Solid methane behaviours under high pressure at room temperature

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Abstract. High pressure behaviours of solid methane were examined in a pressure range of 0.5 GPa to 86 GPa at room temperature using diamond anvil cell. In-situ X-ray diffractometry and Raman spectroscopy revealed existence of two high pressure phases above 35 GPa. The Raman spectra showed clear peak splitting and appearance of new vibration modes at 35 GPa and 62 GPa. The XRD patterns of the high pressure phases were basically similar to those of the known phases B and HP. These results indicate that the observed high pressure phases have a similar fundamental structure but have different molecular orientations. In addition, an intermediate metastable phase was found between phases A and B. This phase can be thought as that: the configuration of the methane molecules almost attains as that in phase B, and the rotation of molecules still remains as that in phase A.

1. Introduction

Solid methane exhibits a wide variety of phases due to molecular orientational ordering. Many phases with different molecular orientations were reported in low temperature region [e.g. 1-5]. After that, also in high pressure region at room temperature, X-ray diffractometry using synchrotron radiation and Raman spectroscopy revealed phase changes as follows. Fluid methane crystallizes to phase I (cubic) at 1.7 GPa [6,7], phase I transforms to phase A (rhombohedral or tetragonal) at 5.2 GPa [3,8,9], phase A to phase to B (cubic or hcp) at 10-18 GPa [3,10], phase B to a high-pressure phase (HP) (cubic or hcp) at 25 GPa [4,10], HP retains at least up to 37 GPa [10]. Recently, an optical study made up to 288 GPa reported change of refractive index suggesting insulator-semiconductor transformation [11]. Under high temperatures and high pressure, a few shock compression studies reported dissociation of the methane molecule to form diamond at 20 GPa and 2000 K [12], while a theoretical study predicted polymerization of solid methane to produce ethane and propane at 100 to 300 GPa and 4000 K rather than dissociation of the methane molecule [13]. An experiment using laser-heating diamond anvil cells observed the formation of both polymerized hydrocarbons and diamond at 19 GPa and 2000 to 3000 K [14]. Thus, solid methane behaviours under high pressure have not yet been clarified both at room temperature and high temperatures.

In this study high pressure experiments at room temperature of solid methane were carried out using combined Raman spectroscopy with X-ray diffractometry (XRD), and existence of another two high-pressure phases were shown above 35 GPa. And, an intermediate metastable phase was found.
between the known phase A and phase B. The nature of the intermediate phase was discussed in relation to the sluggish transition between phases A and B.

2. Experimental

A lever-and-spring type diamond anvil cell was used in the high-pressure experiments. The ruby fluorescence method was used for the pressure measurements. The accuracy of the present measurement system is 0.1 GPa, taking the resolution of the spectrometer and the analytical procedure into account. The samples of methane were filled into the gasket hole by a gas loading vessel in which methane gas (99.99%) was compressed to supercritical fluid at approximately 0.15 GPa at room temperature (Critical point of methane is 190.6K, 4.60MPa, so the filling condition is above the point). The XRD study was performed using synchrotron radiation on BL-18C and BL-13A at the Photon Factory, High Energy Accelerator Research Organization (KEK). A monochromatized beam with a wavelength of 0.6198 Å was used. XRD and Raman studies and optical observations were conducted for twelve samples at room temperature in a pressure range from 0.5 to 86 GPa.

