

RAMAN STUDY OF TYPE-I GERMANIUM CLATHRATE $I_8Sb_8Ge_{38}$ AT 1 BAR AND HIGH PRESSURES

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Raman spectra of iodine-containing cationic type-I clathrate $I_8Sb_8Ge_{38}$ have been measured at 1 bar and high pressures up to 44 GPa at room temperature, by using a diamond anvil cell. The guest-iodine rattling vibrations were observed at 53 and 58 cm^{-1} at ambient conditions. High-pressure Raman experiments show two spectral changes at 16 and 35 GPa, which are respectively due to a change in guest-host interaction and to an irreversible amorphization.

1. Introduction

In the last decade, group-IV clathrates, which are open-structured Si, Ge, and Sn cage-like compounds, have attracted increasing attention because of their potential applications for thermoelectric devices,[1, 2] in particular for Ge based clathrates due to the behaviour of phonon-glass and electron-crystal (PGEC). One of the keys for the intriguing properties is the vibrations of the guest atoms encapsulated in the host nano-cages (so called “rattling” vibrations).[2-4] This rattling is responsible for the glass-like low thermal conductivities of the clathrates. The direct observation of the rattling is important for understanding of the clathrate properties. The systematic observations of the rattling vibrations as a function of volume (or pressure) are very significant to investigate the guest-host interaction.[4, 5]

In this report, we present Raman experiments of the iodine-containing cationic type-I clathrate $I_8Sb_8Ge_{38}$ at 1 bar and high pressures using a diamond anvil cell (DAC), in order to study its vibrational properties. In the Raman spectra, we have clearly observed vibrational bands which include the guest-I vibrations in a low frequency region around 55 cm^{-1} as well as the host (Ge, Sb) vibrations in the higher frequency region of 75-270 cm^{-1} .

2. Experimental

The $I_8Sb_8Ge_{38}$ sample was prepared by the powder metallurgy method as follows: [6] Raw powder or grain of stoichiometric I, Sb, and Ge was pulverized together using a planetary mill, and fully mechanically alloyed. The obtained fine powder was then sintered in a graphite die by spark plasma sintering (SPS) carried out at a pressing pressure of 40 MPa in argon of 400 Torr and $T=873$ K.

Raman measurements have been performed with an apparatus which has been improved through detecting the low-frequency Raman signals for various clathrate compounds.[4, 5] Radiation of 532 nm from a solid-state laser (Verdi2W) was incident on the sample with a power of 5 mW. The backscattered Raman spectrum was measured with a spectrometer (JASCO NR1800) equipped with a triple polychromator and a charge coupled device detector. The illuminated spot was less than 5 μm in size. The resolution of Raman spectra was about 1 cm^{-1} . High-pressure experiments were carried out by using DAC. The hole of the tungsten-metal gasket serving as the sample chamber was set to 100 μm in diameter and 50 μm in thickness. A tiny sample was placed into the chamber of DAC and loaded with a ruby chip for pressure measurements.[7]

3. Results and discussion

The Raman spectrum of $I_8Sb_8Ge_{38}$ at ambient conditions is shown in Fig. 1 with those of type-I Ba_8Ge_{43} , $Ba_8Ga_{16}Ge_{30}$, and $Sr_8Ga_{16}Ge_{30}$ clathrates for comparison. For $I_8Sb_8Ge_{38}$, the rattling vibrations of guest-I in the large cage were observed in a low frequency region around 55 cm^{-1} , and the framework vibrations in the high frequency region of $75\text{-}270\text{ cm}^{-1}$. Although the mass of guest-I is almost close to Ba atom, the rattling vibrations of I (53 and 58 cm^{-1}) are located at higher frequencies than the Ba vibration as seen in Fig. 1. This suggests the strong guest-host interaction in $I_8Sb_8Ge_{38}$, i.e., the Sb atom, donating its valence electron to the electronegative guest-I for the covalent bonding, attracts the guest-I atom towards the host framework. This guest-host polarity is reversed comparing with anionic clathrates, e.g., $Ba_8Ga_{16}Ge_{30}$.

The rattling frequency can be estimated by the Einstein temperature (Θ_E), which is

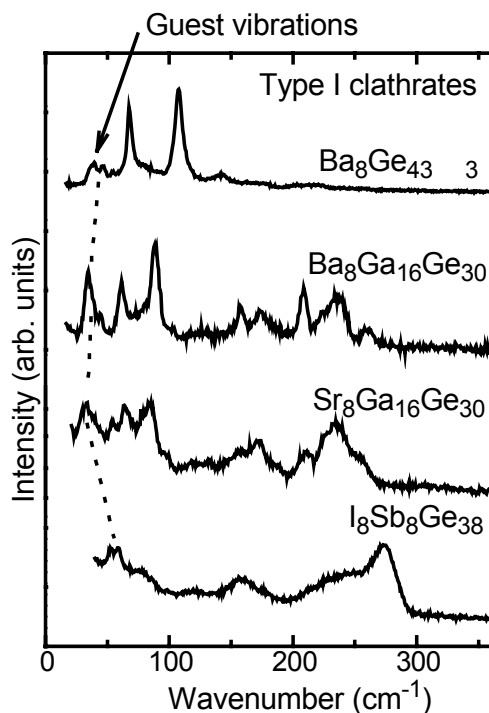


Fig. 1. Raman spectrum of cationic type-I clathrate $I_8Sb_8Ge_{38}$ at ambient conditions with those of anionic type-I Ba_8Ge_{43} , $Ba_8Ga_{16}Ge_{30}$, and $Sr_8Ga_{16}Ge_{30}$ clathrates for comparison. Dotted lines indicate their rattling vibrational region.

