High-pressure Raman study of the Ba-doped silicon clathrate Ba$_{24}$Si$_{100}$ up to 27 GPa

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High-pressure Raman scattering of type-III silicon clathrate Ba$_{24}$Si$_{100}$ has been measured up to 27 GPa at room temperature. Low-frequency vibrational modes associated with Ba atoms inside three kinds of cages were found around 45–90 cm^{-1}. The Si framework Raman bands were observed around 115–415 cm^{-1}, which are altogether shifted toward lower frequencies as compared to those of type-I Ba$_8$Si$_{46}$. High-pressure phase transition occurs at 6.5 GPa, which seems to be due to the structural distortion induced by the increasing guest(Ba)-host(Si) couplings. Ba$_{24}$Si$_{100}$ becomes irreversibly amorphous above 23 GPa. This pressure is lower than those of type-I Si clathrates, which suggests that type-III structure is less stable than type-I under high pressures.

I. INTRODUCTION

Silicon (Si), germanium (Ge), and tin (Sn) form clathrate structures in which the guest atoms are alkali and alkaline earth metals,[1,2] 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$_2$O clathrates.[3] 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$_8$Si$_{46}$ if host Si cages are fully occupied by guest atoms (M). The type-II structure is formed by 16 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 a superconductor,[4–7] unusual wide-band-gap semiconductor,[8,9] and a class of thermoelectric materials.[10,11] Most recently, we have found vibrational modes of guest atoms (Ba, K, and I) in type-I Ba$_8$Si$_{46}$,[12] K$_8$Si$_{46}$,[13] and I$_8$Si$_{44}$I$_2$[14] compounds by Raman spectroscopy, and observed some phase transitions at pressures up to 30 GPa.

Recently, type-III Ge and Si clathrates, Ba$_{24}$Ge$_{100}$ and Ba$_{24}$Si$_{100}$ were prepared by several authors.[15–18] Ba$_{24}$Si$_{100}$ is cubic with the room-temperature lattice constant a =14.0685 Å. Each unit cell contains four Ba$_6$Si$_{25}$ formula units. Figure 1 shows symbolic representation of face-sharing Si$_{20}$ dodecahedron, Si$_8$ distorted cube, and Si$_{20}$ open cage as building units of type-III clathrates.[16] In the structure there are three sites for the Ba atoms, each having a different coordination environment. Each of the Si$_{20}$ polyhedra is centered by a Ba atom (Ba1 site), and the two remaining Ba atoms occupy cavities in the zeolitelike 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 20 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$_6$Si$_{25}$ formula unit.[15,16] It is worth noting 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 and 180 K from metallic behavior to a high-resistivity state,[19,20] which is due to the Ge—Ge bond breaking combined with the displacement of neighboring Ba atoms to the split positions.[21–23] 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
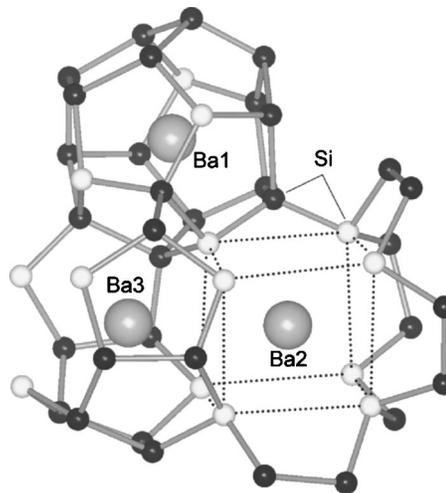
FIG. 1. Symbolic representation of face-sharing Si$_{20}$ dodecahedron, Si$_8$ distorted cube, and Si$_{20}$ open cage as building unit of type-III clathrates.[16] There are three different sites for the Ba atoms: Ba1, Ba2, and Ba3 are enclosed inside Si$_{20}$, Si$_8$, and Si$_{20}$ open cages, respectively. Black and white spheres are four- and three-bonded Si atoms, respectively. 68 out of 100 Si atoms in the unit cell are four-bonded and the remaining 32 Si atoms are three-bonded.

increases remarkably to 3.8 K at 2.8 GPa.[19–22] These unusual properties are understood by the density of states at the Fermi energy.[22,24] On the other hand, $Ba_{24}Si_{100}$ showed a metallic conductivity without the phase transition down to 2 K at atmospheric pressure.[16] Very recently, Tanigaki and others found the superconductivity on $Ba_{24}Si_{100}$ at about T_c =1.4 K.[25] 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 first Raman study of type-III $Ba_{24}Si_{100}$ clathrate at ambient pressure and high pressures up to 27 GPa at room temperature. 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}.[12] The Si framework vibrational bands of $Ba_{24}Si_{100}$ are observed around 115–415 cm^{-1}, which are altogether shifted toward lower frequencies as compared to those of type-I Ba_8Si_{46} clathrate. 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 to amorphous Si and the amorphization observed in type-I Ba_8Si_{46},[26] K_8Si_{46},[27] and $I_8Si_{44}I_2$[14,28] compounds.

