RAMAN AND XRD STUDY OF TYPE-I CLATHRATE $Ba_8Ga_{16}Ge_{30}$ UNDER HIGH PRESSURE

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Raman and synchrotron XRD study of clathrate compound $Ba_8Ga_{16}Ge_{30}$ have been performed under high pressures. A reversible phase transition was observed at 33 GPa, at which Raman and XRD peaks become weak and broad. The vibrations of guest Ba atoms encapsulated in the host cage structure formed with Ga/Ge were clearly observed up to 30 GPa by Raman measurements. An anomalous behavior of the Ba vibrational frequency suggests a change of the guest-host interaction at high pressure.

1. Introduction

Group IV elements are known to form clathrate compounds which consist of three-dimensional arrangements of nano-scaled polyhedrons including guest atoms (M) such as Ba, Na, and so on[1]. The most intensively studied clathrate is of the type I formulated with M_8IV_{46}. The group IV atoms can be partially replaced with III or V elements in order to compensate the excess or missing of charges of the guest atoms. The $Ba_8Ga_{16}Ge_{30}$, which belongs to type I structure, is one of the most intensively studied clathrate, because of its potential application for thermoelectric devices due to the behaviour of phonon-glass and electron-crystal (PGEC)[2,3]. The low thermal conductivity is attributed to the rattling vibration of the guest atoms, which weakly interact with the host cage. The guest-host interaction can be changed by reduction of the cage size, which is realized by pressurization. Since the guest vibration is influenced by the guest-host interaction, the high pressure study on the guest vibration is important for understanding the guest-host interaction. The direct measurement of the guest vibration can be carried out by Raman spectroscopy, as reported for various clathrates[4-7].

The guest-host interaction also contributes to a characteristic phase transition of various clathrates under high pressure[4,5,8,9]. San-Miguel et al. have observed a discontinuous volume reduction without any structural change at 15 GPa for Ba_8Si_{46}. This isostructural transformation has been commonly observed for various Si clathrates[8-10]. The transformation pressure depends strongly on the guest element, suggesting that the guest-host interaction plays an important roles for the isostructural transition.

In this paper, we present a systematic study of $Ba_8Ga_{16}Ge_{30}$ clathrate by means of Raman spectroscopy and synchrotron powder XRD measurements under high pressures up to about 40 GPa. As a result, we clearly observed the volume collapse transition at 33 GPa, and identified the transition to be reversible. At least up to 30 GPa, the clathrate structure was found to be maintained. The Raman spectra clearly showed the Ba guest vibrations (30-50 cm^{-1}) as well as the host cage vibrations (>50 cm^{-1}) up to 30 GPa. The unusual behaviour of guest vibration, which takes a maximum frequency around 20 GPa, suggests a change of the guest-host interaction.

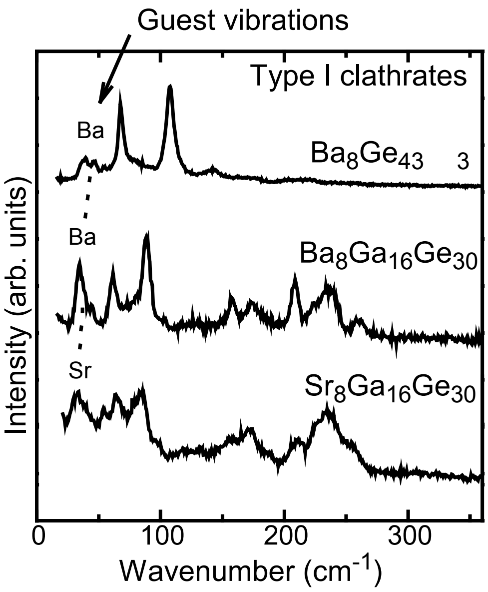

Fig. 1 Raman spectra of Ge based clathrates at 1 atm.