calculated from the atomic displacement parameter (ADP) determined by X-ray crystallographic data, if the static disorder is small and the Θ_E is less than about 300 K.[8] Recently, Kishimoto *et al.*[6] had reported $\Theta_E=78\text{ K}$ ($=54.2\text{ cm}^{-1}$) for $I_8Sb_8Ge_{38}$ and $\Theta_E=51\text{ K}$ ($=35.4\text{ cm}^{-1}$) for $Ba_8Ga_{16}Ge_{30}$. [9] The value of 54.2 cm^{-1} for $I_8Sb_8Ge_{38}$ is good agreement with the present Raman results as seen in Fig. 1. For the framework vibrations, it is remarkable that the highest-frequency Raman band locates at about 270 cm^{-1} , which is higher than the others in Fig. 1. This highest framework frequency of $I_8Sb_8Ge_{38}$ can be affected directly by the Ge-Ge bonding nature, therefore, the electron transfers from the host framework to the electronegative guest-I strengthen Ge(Sb)-Ge(Sb) bonds. Similar phenomenon was observed for the guest-I cationic type-I Si clathrate; [10] 461 cm^{-1} for $I_8I_2Si_{44}$, 438 cm^{-1} for Ba_8Si_{46} , and 440 cm^{-1} for K_8Si_{46} .

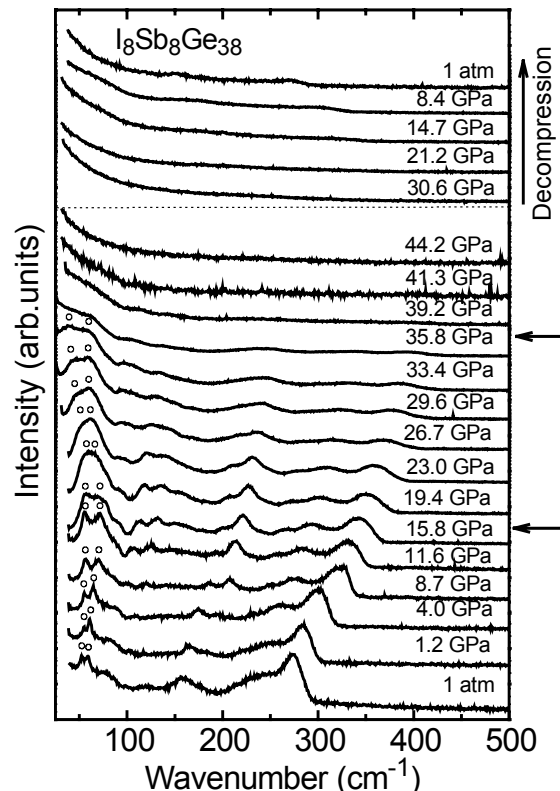


Fig. 2. Pressure dependence of Raman spectra of $I_8Sb_8Ge_{38}$ up to 44 GPa at room temperature, showing the compression and decompression processes. Horizontal arrows indicate the point of spectral change.

The Raman spectra obtained at high pressures up to 44 GPa show three remarkable changes as seen in Fig. 2 with the processes of the compression and the decompression: (1) at above 10 GPa, two Raman bands appear around 110-130 cm^{-1} , (2) above 16 GPa, rattling vibrations show the frequency softening with increasing pressure, which is likely due to a change in the guest-host interaction, (3) at about 35 GPa, all Raman bands disappear, indicating an irreversible amorphization.

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References

- [1] G.S. Nolas, J.L. Cohn, G.A. Slack, and S.B. Schujman, *Appl. Phys. Lett.* **73**, 178 (1998).
- [2] G.J. Snyder and E.S. Toberer, *Nature Mater.* **7**, 105 (2008).
- [3] B.C. Sales, D. Mandrus, and R.K. Williams, *Science* **272**, 1325 (1996).
- [4] T. Kume, H. Fukuoka, T. Koda, S. Sasaki, H. Shimizu, and S. Yamanaka, *Phys. Rev. Lett.* **90**, 155503 (2003).
- [5] H. Shimizu, T. Iitaka, T. Fukushima, T. Kume, S. Sasaki, N. Sata, Y. Ohishi, H. Fukuoka, and S. Yamanaka, *J. Appl. Phys.* **101**, 063549 (2007).
- [6] K. Kishimoto, S. Arimura, and T. Koyanagi, *Appl. Phys. Lett.* **88**, 222115 (2006).
- [7] H.K. Mao, P.M. Bell, J.W. Shaner, and D.J. Steinberg, *J. Appl. Phys.* **49**, 3276 (1978).
- [8] B.C. Sales, B.C. Chakoumakos, and D. Mandrus, *J. Solid State Chem.* **146**, 528 (1999).
- [9] B. Eisenmann, H. Schafer, and R. Zagler, *J. Less-Common Met.* **118**, 43 (1986).
- [10] H. Shimizu, T. Kume, T. Kuroda, S. Sasaki, H. Fukuoka, and S. Yamanaka, *Phys. Rev. B* **68**, 212102 (2003).