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Abstract

In order to examine the pressure-induced structural change of liquid silver iodide (AgI), high-pressure and high-temperature *in situ* x-ray absorption fine structure (XAFS) and x-ray diffraction (XRD) studies have been carried out up to 1200 K and 6 GPa. The modifications in the x-ray absorption near edge structure (XANES) spectra and x-ray structure factors, $S(Q)$, with increasing pressure provide evidence for changes in the short-range order of liquid AgI. The I–Ag bond length in liquid AgI increases by compression up to 2 GPa, which proposes that components with higher coordination than fourfold are introduced. The I–Ag bond length decreases monotonically with compression above 2 GPa, indicating that the structural change involving a coordination-number change is completed below 2 GPa and then a high-pressure form of liquid AgI is stabilized. Comparing the I–Ag bond lengths of liquid AgI with those of crystalline phases, we conclude that the high-pressure form of liquid AgI has a rocksalt-like structure with large vacancies.

1. Introduction

Like those of crystalline phases, it has been proposed that structures of liquid phase change with pressure. Growing evidence for liquid polymorphism has come from experimental and theoretical studies [1–3], although liquid polymorphism was not considered seriously for a long time due to the absence of long-range structural order in the liquid phase. Recent synchrotron radiation studies have revealed a first-order liquid–liquid phase transition for phosphorus [4, 5]. Liquids with a locally tetrahedral molecular structure, such as SiO_2 and GeO_2, have possibilities for observing pressure-induced polymorphism [2]. However, direct structural studies have not been successful to date.
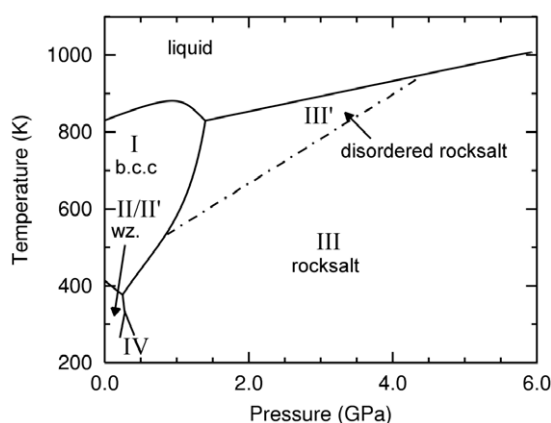
Figure 1. *P–T* phase diagram of AgI after [6–10]. The solid lines are the thermodynamic equilibrium phase boundaries, while the chained line indicates the approximate boundary between AgI-III and AgI-III′ [8–10].

AgI is one of the most promising candidates for observing pressure-induced liquid polymorphism. Figure 1 summarizes the *P–T* phase diagram of AgI reported so far [6–10]. As shown in figure 1, the melting curve of body-centred cubic (bcc) structured phase (AgI-I) has a temperature maximum at around 1.0 GPa. The melting curve with negative slope indicates, by the Clapeyron relation ($dT_m/dP = \Delta V/\Delta S$), the existence of a liquid phase that is denser than AgI-I [10]. Liquid polymorphism of AgI is also suggested by solid phase relations of AgI. AgI has both ionic and covalent bonding character and ionicity of 0.770 on the Phillips scale [11], hence a large number of pressure-induced polymorphisms are possible. At room temperature and room pressure, two fourfold coordinated phases exist in AgI: AgI-II with wurtzite structure and AgI-II′ with zincblende structure. On room-temperature compression, AgI shows a structural phase transition from fourfold coordinated structure (AgI-II or AgI-II′) to sixfold coordinated structure (rocksalt structured phase AgI-III). With increasing temperature at room pressure, it transforms to AgI-I and then melts. Since the disordered rocksalt phase (AgI-III′) or AgI-III melts at pressures above 1.5 GPa, the liquid AgI would undergo a structural change corresponding to the solid state transformation from fourfold to sixfold coordinated structure.

There have been only a few structural studies on liquid AgI under pressure. Previous x-ray absorption fine structure (XAFS) measurements for liquid AgI up to 1.8 GPa report a frequency shift of the XAFS signal towards lower frequency with pressure, in a rough approximation, which corresponds to the shortening of the I–Ag bond length [12]. However, quantitative analysis was not carried out and the details of the pressure-induced structural change of liquid AgI have never been examined precisely. In this study, we have performed *in situ* XAFS and x-ray diffraction (XRD) measurements on liquid AgI up to 6 GPa and 1200 K using a cubic-type multi-anvil high-pressure apparatus and synchrotron radiation in order to investigate the pressure-induced structural change of liquid AgI.

