High-pressure Raman study on type III clathrate compounds

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Summary

High-pressure Raman measurements of type-III silicon clathrate $Ba_{24}Si_{100}$ and $Ba_{24}Ge_{100}$ have been performed up to 27 GPa and 20 GPa, respectively. The Raman spectra were clearly measured in a region above 40 cm^{-1}. For $Ba_{24}Si_{100}$, a phase transition was identified at 6.5 GPa as splitting of a Raman peak arising from Si frame. Also for $Ba_{24}Ge_{100}$, a similar phase transition was observed around 5-7 GPa. In the high pressures above 23 GPa, $Ba_{24}Si_{100}$ becomes irreversibly amorphous. In the case of $Ba_{24}Ge_{100}$, the amorphization was observed until 20 GPa.

Introduction

Silicon (Si), germanium (Ge), and tin (Sn) form clathrate structures in which the guest atoms are alkali and alkaline earth metals,(Kasper 1965, Bobey 2000) showing more open structures than the diamond-type. In these materials, the host lattice is formed by one kind of atoms bonded by strong covalent forces, and its bond lengths are almost similar to those in diamond-structured Si, Ge, and Sn. The most common forms of clathrates are known as type-I and type-II, which are isostructural with hydrogen-bonded H_2O clathrates.(Sloan 1998) For silicon clathrates, the type-I structure is formed by two Si_{20} dodecahedra and six Si_{24} tetrakaidecahedra in a cubic unit cell connected by the face-sharing manner, which can be represented by the general formula of M_8Si_{46} if host Si cages are fully occupied by guest atoms (M). The type-II structure is formed by sixteen Si_{20} dodecahedra and eight Si_{28} hexakaidecahedra also connected by shared faces in its larger cubic unit cell. These compounds continue to attract much attention as new superconductor,(Kawaji 1995, Yamanaka 2000, Tanigaki 2003) unusual wide-bandgap semiconductor (Gryko 2000) and a new class of thermoelectric materials.(Nolas 2000, Tse 2000) Most recently, we have found vibrational modes of guest atoms (Ba, K, and I) in type-I Ba_8Si_{46},(Kume 2003) K_8Si_{46},(Kume 2004) and $I_8Si_{44}I_2$(Kume 2003) compounds by Raman spectroscopy, and observed some phase transitions at pressures up to 30 GPa.

Recently, type-III new Ge and Si clathrates, $Ba_{24}Ge_{100}$ and $Ba_{24}Si_{100}$ were prepared by several authors.(Fukuoka 2000a, 2000b, C-Cabrera 2000, Kim 2000) $Ba_{24}Si_{100}$ is cubic with the room-temperature lattice constant a = 14.0685 Å. Each unit cell contains four Ba_6Si_{25} formula units. Figure 1 shows symbolic representation of face sharing Si_{20} dodecahedron, Si_8 distorted cube, and Si_{20} open cage as building unit of type-III clathrates. In the structure there are three sites for the Ba atoms each having a different coordination environment. Each of the Si_{20} polyhedra is centred by a Ba atom (Ba1 site) and the two remaining Ba atoms occupy cavities in the zeolite-like channels, because the Si_{20} units alone cannot fill all spaces; therefore, this structure has two interstitial sites of Ba2 and Ba3, which are coordinated with eight Si atoms and twenty Si atoms (open Si_{20}; four Si atoms are removed from a Si_{24} cage), respectively. There are two Ba1 sites, one Ba2 site, and three Ba3 sites per Ba_6Si_{25} formula unit.(Fukuoka, 2000a, 2000b) It is worth to note that 32 out of 100 Si atoms in the unit cell are three-bonded and the remaining 68 Si atoms are four-bonded (see Fig. 1), in contrast to type-I Si clathrates having all four-bonded Si atoms. $Ba_{24}Ge_{100}$ undergoes a two-step first-order phase transition between 230 K and 180 K from metallic behaviour to a high-resistivity state,(Grosche 2001, Paschen 2002) which is due to the Ge-Ge bond breaking combined with the displacement of neighbouring Ba atoms to the split positions.(Petkov 2003, Yuan 2004, C-Cabrera 2005, Zeree 2002) However, BCS-like superconductivity occurs at low temperature T_c=0.24 K. By applying pressure, the phase transition is shifted to lower temperature but T_c increases remarkably to 3.8 K at 2.8 GPa. These unusual properties are understood by the density of states at the Fermi energy. (Yuan

2004, Zeree 2002) According to Tanigaki, the superconductivity is observed below T_c=1.4 K also for $Ba_{24}Si_{100}$. However, there is only a few experiments on vibrational spectroscopy and high-pressure studies for type-III Si and Ge clathrates.

