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Vibrational properties of $Ba_8Ga_{16}Sn_{30}$ under high pressure

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Abstract. High-pressure Raman scattering experiments were performed for type-I Sn based clathrates, $Ba_8Ga_{16}Sn_{30}$, at room temperature up to 6.9 GPa. We observed irreversible amorphization at 6 GPa. The rattling vibrations of the guest atoms in the cages were investigated up to 5.8 GPa. Pressure induced evolution of spectral shape of the rattling suggested that the reduction in the cage size causes the displacement of the guest atoms from the off center to the center in the cage.

1. Introduction

Semiconductor clathrates consist of polyhedron cages formed by the host atoms which are usually group 14 and/or 13 elements [1-3]. Each cage can accommodate alkali, alkali-earth or halogen atom as the guest atom. There are several types of the crystal structures in the clathrates, such as type I, II and VIII. Figure 1 shows the type-I structure (Pm-3n, No. 223 space group) which consists of 8 guest atoms (G) and 46 host atoms (E). The G_8E_{46} type-I clathrate has two types of cages, the E_{20} dodecahedra and the larger E_{24} tetrakaidecahedra. Thus, there are two sites for the guest atoms; one is the 2a site in the E_{20} cage (G_1) and the other is the 6d site in the E_{24} cage (G_2). For Sn based clathrate $Ba_8Ga_{16}Sn_{30}$ in which the host cages consist of Ga and Sn atoms, there are two structures, *i.e.*, type I and type VIII. Those are selectively synthesized by controlling the temperature [4,5]. The E_{24} cage in type I is larger than the cage in type VIII which has one kind of cage. The E_{24} cage can loosely confine the guest atom. This condition makes the guest atom feel a multi-minima potential of which the minima are located at off-centered positions in the cage, and yields characteristic vibrational states, *i.e.*, so-called off-center rattling vibrations. The off-center rattling vibrations were actually observed in the type I $Ba_8Ga_{16}Sn_{30}$ by THz spectroscopy, and the spectral shapes depending strongly on the temperature have attracted a lot of attention [6]. The off-center rattling vibrations were also studied by Raman scattering under the ambient pressure; Takasu *et al.* have observed the off-center rattling vibrations for Ge based clathrates [7, 8].

Applying the pressure to the clathrate decreases the cage size, which is expected to change the equilibrium position of the off-centered guest atoms. Namely, the guest atoms will move toward the center of the cage. The study of the guest vibrations on this situation will be important for understanding of the rattling.

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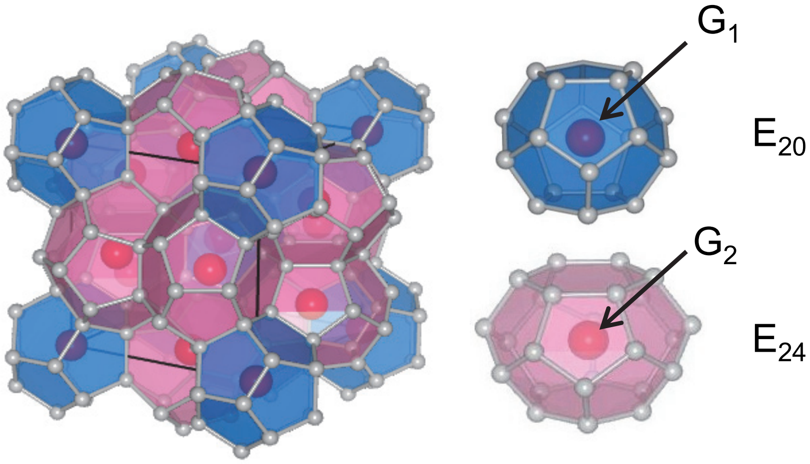

Figure 1. Crystal structure of type-I clathrate.

In this study, we carried out high-pressure Raman measurements of type I $Ba_8Ga_{16}Sn_{30}$ clathrate in order to clarify the rattling vibrations and the structural stability under high pressure. As a result, the irreversible spectral changes were observed at 6.2 GPa, which can be interpreted with irreversible amorphization. The Raman signals corresponding to the rattling vibrations were measured up to 5.8 GPa. A spectral analysis performed on the rattling vibrations suggests that the equilibrium position of the guest in E_{24} cage moves toward the center with increasing pressure.