2. Experimental details

Polycrystalline AgI powder with a nominal purity of 99.99% was provided by Furuuchi Chemical Co. (Tokyo, Japan). The powder was finely ground and mixed with BN powder to dilute the sample. The ratio of AgI and BN was 1:6 and 1:1 in weight ratio for XAFS and XRD measurements, respectively. The mixture was charged in a BN sample chamber.

The chamber was put between a pair of graphite-disc heaters and encased in a cubic-shaped pressure-transmitting medium made of boron-epoxy resin. Details of the high-pressure cell assembly have been described elsewhere [13].

XAFS measurements were performed on a bending magnet beamline, BL14B1, at the SPring-8. High-pressure and high-temperature conditions were generated using a cubic-type 180 ton apparatus, SMAP2 [14], installed on the beamline. The generated pressure was determined using a pressure-load calibration curve based on a NaCl pressure marker [15] with an uncertainty within 0.5 GPa. Temperature was monitored with a W97Re3–W75Re25 thermocouple inserted between the two graphite-disc heaters. The temperature fluctuation was within ±1%. The effect of pressure on the thermal electromotive force was neglected.

XAFS spectra near the I K-edge were recorded using the transmission mode. The x-ray beam was monochromatized by a Si(111) double-crystal monochromator and focused vertically by two millers. The beam size was 0.2 mm in the vertical direction and 0.3 mm in the horizontal direction. The intensities of the incident and transmitted beam were measured by ionization chambers filled with pure Ar and pure Kr gases, respectively. XAFS spectra were collected up to 1200 K and 6 GPa. The data acquisition time for one spectrum was about 20 min. The extended x-ray absorption fine structure (EXAFS) interference function was extracted from the measured x-ray absorption spectra using the standard procedure [16] and normalized using MacMaster coefficients [17]. For further quantitative analysis, the distance range of interest was filtered with a smooth filtering window, and transformed back to k-space. We carried out a nonlinear least-squares fitting method by comparing Fourier-filtered observed and calculated EXAFS interference functions. Parameter fitting was performed with an anharmonic potential model in single scattering theory with the cumulant expansion up to the third-order term [18]. Details on the EXAFS data analysis have been shown elsewhere [19].

Angular dispersive XRD data were collected on an undulator beamline, BL11XU, at the SPring-8. Samples of AgI put in the high-pressure cell were compressed using a cubic-type 180 ton apparatus, SMAP 180 [20], installed on the beamline. A monochromatized x-ray beam of 25 keV was collimated by slits to 0.1 mm height and 0.1 mm width. The diffracted x-ray beams were recorded using a multichannel collimator [21] and imaging plate with a typical exposure of 10 min. Further details of the XRD experimental procedure are described elsewhere [10]. We obtained an x-ray structure factor, $S(Q)$, of liquid AgI from the measured XRD pattern. The data analysis method has been given elsewhere [22].

3. Results and discussion

The $S(Q)$ obtained from XRD measurements for liquid AgI at 1000 K is shown for a series of pressures in figure 2. The $S(Q)$ for liquid CdTe at 0.5 and 3.0 GPa [22], which have zincblende-like and rocksalt-like local structures respectively, are also shown. The $S(Q)$ curve of liquid AgI at 1.4 GPa exhibits two discernible shallow peaks at 1.8 and 3.0 Å^{-1}. With increasing pressure, these two peaks depress and become weaker, whereas a new peak appears at 2.2 Å^{-1}. The variation of $S(Q)$ on compression is comparable to that of liquid CdTe. Overall features of $S(Q)$ for liquid AgI obtained at 1.4 GPa are similar to the $S(Q)$ for liquid CdTe at 0.5 GPa. On the other hand, the shape of the $S(Q)$ for liquid AgI obtained at 4.4 GPa is similar to that of liquid CdTe at 3.0 GPa. These similarities of $S(Q)$ between liquid AgI and liquid CdTe suggest that the short-range order in liquid AgI changes from a low-density form with zincblende-like local structure into a high-density form with rocksalt-like local structure under high pressure.