II. EXPERIMENTAL

The sample of a single-phase $Ba_{24}Si_{100}$ was synthesized at 1.5 GPa and 800 °C from 24 $BaSi_2$ and 52 Si.[16] This applied pressure is lower than $P=3$ GPa at 800 °C previously used for the synthesis of Ba_8Si_{46}.[5] $Ba_{24}Si_{100}$ showed a metallic conductivity and a blackish or metalliclike luster.[16] High-pressure experiments were carried out by using a diamond anvil cell (DAC) with a metal gasket. The hole of the gasket serving as the sample chamber was set to about 100 μm in diameter and 100 μm in thickness. Since the pressure synthesized $Ba_{24}Si_{100}$ was obtained as a single phase of 20 μm in size, a few pieces of the samples were placed into the chamber of DAC and loaded with a ruby chip for pressure measurements. For fine Raman measurements of $Ba_{24}Si_{100}$, 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.[12–14,29] Raman spectra were measured in a backscattering 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}.

III. RESULTS AND DISCUSSION

The type-III Si clathrate crystallizes in the cubic space group $P4_132(O^7)$.[15–18] The group theoretical analysis predicts that the first-order (one-phonon) Raman-active modes of Si framework vibrations are $12A_1+25E+37T_2$ (74 peaks), where A_1 modes are singly degenerate, E are doubly degen-
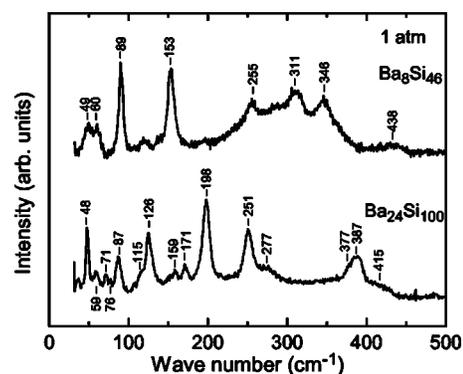
FIG. 2. Raman spectrum of $Ba_{24}Si_{100}$ at 1 bar and 296 K with that of Ba_8Si_{46} clathrate[12] for comparison.

erate, 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 spectrum of $Ba_{24}Si_{100}$ at ambient pressure and 296 K is shown in Fig. 2 with that of Ba_8Si_{46} clathrate[12] 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. Furthermore, our $Ba_{24}Si_{100}$ specimen is not a single crystal, therefore, we cannot make the symmetry-specific polarization measurement at present, which is necessary for mode assignments. Raman spectra at various pressures up to 27 GPa and their Raman frequencies as a function of pressure are shown in Figs. 3 and 4, respectively. The peak at 115 cm^{-1} can be assigned to the lowest frequency framework vibration (see open circles in Fig. 3), because it shows the softening with pressure (Fig. 4), similar to the following four cases; a peak at 153 cm^{-1} of Ba_8Si_{46}[12] (Fig. 2), a peak at 177 cm^{-1} of K_8Si_{46},[13] a peak at 133 cm^{-1} of $I_8Si_{44}I_2$,[14] and a peak near 134 cm^{-1} in Si-136 clathrate studied by the theory[30] and Raman measurement.[31] These mode softenings seem to be the benchmark of Si clathrates and also of cubic-diamond Si,[32] showing tetrahedral bonds.