In this paper, we present the Raman study of new type-III $Ba_{24}Si_{100}$ and $Ba_{24}Ge_{100}$ clathrates at high-pressures and room temperature. For $Ba_{24}Si_{100}$, the Raman signals arising from vibrations of Ba atoms inside three kinds of cages are measured around 45-90 cm^{-1} and identified by comparison with the spectra of Ba_8Si_{46}. We present and discuss the pressure-induced phase transition at about 6.5 GPa and the pressure-amorphized irreversible transition at about 23 GPa by comparing with amorphous Si and the amorphization observed in type-I Ba_8Si_{46},(San Miguel 2005) K_8Si_{46},(Tse 2002) and $I_8Si_{44}I_2$ (Shimizu 2003, Kume 2004) compounds. Also for $Ba_{24}Ge_{100}$, a similar phase transition was observed around 6 GPa, at which the Raman peak splitting occurs for a Ge cage mode.

Experimental

The samples of single phases $Ba_{24}Si_{100}$ and $Ba_{24}Ge_{100}$ were prepared for high pressure experiments. The details for the sample preparation were described elsewhere (Fukuoka 2000a, 2000b). For high pressure Raman experiments, small pieces of the sample were placed into the chamber of a a diamond anvil cell (DAC). The hole of the gasket was set to about 100 μm in diameter and 100 μm in thickness. For fine Raman measurements of the clathrate compounds which shows very weak Raman signals due to its metallic property, we used the dense argon as the pressure transmitting medium that is free from Raman signals. Raman spectra were measured in a back-scattering geometry with a micro-Raman spectrometer (JASCO NR 1800) equipped with a triple polychromator and a charge-coupled device (CCD) detector. The 532 nm line of a solid laser (Coherent Verdi2W) was used for the excitation. The spectral resolution was about 1 cm^{-1}. In the Raman measurements at ambient pressure without DAC, the sample was placed in a cell filled with He gas to remove undesirable Raman lines of gaseous N_2 and O_2 rotation below 200 cm^{-1}.

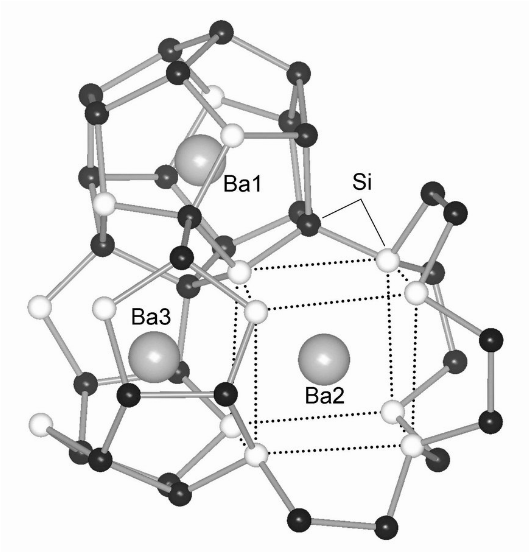

Figure 1. Local structure of Type III clathrate $Ba_{24}Si_{100}$ with space group $P4_132$. There are three Ba sites, Ba1 in Si_{20}, Ba2 in Si_8, and Ba3 in open Si_{20} cages. Black and white balls are four- and three bonded Si respectively. Ge clathrate $Ba_{24}Ge_{100}$ also takes the identical structure.

Results and Discussion

- Raman spectra at 1 bar -

The type-III clathrate crystallizes in the cubic space group $P4_132$ (O^7). The group theoretical analysis predicts that the first-order (one-phonon) Raman-active modes of Si or Ge framework vibrations are $12A_1 + 25E + 37T_2$ (74 peaks), where A_1 modes are singly degenerate, E are doubly degenerate, and T_2 are triply degenerate. In addition, the guest Ba atoms enclosed inside three distinct cages also contribute to Raman-active modes of $2A_1 + 6E + 8T_2$ (16 peaks); consisting of $A_1 + 2E + 3T_2$ associated with Ba1 atoms, $E + T_2$ associated with Ba2 atoms, and $A_1 + 3E + 4T_2$ associated with Ba3 atoms.