Since x-ray near edge structure (XANES) spectra are sensitive to the electronic states and three-dimensional atomic configuration around x-ray absorbing atoms, they are useful
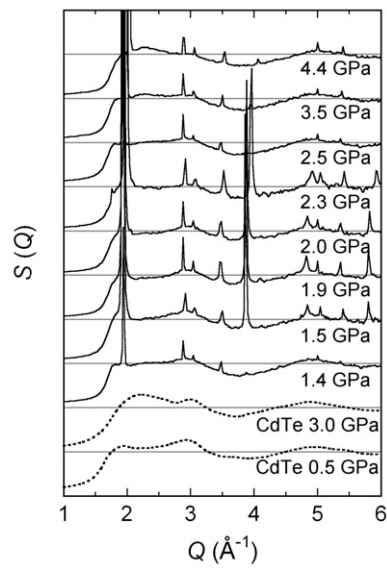
Figure 2. $S(Q)$ of liquid AgI at high pressures and 1000 K. The sharp peaks are Bragg reflections of BN mixed with sample. $S(Q)$ for liquid CdTe at 0.5 and 3.0 GPa [22] are also shown for comparison.
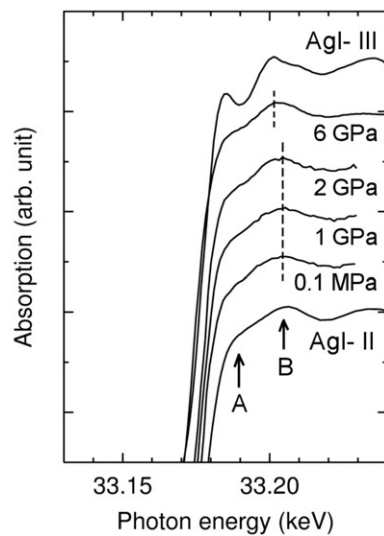

Figure 3. I K-edge XANES spectra of liquid AgI at 1000 K and 6, 2, 1 GPa and 0.1 MPa, together with those of AgI-II and -III. The arrows indicate the peaks A and B, as discussed in the text.

for determining the coordination environments of I atoms in liquid AgI. Figure 3 shows the pressure variation of XANES spectra of the I K edge in liquid AgI up to 6 GPa at 1000 K. The XANES spectra of AgI-II (fourfold) and AgI-III (sixfold) recorded under ambient conditions and 3 GPa and 300 K, respectively, are also shown in figure 3 for comparison. At 0.1 MPa, the edge features of the liquid AgI spectrum, which are characterized by the two peaks indicated
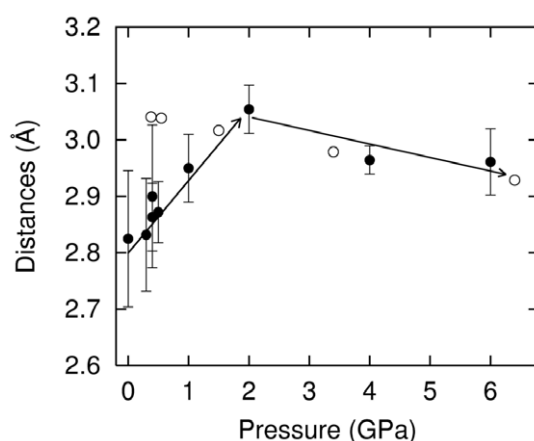
Figure 4. Pressure variation of the first-neighbour I–Ag bond lengths in liquid AgI at 1000 K (solid circles). For comparison, values of the rocksalt-structured phase AgI-III at room temperature [23, 24] (open circles) are also shown. The arrows are only a guide for the eye.

by the arrows A and B in the figure, are comparable to that of AgI-II. This result indicates that fourfold-coordinated I atoms are dominant at this pressure. The position of the main peak (arrow B) is almost unchanged up to 2 GPa, whereas it shifts to lower energies and the relative intensities of peaks A and B change close to the pattern of the AgI-III spectrum at 6 GPa. The observed change of the XANES spectra implies that liquid AgI has two distinct local structures within the present experimental pressure regime.