As seen in Fig. 1, there are three different sites for the guest Ba atoms. Hence we can expect three kinds of vibrations associated with the Ba atoms at low-frequency region. Ba1 occupies a Si_{20} cage, which is the same as the small cages (Si_{20}) of Ba_8Si_{46}. We can find that a peak of 87 cm^{-1} of $Ba_{24}Si_{100}$ shows good correspondence to the 89 cm^{-1} peak of Ba_8Si_{46}, which is due to Ba vibrations in Si_{20} small cages.[12] Ba3 occupies a Si_{20} open cage, which is closely related to the Si_{24} cage in type-I structure because the Si_{20} open cage can be made by removing four Si atoms from the Si_{24} cage. Thus, the local structure surrounding the Ba3 atom can be regarded as the same as that for Si_{24} cage in Ba_8Si_{46}. Therefore, we
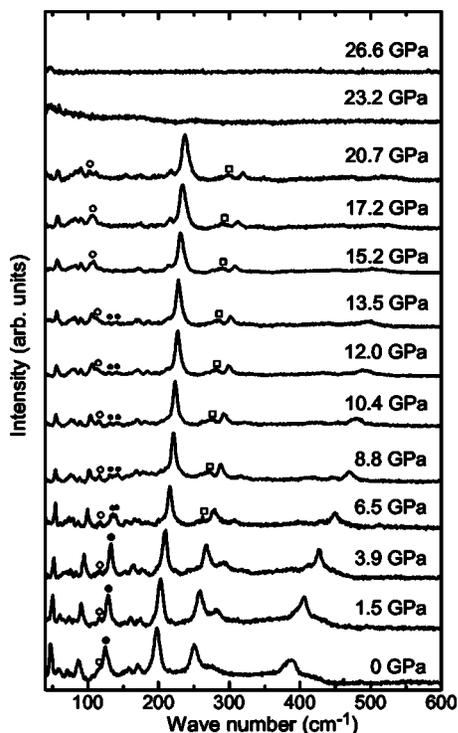
FIG. 3. Raman spectra of $Ba_{24}Si_{100}$ at various pressures up to 27 GPa and 296 K. For open and solid circles and open squares, see text.

also confirm that 59 cm^{-1} and 48 cm^{-1} peaks of $Ba_{24}Si_{100}$ are associated with the vibrations of Ba3 atoms in Si_{20} open cages, by comparison with 60 cm^{-1} and 49 cm^{-1} bands in Si_{24} large cages of Ba_8Si_{46}.[12] Here, the corresponding vibra-
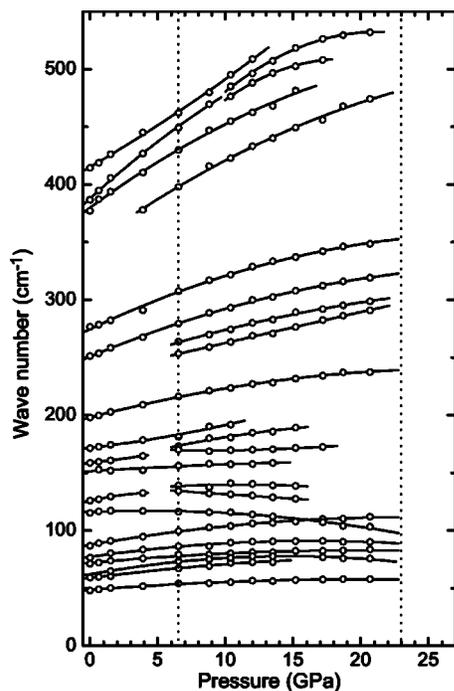
FIG. 4. Pressure dependence of Raman frequency shifts of $Ba_{24}Si_{100}$ at 296 K. Vertical dotted lines indicate phase transition pressures. Solid lines are drawn to guide the eye.

tional frequencies in $Ba_{24}Si_{100}$ and Ba_8Si_{46} are surprisingly close to each other, because this is reasonable by considering that the corresponding sizes of cages in $Ba_{24}Si_{100}$ and Ba_8Si_{46} are very close to each other:[16] Si_{20}; average bond lengths of Ba1-Si, 3.408 Å and of Ba-Si, 3.362 Å, respectively, Si_{24}; (open Si_{20}) average bond lengths of Ba3-Si, 3.748 Å and of (Si_{24}) Ba-Si, 3.706 Å, respectively. The remaining assignment is the vibrations at 76 cm^{-1} and 71 cm^{-1}. Let us investigate a Ba2 atom inside a Si_8 distorted cube. The distances between Ba2 and host Si atoms are in a range of 3.429–3.928 Å.[16] The space of Ba2 atoms inside the channels are much ampler than those located inside the Si_{20} cage, and there exist only eight Si atoms enclosing a guest Ba2 atom (see Fig. 1). Therefore, it seems that the vibrational bands associated with Ba2 atoms are at 76 cm^{-1} and 71 cm^{-1}. In general, Raman intensities of guest vibrational bands are proportional to the number of atom or molecule inside each cage in the unit cell; this is the successful case for gas clathrate hydrates.[33] For Si clathrates we cannot estimate Raman bands by this standard because of strong guest-host couplings.[12–14] For exact assignment of 76 cm^{-1} and 71 cm^{-1} bands, the theoretical calculation of phonon density of states[27] is needed in a future.