Raman scattering spectra of $Ba_{24}Si_{100}$ and $Ba_{24}Ge_{100}$ at ambient pressure and 296 K are shown in Fig. 2 with that of Ba_8Si_{46} type I clathrate (Kume 2003) for comparison. For $Ba_{24}Si_{100}$, just looking different from Ba_8Si_{46}, we can find many peaks at low-frequency region around 45-90 cm^{-1}, and the Si framework vibrational bands distribute separately around

115-415 cm^{-1}. Their frequencies of framework vibrations are altogether lower than those of Ba_8Si_{46}. For these framework vibrations, we calculate 74 Raman-active modes, but we cannot unambiguously make the mode assignments because of relatively broad bands containing more than one Raman mode. In the low frequency region below 100 cm^{-1}, there are five peaks in the $Ba_{24}Si_{100}$. We can see that some peaks among them are located at almost the same position as the Ba_8Si_{46}. This is probably due to the similarity in the local structure. As seen in Fig. 1, there are three different sites for the guest Ba atoms in the type III structure. The Ba1 occupies a Si_{20} cage, which is the same as the small cages (Si_{20}) of Ba_8Si_{46}. The Ba3 atoms is located at a Si_{20} open cage, which is closely related with the large cages (Si_{24}) in Ba_8Si_{46} because removing four Si atoms from the Si_{24} cage causes the Si_{20} open cage. Thus, we see that there is Si_{20} and broken Si_{24} cage in $Ba_{24}Si_{100}$. The remaining small peaks of 76 cm^{-1} and 71 cm^{-1} which are not observed for Ba_8Si_{46} may come from Ba2 in Si_8 distorted cube.

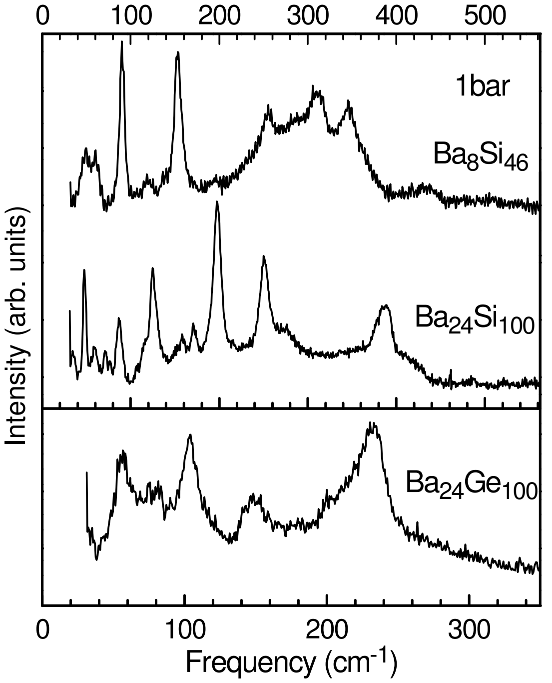

Figure 2. Raman spectra of $Ba_{24}Si_{100}$, Ba_8Si_{46}, and $Ba_{24}Ge_{100}$. The frequency scale for $Ba_{24}Ge_{100}$ is reduced by a factor of the square of root of atomic mass ratio (M_{Ge}/M_{Si}).

We now compare $Ba_{24}Si_{100}$ with $Ba_{24}Ge_{100}$ whose spectrum is indicated with a different scale reduced by a factor of square root of atomic weight $(M_{Ge}/M_{Si})^{0.5} = (72.6/28.1)^{0.5} = 1.61$. The spectral correspondence between the two type III clathrates is not observed although the crystal structures are the same. This is though to result from the presence of Ba guest atoms. The heavy Ba atoms (M_{Ba} =137.3) affect more the lower frequency modes. Furthermore, the Ba atom in each clathrate contributes to the vibration in different ways because the guest-host mass ratio is different and the guest-host interaction is likely to be also different. Since, however, the highest-frequency band is located at almost the same position in Fig. 2, the highest frequency modes is seen to arise only from the host Si or Ge frame.

- Phase transition of $Ba_{24}Si_{100}$ -

Figs. 3 and 4 are Raman spectra of $Ba_{24}Si_{100}$ at various pressures up to 27 GPa and pressure dependence of Raman frequencies, respectively. We note that the peak marked with open circles shift to lower frequencies. This behaviour has been observed also for other Si clathrates Ba_8Si_{46}, K_8Si_{46}, $I_8Si_{44}I_2$, and Si_{136} clathrate (Guyot 1999). All the modes showing the softening are believed to be Si framework vibarations. The softenings seem to be the benchmark of Si clathrates and also of cubic-diamond Si,(Weinstein 1975) showing tetrahedral bonds.