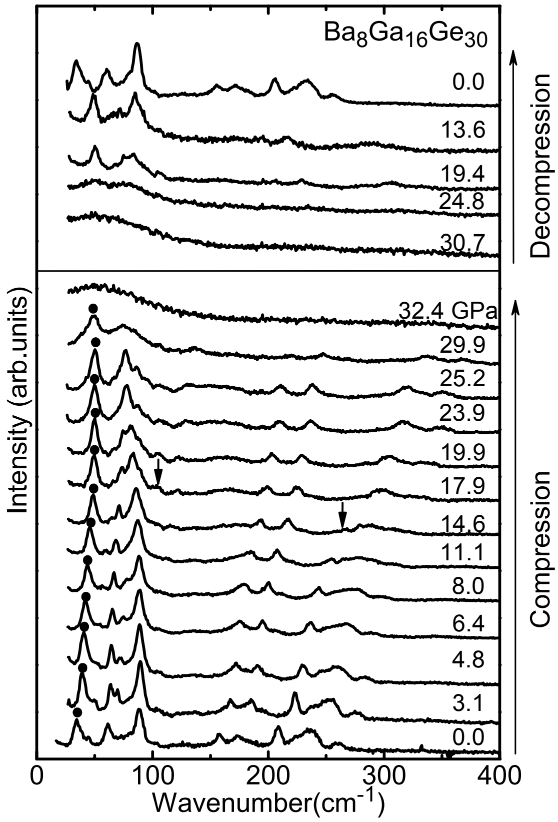

Fig. 2 Pressure dependence of Raman spectrum of $Ba_8Ga_{16}Ge_{30}$. The lower and upper panels correspond to compression and decompression processes, respectively. The lowest frequency peaks denoted with solid circles correspond to Ba vibrations.

2. Experimental

$Ba_8Ga_{16}Ge_{30}$ samples were prepared by Ar arc melting. After arc melting, specimens were annealed at 790 °C in vacuum for 12 h followed either by oil quenching or by furnace cooling. Details for the sample preparation are described elsewhere[3]. High pressure experiments were carried out by using a diamond anvil cell (DAC) with a metal gasket. The hole made by drilling the metal gasket serving as the sample chamber was set to about 100 μm in diameter and 50 μm in thickness. A single-phase sample of 40 μm in size was placed into the chamber of the DAC with a ruby chip for pressure measurements. For fine Raman measurements, we used the dense argon as the pressure-transmitting medium that is free from Raman signals[4-6].

Raman spectra were measured with a triple polychromator and a charge-coupled device (CCD) detector. The 532 nm line of a solid laser (Coherent Verdi2W) with its intensities of less than 10 mW was used for the excitation. The resolution of the Raman spectra was about 1 cm^{-1}.

To make the powder XRD measurements, the sample of $Ba_8Ga_{16}Ge_{30}$ was ground to fine powder, and the powder and a ruby chip were put into the sample chamber of DAC which was prepared in the same manner as that for Raman measurements. The pressure medium was dense argon or helium. Synchrotron powder XRD measurements were carried out with an imaging plate detector installed at the BL10XU beam line of the SPring-8. The wavelength of the incident x-ray was 0.04136 nm. The exposure time for obtaining the diffraction pattern was typically 3 min.

3. Results and Discussion

Figure 1 shows Raman spectra of $Ba_8Ga_{16}Ge_{30}$ obtained for atmospheric pressure. For comparison, the results of Ba_8Ge_{43}, and $Sr_8Ga_{16}Ge_{30}$ are also shown in this figure. The Raman band located below 50 cm^{-1} are due to the rattling vibration of the guest Ba or Sr in the large cage[7]. The

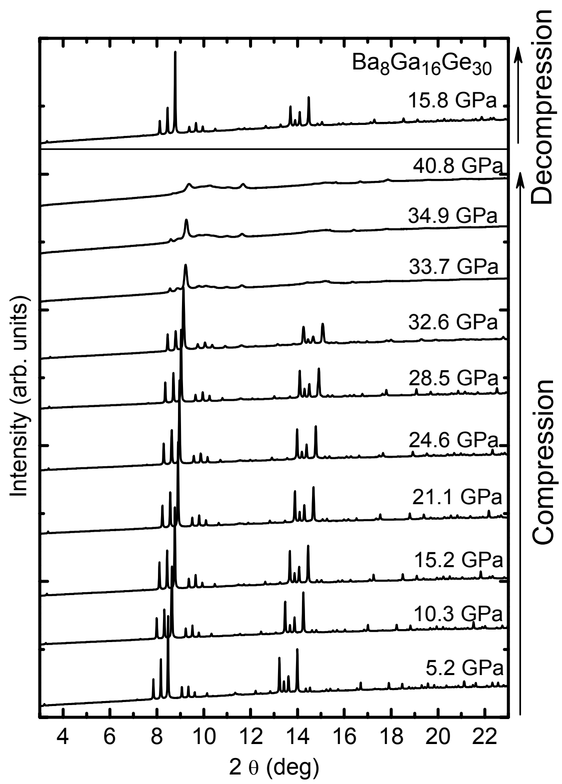

Fig. 3 Pressure dependence of XRD pattern of $Ba_8Ga_{16}Ge_{30}$. The lower and upper panels correspond to compression and decompression processes, respectively.