Next, we investigate pressure-induced phase transitions. As indicated by large and small solid circles in Fig. 3, the framework vibration of 126 cm^{-1} at ambient pressure, with increasing pressure, splits into two peaks at about P =6.5 GPa and their peak frequencies show softening with pressure (Fig. 4). This splitting is due to the resolution of degenerate E or T_2 mode. At the same time, new band appeared at about 260 cm^{-1} as indicated by open squares (Fig. 3). Furthermore, the band intensities associated with the vibrations of Ba atoms become weak above 7 GPa at low-frequency region, particulary 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[12] has been recently interpreted by the off-center displacement of Ba atoms in the large Si_{24} cages, confirmed by the x-ray absorption.[26] Furthermore, we are also interested in the phase transition of $Ba_{24}Ge_{100}$ around 200 K at 1 bar, which is due to the Ge—Ge bond breaking combined with the displacement of neighboring Ba atoms to the split positions.[20,22,23] However, we cannot compare these results to our present study because there is no phase transition for $Ba_{24}Si_{100}$ at 1 bar. Therefore, we need high-pressure Raman studies for $Ba_{24}Si_{100}$ at low temperatures and for $Ba_{24}Ge_{100}$ at room and low temperatures.

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 or not the disappeared Raman spectra of $Ba_{24}Si_{100}$ can recover. As seen in Fig. 5, Raman spectrum did not re-
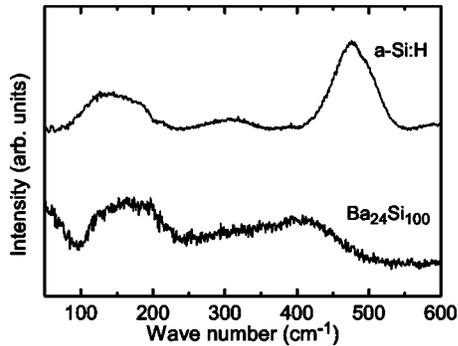
FIG. 5. Raman spectra at 1 bar for hydrogenated amorphous Si (a-Si:H) and for amorphous $Ba_{24}Si_{100}$ decompressed from P =27 GPa (an amorphous phase) to ambient pressure.

cover to those before compression and looks like the spectrum of an amorphous Si.[34–36] 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 is due to its metallic property at high pressures. This irreversible transformation to the amorphous phase is a marked contrast to the case of H_2O clathrates,[37] where the repulsive forces between the guest and the water host are mainly responsible for the reversible transition to the original structure under decompression. The irreversible phenomena of the pressure-induced amorphization had been commonly observed on type-I Si clathrates: Ba_8Si_{46} at about 40 GPa by x-ray,[26] K_8Si_{46} at 32 GPa by x-ray,[27] and $I_8Si_{44}I_2$ at 40 GPa by Raman scattering.[14,28] On a recent study of K_8Si_{46}, Tse *et al.*[27] suggested that the guest-host interaction in the amorphous phase is different from that in water clathrates. We like to emphasize that the amorphization pressure of 23 GPa for type-III $Ba_{24}Si_{100}$ is significantly lower than those of 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).

To investigate the amorphous state in $Ba_{24}Si_{100}$, we measured the Raman spectrum of hydrogenated amorphous Si (a-Si;H) for the comparison. As shown in Fig. 5, we observed a-Si:H Raman spectrum, which is almost the same as previous results;[34–36] we confirmed TA-, LA-, LO-, and TO-like phonon bands around 145, 310, 385, and 475 cm^{-1}, respectively, where the Raman selection rule is relaxed owing to the structural disorder of amorphous states. For the spectrum of amorphous $Ba_{24}Si_{100}$, we can point out that (i) TA-like phonon band shifted to higher frequency at about 170 cm^{-1} and (ii) TO-like phonon band shifted to lower frequency at about 415 cm^{-1}, and it shows weak Raman inten-

sity by comparing to 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.*[35] 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 cagelike 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,[16] 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.

IV. SUMMARY

We performed the first Raman studies of type-III silicon clathrates ($Ba_{24}Si_{100}$) at ambient pressure and high pressures up to 27 GPa and assigned low-frequency vibrations associated with Ba atoms inside three kinds of Si_{20} cage, Si pseudocubic space, and Si_{20} open cage by comparing to those of type-I Ba_8Si_{46}. The Si framework vibrations of $Ba_{24}Si_{100}$ 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. $Ba_{24}Si_{100}$ clathrate becomes irreversibly amorphous at pressures above 23 GPa. This pressure is compared to those of 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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