3. Results

Figure 1 shows a series of optical micrographs with pressure change. The microscopic observation detected crystallization from fluid at 1.7 GPa and the transition at 5.2 GPa. Above the pressure range up to 86 GPa any transition or change in refractive index was not observed with increasing and decreasing pressure by a conventional optical observation (Figure1). The XRD study confirmed crystallization to phase I (fcc) at 1.7 GPa and the transition from phase I to phase A (rhombohedral) at 5.2 GPa. The transition from phase A to B was very sluggish as reported before [2,3]. The process of the transition was traced by peak splitting of a C-H symmetric stretching mode of the methane molecule, $\nu_1$, in the Raman spectra as reported previously by IR spectroscopy [3]. After confirming completion of the A-B transition by Raman and XRD, higher pressure was loaded to the samples. Figure 2(a) shows changes in XRD patterns with pressure after the A-B transition. In the XRD patterns of phase B, five distinct diffraction lines were observed, which agreed with the previous XRD study [10]. The XRD lines were indexed as a simple cubic system with a lattice parameter of $a=8.047\quad\ang$ at 17.4 GPa using a software indexing XRD pattern, LTC. Deviations between the observed d-values and the calculated ones were very small within 0.1 %. At higher pressures above the A-B transition, the diffraction patterns were basically unchanged up to 86 GPa, so the XRD patterns were also indexed as the same simple cubic lattice. But, above 63.5 GPa, several diffraction lines shift slightly to lower angle, comparing with the continuous shift of those from Re gasket to higher angle (Figure 1(a)). The result suggested some structural change at approximately 62 GPa. Fig. 2(b) shows variation of volume as the simple cubic lattice with pressure change. In the figure 2(b), changes in slope of volume with pressure were not clearly distinguished at approximately 35 GPa and 62 GPa. That is similar to that of the B-HP transition at 25 GPa reported by Umemoto et al. [10]. On the other hand, distinct changes were observed by Raman spectroscopy at these pressures, as described below.
Raman spectra of C-H symmetric stretching modes of methane molecules, $\nu_1$ and $\nu_3$, with pressure change are given in Figure 3(a, b). The variations in the Raman frequency shift of these vibration modes with pressure change are shown in Figure 3(c). Peak splitting and changes in peak intensities were clearly observed at approximately 35 GPa and 62 GPa in Figure 3(a, b). The changes of each peak were easily traced throughout the pressure range in Figure 3(c). In addition, changes in slope of the Raman frequency shift with pressure were distinguished at 25 GPa, 35 GPa and 62 GPa. All changes observed in increasing pressure reverted in decreasing pressure. Above phase B, the transitions proceed in a relatively shorter time than the A-B transition.

The transition from Phase A to B was sluggish. At 17.4 GPa the transition started 4 hours after the pressure had reached this value and the transition was completed after 10 hours. In the case of 12.7 GPa, more than 10 hours and heating at about 330 K were necessary to accomplish this transition. The process of change had been detected by IR spectroscopy [3]. In this study, the process of change was tracked by XRD combined with Raman spectroscopy. The XRD study revealed the existence of an intermediate phase, or rather, a “state”, having another diffraction pattern different both from phase A and phase B. This phase is tentatively referred to in this paper as phase pre-B. Figure 4 (a) shows the XRD patterns of phases A, pre-B and B. The diffraction pattern of phase pre-B was totally different from A, but rather related to that of phase B. Four diffraction lines were observed, which were indexed as a simple cubic system. The lattice parameter for phase pre-B was almost similar but a little smaller than that of phase B. The diffraction lines that appeared and their intensities were different from those of phase B. This indicated that the fundamental structure of phase pre-B is similar or closely related to that of phase B. The transition from phase A to pre-B occurred within a short time, approximately one hour after increasing pressure; on the other hand, the transition from phase pre-B to B was sluggish, as described above. During peak splitting observed in Raman spectra (Figure 4 (b)), both diffraction patterns of phase pre-B and B were superimposed. At the completion of the transition, only the pattern of phase B was observed. When phase pre-B was compressed without transition to phase B, the diffraction patterns were basically unchanged up to 81 GPa, and the transition to phase B did not occur (Figure 5(a)). The Raman spectrum of phase pre-B showed a single peak each for $\nu_1$ and $\nu_3$, which was similar to that of phase A (Figures 4(b), 5(b)). This spectrum was retained up to 78 GPa without any peak splitting (Figure 5(b)).
4. Discussion