other higher frequency modes are attributed to the Ge/Ga frame work. The comparison between $Ba_8Ga_{16}Ge_{30}$ and $Sr_8Ga_{16}Ge_{30}$ allows us to be aware that the Ba vibrations (35 cm^{-1}) are located at the same frequencies as the Sr ones (33 cm^{-1}) in spite of the Ba atom heavier than Sr one (M_{Ba}/M_{Sr} = 137.3/87.6). This is believed to be due to the stronger guest-host interaction of $Ba_8Ga_{16}Ge_{30}$ than $Sr_8Ga_{16}Ge_{30}$ [11].

The host vibration (>50 cm^{-1}) of Ba_8Ge_{43} is weak in intensity, which can be understand by the effect of vacancies existing in Ba_8Ge_{43}, but not in $Ba_8Ga_{16}Ge_{30}$. We also note that the guest Ba frequencies (located around 30-40 cm^{-1}) are different in between Ba_8Ge_{43} and $Ba_8Ga_{16}Ge_{30}$; the frequencies of the $Ba_8Ga_{16}Ge_{30}$ shows lower frequency than that of Ba_8Ge_{43}. This can be simply understand by the different of the molar volume which is 3.7 % larger for $Ba_8Ga_{16}Ge_{30}$ than Ba_8Ge_{43}[3]; as is shown later in the high pressure Raman results, the volume reduction causes higher frequency shifts of Ba vibration modes.

Figure 2 shows Raman spectra of $Ba_8Ga_{16}Ge_{30}$ obtained at high pressures up to 32 GPa. The lower and upper panels correspond to the data on the compression and decompression processes, respectively. The drastic spectral change is found at 32 GPa on the compression process; all the Raman peak vanish, and only a very weak and broad band is observed around 70 cm^{-1}. The corresponding change also observed in the XRD measurements, as is indicated in Fig. 3. The Raman and XRD results suggest an amorphization of the clathrate above 30 GPa. However, the amorphization is immediately denied because “the reversibility” was observed; when the pressure decreases (upper panels of Figs. 2 and 3), the Raman and XRD peaks were observed again as observed on the compression process. In general, the amorphization for the covalent materials is irreversible at the room temperature[12]. The XRD peaks weakly remaining above 33 GPa can be explained with the same symmetry as those at 1 atm with space group of Pm3n although the clathrate structure is likely to be highly distorted. The XRD peaks shifted discontinuously at 33 GPa, corresponding to 3 % reduction of the molar volume under the assumption of the same structure.

The XRD results demonstrate that the clatharate structure is maintained up to 30 GPa. In spite of no structural transformation, the anomaly was found in the guest Ba vibration (denoted with solid circles in Fig. 2). The Ba mode shows higher-frequency shifts up to around 17 GPa, and then turns to lower frequencies. This behaviour may be interpreted with the evolution of the guest-host interaction. The decreasing of the cage size at high pressures may cause a charge transfer between the host and guest. Actually, Tse et al.[10] has recently reported the charge transfer from Ba to Si in the Ba_8Si_{46} under high pressure. The charge transfer can be responsible for the change of the guest-host interaction. The occurrence of the charge transfer will also change the Raman intensities because the electronic polarizability, determining the Raman intensities, can be changed. In fact, at 15 GPa, the Raman peaks denoted by arrows decrease or increases in intensity (see Fig. 2).

4. Conclusion

High pressure Raman and XRD study of Ge based clathrate $Ba_8Ga_{16}Ge_{30}$ has been performed for understanding stability of clathrate structure and behavior of guest and host vibration under high pressure. The clathrate $Ba_8Ga_{16}Ge_{30}$ shows a reversible phase transition at 32 GPa. In the high pressure phase, the host cage is likely to be highly distorted. The vibrational property indicates some anomalies 15-20 GPa, suggesting the evolution of the guest-host interaction induced by decreasing of the cage size.

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