffraction patterns were collected at several diffraction angles between 3° and 16° as a function of photon energy at a given P-T condition. The structure factor $S(Q)$ was constructed as a function of wave number $Q$ from those diffraction data using a procedure similar to that developed in Ref. [8].

Figure 1. Schematic drawing of the cross section of a sample container for x-ray diffraction measurement of liquid SnI₄ developed in this study. A diamond piston, 0.5 mm diameter and 0.2 mm thick, can be slid in the bore of a diamond sleeve.

Figure 2. Typical example of measured diffraction patterns of the LPL of SnI₄ at 0.94 GPa and 850K at several angles indicated. Patterns are entirely free from contamination with diffraction peaks from materials surrounding the sample.
3. Results and Discussion

Figure 2 illustrates typical diffraction patterns measured at several diffraction angles indicated in the figure. By the use of the diamond container, we were able to obtain clear diffraction patterns consisting of only scattering from a liquid sample. Strong characteristic x-rays and the K-absorption edge of the sample itself appear below ~35 keV.

Figure 3 shows the structure factors constructed from diffraction patterns measured at P-T conditions indicated. The structure factor illustrated at the bottom is for liquid SnI$_4$ at 1 atm and taken from Ref.[9] for comparison. We can distinguish two different liquid structures on the basis of following features of $S(Q)$. First, the oscillation on the larger wave number side is well developed at 1 atm, 0.94 GPa and 1.35 GPa, while it is considerably damped at higher pressures. This oscillation arises from intramolecular interference term; therefore, we can expect the LPL form stable below 1.35 GPa to have the SnI$_4$ molecules as a structural unit. Let us refer the liquid structure above 2.03 GPa to as HPL. Secondly, only the fourth peak exhibits an anomalous pressure dependence of its position. When a simple liquid is uniformly compressed, all peaks in $S(Q)$ will shift to the larger wave number side with increasing pressure. In the present case, the forth peak stays at an almost constant wave number in the LPL conditions; 7.57 Å$^{-1}$ at 1 atm, 7.52 Å$^{-1}$ at 0.94 GPa, 7.49 Å$^{-1}$ at 1.35 GPa. Those values were obtained by fitting the data near the maximum position to parabola. An increase of ~0.7 GPa forces the fourth peak to shift abruptly to smaller wave number; 7.11Å$^{-1}$ at 2.03 GPa, 7.10 Å$^{-1}$ at 2.22 GPa. Other peaks behave normally by compression. The breakdown of the tetrahedral molecules in the HPL state may be inferred from those results. It should be mentioned at this point that the shift of the fourth peak toward the low wave number side has been detected at 1.8 GPa, 970 K [7], although the quality of their $S(Q)$ is poor owing to the use of a boron nitride sample container. It is highly desirable to re-examine $S(Q)$ at around the condition with this newly designed sample container.

Direct information about the breakdown of the molecule can be obtained from the reduced radial distribution function $G(r)$, calculated from $S(Q)$ by Fourier sine-transform. The results are shown in figure 4. The vertical line at 2.65 Å in the figure indicates the distance, $r_{\text{Sn-I}}$, between the tin and iodine

\textbf{Figure 3.} Experimental structure factors for the LPL form of SnI$_4$ at 1 atm, 0.94 GPa, 1.35 GPa and for the HPL form at 2.03 GPa and 2.22 GPa. Thermodynamic conditions for each measurement are indicated.

\textbf{Figure 4.} Reduced radial distribution functions for the LPL form of SnI$_4$ at 1 atm, 0.94 GPa, 1.35 GPa and for the HPL form at 2.03 GPa and 2.22 GPa. Lines at 2.65 Å and 4.33 Å indicate the distances between tin and iodine atoms, $r_{\text{Sn-I}}$, and iodine atoms, $r_{\text{I-I}}$, in the molecule, respectively.
atoms in the tetrahedral molecule and the line at 4.33 Å corresponds to the distance, $r_{I-I}$, between iodine atoms, that is, the edge length of the tetrahedron. It is clear that the tetrahedral molecules exist in the LPL structure below 1.35 GPa. Note that the shoulder peak in $G(r)$ at ~3.5 Å grows up with increased pressure. This indicates an increase in intermolecular I-I correlation for the vertex-to-face orientation of tetrahedral molecules[7] with densification of the liquid structure.

In the HPL form, the Sn-I distance elongates and the average I-I distance shortens, suggesting the occurrence of deformation of the molecules. The ratio $\sigma = r_{I-I} / r_{Sn-I}$ is a good parameter to measure the degree of deformation from the ideal tetrahedron with $\sigma = (8/3)^{1/2} = 1.63$. Experimentally obtained values of $\sigma$ are as follows; 1.64, 1.60, 1.57, 1.46, 1.38 in the order of increased pressure. From these results, we speculate that the HPL structure is characterized by the polymerization of heavily deformed SnI$_4$ molecules, which still have anisotropic chemical bonds.

4. Conclusion

We managed to collect clear x-ray diffraction data for liquid SnI$_4$ under pressure by the use of a diamond sample container newly developed. The presence of two different liquid forms was verified on the basis of the structure factors and the radial distribution functions constructed from the diffraction data. The structural change between these two liquid forms is expected to take place in a very narrow pressure range between 1.35 GPa at 850K and 2.03 GPa at 1000K. The new container allows us to locate the upper limit of the existence of the LPL at 1.35 GPa, thereby further narrowing the possible transition region than that reported in Ref. [7]. The new container will be used in the density measurement planned in near future.

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