2. Experimental

Single-crystalline sample of type I $Ba_8Ga_{16}Sn_{30}$ was synthesized in the same manner as described elsewhere [5]. We used a diamond anvil cell (DAC) with a stainless steal gasket to generate high

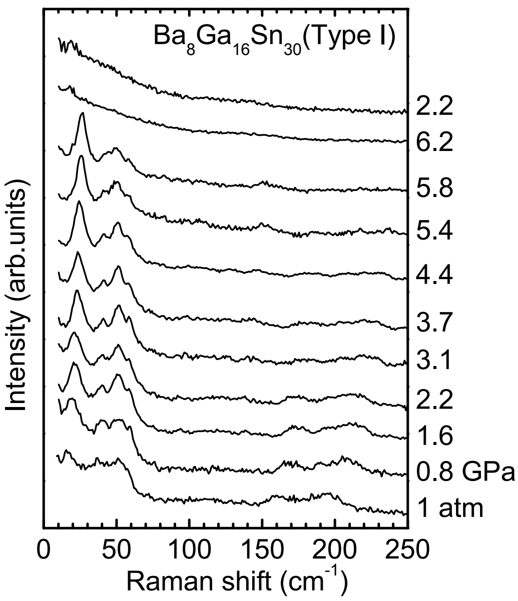

Figure 2. Raman spectra of $Ba_8Ga_{16}Sn_{30}$ type I measured under high pressures at room temperature.

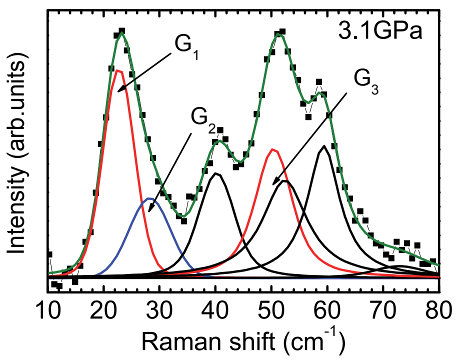

Figure 3. A typical result of peak separation of Raman spectrum. G_1, G_2 and G_3 correspond to the guest related T_{2g} and additional E_g, and E_g modes, respectively. The Rayleigh signal was manually subtracted from the raw spectrum prior to the fitting procedure.

pressure. The hole made by drilling the gasket, served as the sample chamber, was set to about 300 μm in diameter and 80 μm in thickness. The sample was polished to be a smooth plate with 30 μm in thickness to reduce the diffused reflection from the surface. The sample cut into a size of 150 μm was placed into the sample chamber of the DAC. A ruby ball was also placed to measure the pressure. A mixture of methanol and ethanol (methanol:ethanol = 4:1) was used for pressure transmitting medium. Raman measurements have been performed with a spectrometer equipped with a triple polychromator and a CCD detector (JASCO NRS2100G). The 532 nm line of a solid laser with its intensity of less than 10 mW was used for the excitation. To measure the Raman spectra down to about 10 cm^{-1}, we adopted a pseudo-back-scattering geometry. In this geometry, the laser light was incident on the sample surface with an oblique direction, and the light scattered in direction normal to the surface was collected [9].

3. Results and discussion

Figure 2 shows the Raman spectra obtained at high pressure up to 6.2 GPa. All the Raman peaks disappeared and a broad band only was observed above 6 GPa, suggesting the pressure induced amorphization. When the pressure was decreased after achieving the maximum pressure (6.9 GPa), the spectrum was not recovered. Thus, the present amorphization was irreversible. Previously, the pressure induced amorphization was also reported for Si or Ge based clathrates [10, 11]. For most clathrates, however, the amorphizations were reversible in contrast to the present case. The reversible amorphization observed in the Si or Ge clathrate implies that highly distorted structures are achieved in the amorphous states but the atomic bonds of the host cages are not broken. On the other hand, the bonding of Sn weaker than Si or Ge is easier to be broken, leading to the irreversible amorphizaition.

Next, we focus our attention on Raman peaks of guest related vibrations. Previously, Suekuni *et al.* measured Raman spectra using polarized Raman measurements [12]. They assigned peaks at 14 cm^{-1}, 19 cm^{-1}, and 47 cm^{-1} as the guest vibrations at the ambient condition. For type I clathrate, only the guests in the large cages can yield two Raman active modes if the guest atom is positioned on the center of the large cage; one is E_g mode vibrating parallel to the four fold axis of the large cage, and the other is T_{2g} mode vibrating perpendicular to that axis. If, however, the position of the guest atom is deviated from the center, another E_g mode is additionally observed beside the T_{2g} modes.