Next, we investigate pressure-induced phase transitions. As indicated by solid circles in Fig. 3, the framework vibration of 126 cm^{-1} at ambient pressure splits into two peaks at about P=6.5 GPa and then their peak frequencies show softening with pressure (Fig. 4). At the same time as the splitting, new band (open squares in Fig. 3) appeared at about 260 cm^{-1}. Furthermore, the band intensities associated with the vibrations of Ba atoms become weak above 7 GPa at low frequency region, particularly for the lowest band due to the Ba in the large Si_{20} open cage. These phenomena indicate the occurrence of pressure-induced phase transition on $Ba_{24}Si_{100}$. It is probable that the Ba displacement to off-center positions is responsible for this phase transition combined with the enhanced guest-host couplings. We can find the similar phenomenon for Ba_8Si_{46} as follows: The pressure-induced phase transition of Ba_8Si_{46} found by Raman scattering around 7 GPa (Kume 2003) has been interpreted by the off-center displacement of Ba atoms in the large Si_{24} cages.

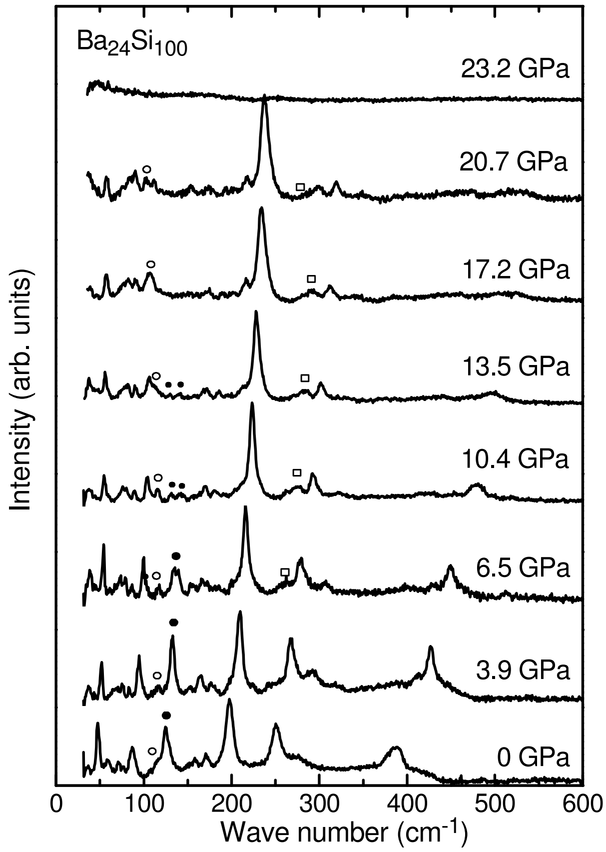

Figure 3. Raman spectra of $Ba_{24}Si_{100}$ clathrates obtained at high pressures.

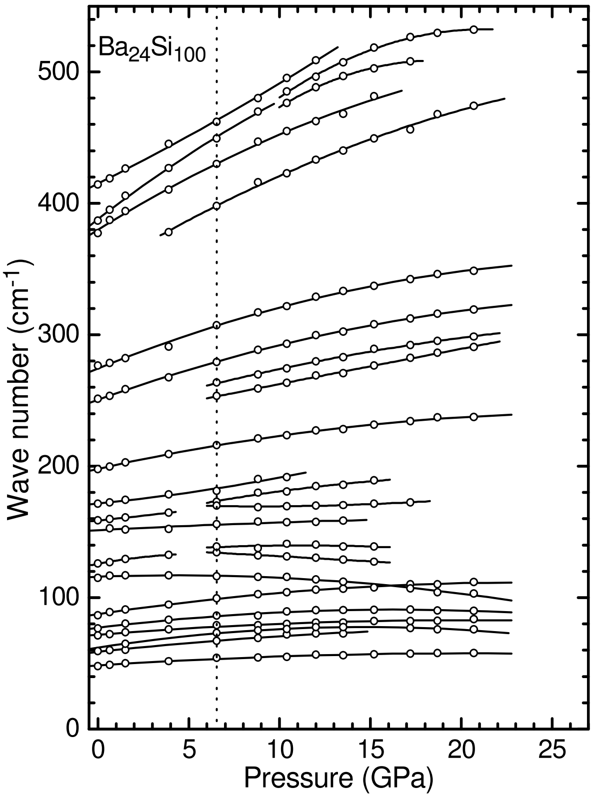

Figure 4. Pressure dependence of Raman frequencies of $Ba_{24}Si_{100}$.