The phase changes of solid methane were observed at approximately at 5.2, 12-18, 25, 35, 62GPa in the present XRD and Raman studies. The former three changes correspond to the known ones as one from phase I to A, from phase A to B and from phase B to HP, respectively. Thus, existence of two additional high pressure phases above 35 GPa up to 86 GPa were revealed in this study. The phase above 25 GPa was previously named phase HP [3, 10], thus the high-pressure phases above 25 GPa were tentatively called HP1, HP2 and HP3 in the order of pressure in this paper (Figure 3(c)). The phase changes at 25 GPa, 35 GPa and 62 GPa were clearly recognized by the changes in the intramolecular vibration modes by Raman spectroscopy. On the other hand, by the X-ray diffractometry they were detected by the relatively slight changes such as the peak shifts at about 62 GPa. Therefore, the observed phase changes above phase B are thought to be caused by the changes in the state of the methane molecules accompanied by no fundamental structural change.

The determination of high-pressure structures has long been an issue [3-5, 10, 15]. The structure for phase I has been established [5], while different reports for structures above phase A exist. The detailed IR and Raman studies by Bini et al. demonstrated that the structure evolved from fcc (phase I) to hcp (phase B and HP) through a tetragonal system (phase A) [3, 4]. On the other hand, the XRD studies showed a rhombohedral structure for phase A [9] and a cubic structure for phases B and HP [10]. The XRD patterns we obtained for phases, B, HP1, HP2 and HP3 were similar to each other and they were indexed as the same simple cubic lattice. Thus, the fundamental structures, i.e. the positions of the molecules, of these phases are thought to resemble to each other. On the other hand, the intramolecular vibration modes were considerably different among these phases. The changes observed in Raman spectra from phase B to HP1, HP2 and HP3 can be interpreted as methane molecules showing different manners of orientational ordering in one phase to another in a similar fundamental structure.

As for the sluggish A-B transition, Bini et al. described, on the basis of their detailed IR studies, that complex reconstruction of molecules may be performed at the A-B transition, thus a prolonged
period of time is required for it [4]. In our study we found an intermediate metastable phase, pre-B, between phases A and B. The transition from A to pre-B was accomplished relatively quickly, unlike the transition from phase pre-B to B, which was very sluggish. The XRD pattern of phase pre-B was similar to that of phase B, indicating that the fundamental structure might be somewhat related to that of phase B. This means that broad configurations of methane molecules as phase B might already be built up at the state of phase pre-B, i.e., immigration of the molecules might be almost completed in a relatively short time span. A longer period might be required for the molecules to arrange themselves into suitable and stable orientations at each molecular position. The phase pre-B can be explained as follows: the configuration of the methane molecules almost attains as that in phase B, and the rotation of molecules still remains as that in phase A without establishing an orientation as observed in phase B.

Figure 4. (a) XRD patterns of phases of A, pre-B and B. (b) Raman spectra from phase pre-B to B.

Figure 5. (a) XRD patterns and (b) Raman spectra of phase Pre-B with pressure change.
The phase changes of solid methane are rather different from analogous materials such as solids CF₄ and CCl₄. Solid CF₄ transforms at 1.86 GPa from a rhombohedral structure to C2/n and at 2.86 GPa it goes to P2₁/c at room temperature [16, 17]. Solid CCl₄ transforms at 0.4 GPa from a rhombohedral or fcc structure to C2/c and at 0.7 GPa to P2₁/c [18, 19]. These phase changes of the analogous materials proceed at lower pressures. The high-pressure structures, monoclinic structures, differ from those of solid methane, although the lower-pressure structures, fcc and rhombohedral, are the same. Methane molecules are small and can be regarded as almost spherical in shape rather than the CCl₄ and CF₄ molecules. Electron negativities differ among these constituent atoms, which results in different multipole interactions among these tetrahedral-shaped molecules. Such differences in the chemical and physical properties of the methane molecule might lead to the different phase change behaviour from the analogous materials.

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