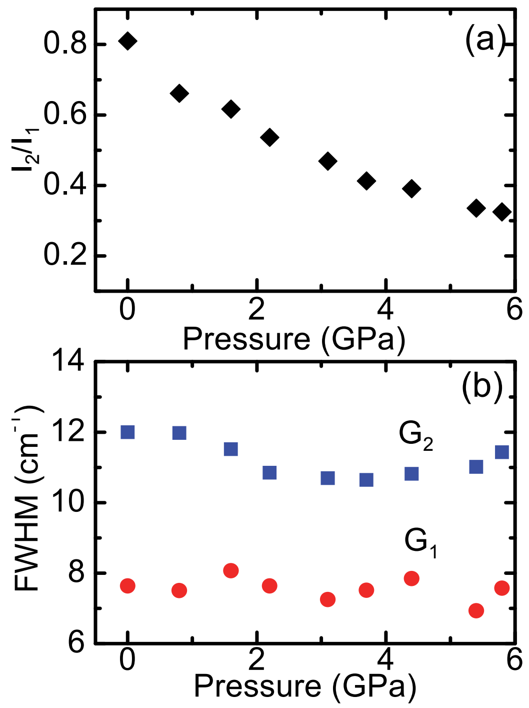

Figure 4. (a) Ratio of intensity of I_2 to I_1. I_1 and I_2 are the integrated intensity of the G_1 (T_{2g}) and G_2 (additional E_g) guest modes, respectively. (b) FWHM of the G_1 and G_2 guest modes as a function of pressure. Solid squares and circles correspond to G_1 and G_2 modes, respectively.

Therefore, three guest vibrational signals (T_{2g}, additional E_g, and E_g) should be included in the present spectra. We thus performed peak separation for the present Raman spectra by a fitting procedure. The typical results of the peak separation for the spectrum at 3.1 GPa are presented in figure 3. The frequencies of the guest vibrations denoted here as G_1, G_2, and G_3 were deduced to be 23 cm^{-1} (T_{2g}), 28 cm^{-1} (additional E_g) and 50 cm^{-1} (E_g), respectively. All the other peaks can be assigned to the host framework modes with T_{2g} or E_g symmetry, according to the previous assignments [12]. The correspondence of these frequencies to the literature ones at 1 atm [12] was reasonable, considering the pressure induced shift. The integrated intensities and the widths were simultaneously obtained as fitting parameters. In figure 4 (a), the relative intensity of G_2 to G_1 modes is plotted as a function of pressure. Figure 4(b) shows peak widths of G_1 and G_2 modes. The peak widths were almost independent of the pressure, indicating neither splitting nor generation of the guest related Raman peaks. From figure 4(a), we see that the relative intensity of G_2 mode decreases as the pressure increases. The G_2 mode, which is the additional mode observable only for the off-center, tends to disappear as the cage size becomes smaller. This is most likely to be because the equilibrium position of the guest in the large cage moves from the off-center to the center with increasing pressure.

4. Summary

Raman spectra for type-I $Ba_8Ga_{16}Sn_{30}$ clathrate were measured under high pressures at room temperature. From a change in the spectral shape, an irreversible amorphizaition was found at 6.2 GPa. We successfully obtained Raman signals related to the guest rattling vibrations up to 5.8 GPa, and clarified the pressure induced evolution of the Raman intensity of the off-center rattling vibration. The signal of the off-center rattling decreased in intensity as pressure increased. It suggests that the equilibrium positions of the guests move from the off-center to the center by decreasing the host cage size.

Acknowledgments

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References

[1] Kasper J S, Hagenmuller P, Pouchard M and Cros C 1965 *Science* **150** 1713
[2] Bobev S and Sevo S C 2000 *J. Solid State Chem.* **153** 92
[3] Kovnir K A and Shevelkov A V 2004 *Rus. Chem. Rev.* **73** 923
[4] Huo D, Sakata T, Sasakawa T, Avila M A, Tsubota M, Iga F, Fukuoka H, Yamanaka S, Aoyagi S and Takabatake T 2005 *Phys. Rev.* B **71** 075113
[5] Suekuni K, Avila M A, Umeo K, Fukuoka H, Yamanaka S, Nakagawa T and Takabatake T 2008 *Phys. Rev.* B **77** 235119
[6] Mori T, Iwamoto K, Kushibiki S, HondaH, Matsumoto H and Toyota N 2011 *Phys. Rev. Lett.* **106** 015501
[7] Takasu Y, Hasegawa T, Ogita N, Udagawa M, Avila M A, Suekuni K, Ishii I, Suzuki T and Takabatake T 2006 *Phys. Rev.* B **74** 174303
[8] Takasu Y, Hasegawa T, Ogita N, Udagawa M, Avila M A, Suekuni K and Takabatake T 2008 *Phys. Rev. Lett.* **100** 165503
[9] Funahashi K, Yajima I, Kume T, Sasaki S, Shimizu H and Takabatake T 2012 *J. Phys:. Conf. Ser.* **377** 012038
[10] Imaeda Y, Kume T, Sasaki S, Shimizu H, Kishimoto K, Ikeda N and Koyanagi T 2012 *J. Phys.: Conf. Ser.* **377** 012037
[11] Kume T, Ohno S, Sasaki S, Shimizu H, Ohishi Y, Okamoto N L, Kishida K, Tanaka K and Inui H 2010 *J. Appl. Phys.* **107** 013517
[12] Suekuni K, Takasu Y, Hasegawa T, Ogita N, Udagawa M, Avila M A and Takabatake T 2010 *Phys. Rev.* B **81** 205207