- *Amorphization of $Ba_{24}Si_{100}$* -

At pressures above 23 GPa, the Raman bands disappeared (see Fig. 3). This is understood as the occurrence of pressure-induced amorphization in $Ba_{24}Si_{100}$ at about 23 GPa, judging from the following observations. After attaining the maximum pressure of 27 GPa, this high-pressure phase was completely decompressed to ambient pressure in order to confirm whether the disappeared Raman spectra of $Ba_{24}Si_{100}$ can recover or not. As seen in Fig. 5, Raman spectrum did not recover to those before compression, and looks like the spectrum of an amorphous Si.(Alben 1975, Ishidate 1982, Deb 2001) Although we observed the Raman bands characterizing the amorphous state of $Ba_{24}Si_{100}$ at ambient pressure (Fig. 5), we could not detect these Raman signals at pressures of 23-27 GPa, i.e., in the amorphous phase (Fig. 3). This irreversible transition to the amorphous state had been commonly observed on type-I Si clathrates: Ba_8Si_{46} at about 40 GPa by x-ray,(San Miguel 2005) K_8Si_{46} at 32 GPa by x-ray,(Tse 2002) and $I_8Si_{44}I_2$ at 40 GPa by Raman scattering.(Shimizu 2002, Kume 2004) We like to emphasize that the amorphization pressure of 23 GPa for type-III $Ba_{24}Si_{100}$ is significantly lower than those of

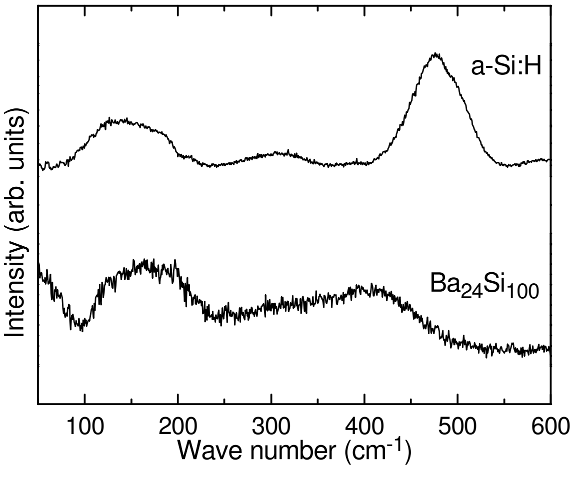

Figure 5. Raman spectra of recovered sample of $Ba_{24}Si_{100}$ and amorphous Si:H.

type-I clathrates. This means that the type-III structure is less stable than the type-I structure under high pressures. This result can be understood from the following structural feature; the type-I structure has the three-dimensional tight Si-network (all four-bonded Si atoms), but the type-III structure contains the channel with ample space (68 % four-bonded and 32 % three-bonded Si atoms).

In Fig. 5, the Raman spectrum of hydrogenated amorphous Si (a-Si;H) (Alben 1975, Ishidate 1982, Deb 2001) is indicated for the comparison. In the amorphous spectrum, we confirmed TA-, LA-, LO-, and TO-like phonon bands around 145, 310, 385, and 475 cm^{-1}, respectively. For the spectrum of amorphous $Ba_{24}Si_{100}$, we can point out that (1) TA-like phonon band shifted to higher frequency at about 170 cm^{-1} and (2) TO-like phonon band shifted to lower frequency at about 415 cm^{-1} and it shows weak Raman intensity, by comparing with those of a-Si:H in Fig. 5. These results show that the states of amorphous $Ba_{24}Si_{100}$ and a-Si:H are different from each other. Ishidate *et al.*(1982) measured high-pressure Raman spectra of a-Si:H up to 2.5 GPa, and reported that the frequencies of TO- and LO-like modes increase, but that of TA-like mode decreases with compression. Therefore, as seen in Fig. 5, the spectrum of the amorphous $Ba_{24}Si_{100}$ is corresponding to that of expanded amorphous Si, and that of a-Si:H is corresponding to the spectrum under compression. The resulting point is that the Si-Si bond length in the amorphous $Ba_{24}Si_{100}$ seems to be larger than that in the amorphous Si, which may significantly suggest that the amorphous $Ba_{24}Si_{100}$ is somewhat composed of cage-like structures enclosing Ba atoms. These investigations are based on that the average Si-Si bond length of $Ba_{24}Si_{100}$ is 2.415 Å (Fukuoka 2000b) which is longer than that of the diamond-type Si (2.352 Å) at room temperature. The amorphous state of Si clathrates is generally interesting in view of the structural constituent of its bonding and the theoretical simulations. The present work can be expected to stimulate more studies of Si clathrates in view of these characteristic properties.