The pressure variation of the I–Ag bond length reveals the details of the pressure-induced structural change of liquid AgI. Figure 4 shows the pressure variation of the first-neighbour I–Ag bond lengths in liquid AgI at 1000 K derived through the EXAFS analysis. The I–Ag bond lengths in AgI-III at room temperature [23, 24] are also shown. At 0.1 MPa, the I–Ag bond length in liquid AgI is 2.82 Å, the value of which is slightly larger than that of AgI-II under ambient conditions (2.81 Å). This result indicates that the local structure of liquid AgI at 0.1 MPa is a fourfold-coordinated structure. On compression, the bond length increases up to 2 GPa and then decreases monotonically with pressure. Generally, the inter-atomic bond length decreases with increasing pressure. As shown in figure 4, however, the I–Ag bond length in liquid AgI increases by compression up to 2 GPa, which indicates that components with higher coordination are introduced. Because the I–Ag bond length decreases with compression above 2 GPa and the bond lengths between 2 and 6 GPa are comparable to those in AgI-III under room-temperature compression, we conclude that the structural change involving coordination-number change is completed below 2 GPa and then a high-pressure polymorph of liquid AgI is stabilized. It should be noted that the structural change of liquid AgI occurs in a narrow pressure range of about 2 GPa, which is consistent with the results of other ionic liquids such as CdTe [22].

To estimate the local structure of the high-pressure form of liquid AgI, we compare the I–Ag bond length of liquid AgI with that of the crystalline phase. The observed bond lengths of liquid AgI between 2 and 6 GPa are almost comparable to those of AgI-III at room temperature [23, 24]. However, considering the thermal expansion of the I–Ag bond length in AgI-III at high temperature, the bond length in corresponding liquid AgI is most probably shorter than that of AgI-III just below the melting temperature. Figure 5 shows the temperature variation of the first-neighbour I–Ag bond lengths at 6 GPa derived by the EXAFS analysis.
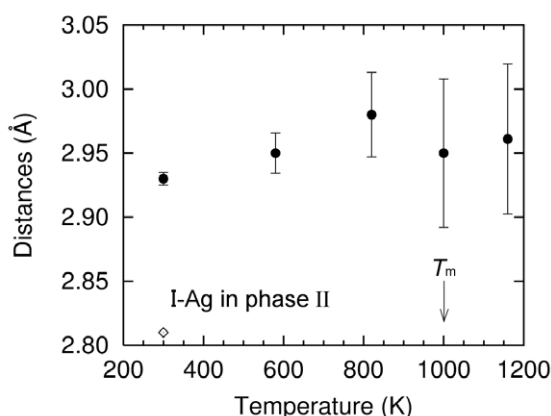
Figure 5. Temperature variation of the I–Ag bond length in AgI at 6 GPa. T_m is the melting temperature of 1000 K for AgI at 6 GPa. The open diamond indicates the I–Ag bond length in phase AgI-II under ambient conditions.

The I–Ag bond length at 6 GPa and 300 K is 2.930(5) Å and in good agreement with that obtained through x-ray diffraction studies [24]. The I–Ag bond length elongates with increasing temperature up to the melting point (1000 K at 6 GPa) [10] and shortens when the sample melts. Based on the difference in I–Ag bond lengths between solid and liquid at 6 GPa, two interpretations can be proposed for the coordination environment of the high-pressure form of liquid AgI. One is that the high-pressure form of liquid AgI consists of a rocksalt-like structure with large vacancies, which has been proposed by Urakawa *et al* [25] for liquid NaCl under pressure using an energy dispersive XRD method. The other interpretation is that the high-pressure form of liquid AgI consists of a mixture of fourfold and sixfold coordination. However, Hattori *et al* [22] reported that two species are not preferable in ionic liquids because the formation of the different bonds causes a marked increase in the potential energy of the system. Accordingly, the coordination changes of ionic liquids are relatively sharp. On the basis of these previous studies, a mixture of fourfold and sixfold coordination is unstable, and it seems reasonable to conclude that the high-pressure form of liquid AgI has a rocksalt-like structure with large vacancies and the average coordination number of the I atom is smaller than six.

4. Conclusions

Liquid AgI has been compressed up to 6 GPa and its short-range order has been examined using *in situ* XAFS and XRD measurements. A structural change in liquid AgI occurs in a pressure range between 0.1 MPa and 2 GPa, whereupon a high-pressure form of liquid AgI is stabilized. The local structure of liquid AgI at 0.1 MPa has a zincblende-like structure characterized by fourfold-coordinated I atoms. The high-pressure form of liquid AgI has a rocksalt-like structure and the average coordination number of I atoms is smaller than six.

Acknowledgments

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