-Phase transition of $Ba_{24}Ge_{100}$-

Figure 6 shows the Raman spectra of $Ba_{24}Ge_{100}$ obtained for various pressures up to 20 GPa. Similarly to the case of $Ba_{24}Si_{100}$, the peak located at 100 cm^{-1} is split into two at 5-6 GPa and then weakened above 10 GPa. Considering that this peak arises from Ge cage, the phase transition causes some changes in the Ge cage structure. This reminds us of the phase transition reported around 200 K at 1 bar, which is due to the Ge-Ge bond breaking combined with the displacement of neighbouring Ba atoms to the split positions.(Paschen 2002, Yuan 2004, C-Cabrera 2005) The peak splitting and vanishing are observed also for $Ba_{24}Si_{100}$ as indicated in Fig. 3. An identical phase transition is likely to govern for $Ba_{24}Si_{100}$ and $Ba_{24}Ge_{100}$. For better understating of this phase transitions, low temperature Raman experiments and structural studies are highly required.

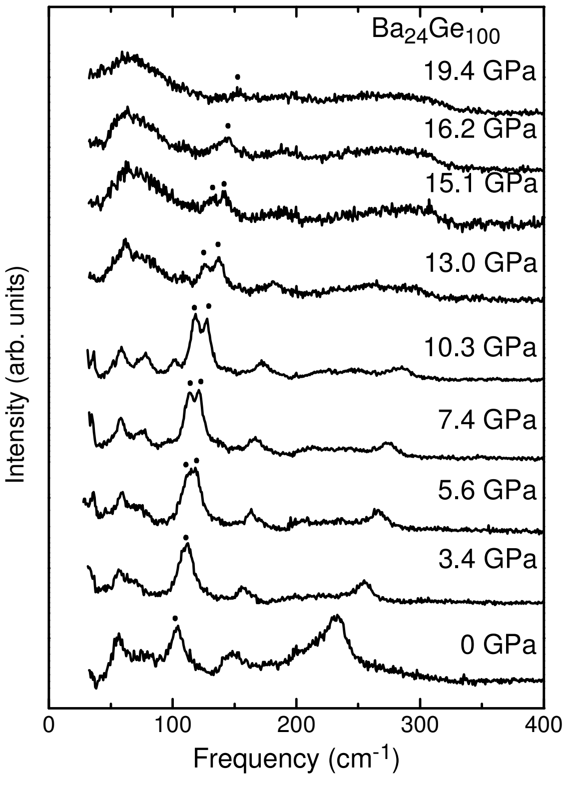

Figure 6. Raman spectra of $Ba_{24}Ge_{100}$ clathrates obtained at high pressures.

Conclusion

We performed the high-pressure Raman studies of type-III clathrates ($Ba_{24}Si_{100}$ and $Ba_{24}Ge_{100}$). For the Raman spectrum of $Ba_{24}Si_{100}$, the Si framework vibrations around 115-415 cm^{-1} shifted altogether to lower frequency as compared to those of Ba_8Si_{46}.

The change in framework vibrations of $Ba_{24}Si_{100}$ indicated the existence of high-pressure phase transition at 6.5 GPa, which seems to be due to the lattice distortion induced by increasing guest (Ba)-host (Si) couplings. The similar spectral changes were observed also for $Ba_{24}Ge_{100}$. $Ba_{24}Si_{100}$ clathrate becomes irreversibly amorphous at pressures above 23 GPa. This pressure was compared with those for type-I clathrates, and the stability of cage structures was investigated. By comparison of TO- and TA-like phonon spectra between an amorphous $Ba_{24}Si_{100}$ and a-Si:H, we discussed a possible local structure of the amorphous $Ba_{24}Si_{100}$ with the partial composition of the Si cage structures enclosing Ba atoms.

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