

High-pressure Raman study of the iodine-doped silicon clathrate $I_8Si_{44}I_2$ Hiroyasu Shimizu,^{1,2*} Tetsuji Kume,¹ Toyoki Kuroda,² Shigeo Sasaki,^{1,2} Hiroshi Fukuoka,³ and Shoji Yamanaka³¹*Department of Materials Science and Technology, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan*²*Environmental and Renewable Energy Systems, Graduate School of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan*³*Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higasi-Hiroshima 739-8527, Japan*

(Received 4 August 2003; published 18 December 2003)

Raman scattering measurements of an iodine-doped $I_8Si_{44}I_2$ clathrate have been performed at pressures up to 28 GPa and 296 K. We found two Raman peaks at 75 and 101 cm^{-1} associated with the vibrations of guest I atoms inside the host Si cages, and observed some framework vibrations around 120–500 cm^{-1} . These characteristic Raman bands and their pressure dependence are investigated in consideration of our recent Ba_8Si_{46} studies. The lowest-frequency framework vibration at 133 cm^{-1} shows the softening with pressure, which seems to be the common feature of Si clathrates. A strong and broad Raman band centered at 461 cm^{-1} is identified to the highest-frequency framework vibration, which is likely intensified and broadened by the considerable framework distortion due to the replacement of framework Si with larger I atom. No obvious pressure-induced phase transition was found up to 28 GPa. The guest-host interactions are investigated by the present vibrational properties and are compared with those of previous neutron studies of $I_8Si_{44}I_2$.

DOI: 10.1103/PhysRevB.68.212102

PACS number(s): 62.50.+p, 63.20.Pw

Silicon clathrates¹ are covalent bonded cagelike crystals composed of face-sharing Si_{20} , Si_{24} , and Si_{28} polyhedra.² Doping of the guest into low-density clathrates can be achieved by filling up the cages by some metals such as Na, K, and Ba. These materials are isostructural with hydrogen-bonded H_2O clathrates (structures I and II).³ In fact, two types of silicon clathrates are commonly observed labeled Si-46 (type-I) and Si-136 (type-II). The Si_{46} is, for example, formed by a simple cubic arrangement of two small Si_{20} and six large Si_{24} polyhedra per unit cell. The resulting formula is M_8Si_{46} if host Si cages are fully occupied by guest atoms (M). In these Si clathrates, the electron-electron, electron-phonon, and phonon-phonon coupling mechanisms between the encaged atoms and the framework Si are key points to understand their characteristic properties such as superconductivity,⁴ wide band gap,⁵ high thermoelectric power,⁶ low compressibility,⁷ and pressure stability.⁸ These couplings can be explored in part by the study of high-pressure Raman scattering through their vibrational properties of both guest atoms inside the cages and the host Si framework.

Recently, an iodine doped $I_8Si_{44}I_2$ clathrate has been prepared by Reny *et al.*⁹ under the conditions of high temperature and high pressure, which is the first case of *p*-type silicon clathrate by doping acceptor I atoms more electronegative than the host Si. In the $I_8Si_{44}I_2$, the I atoms occupy all clathrate cages, and 11% of the Si (2) site (i.e., 16i site in the $Pm\bar{3}n$ space group which presents three distinct crystallographic sites; 6c, 16i, and 24k) in the Si framework are replaced with the larger I atoms than host Si atoms.¹⁰ The “ideal” I_8Si_{46} clathrate is not still found experimentally.

For the experimental studies of $I_8Si_{44}I_2$, Miguel *et al.*¹¹ measured x-ray diffraction at high pressures up to 35 GPa and room temperature, and estimated the pressure dependence of the cell parameter and the average first-neighbor Si-Si distance. They found only the slight change in the cell parameter at 17 GPa and confirmed more stable cage struc-

ture than Na_8Si_{46} and Ba_8Si_{46} . Reny *et al.*¹² measured the inelastic neutron scattering at ambient pressure and 300 K, and provided the spectra responsible to the phonon density of states (PDOS). More importantly, they concluded the increase of the hybridization between guest and framework in order of Na, K, Ba, and I guest atoms by comparing the intensities (i.e., PDOS) of low-frequency modes, corresponding to the vibrations of encaged atoms.

For the theoretical study of “ideal” I_8Si_{46} , Connétable *et al.*¹³ presented first-principles calculations of the structural and electronic properties and predicted that the strong hybridizations between the iodine and Si network orbitals result in a large opening of a 1.75 eV band gap, in contrast with Na- and Ba-doped clathrates showing metallic behavior.

In this paper, we present the high-pressure Raman study of the iodine-doped $I_8Si_{44}I_2$ clathrate at pressures up to 28 GPa and 296 K. Two Raman peaks at 75 and 101 cm^{-1} are found to be responsible to the low-frequency vibrations of guest I atoms inside the large Si_{24} and small Si_{20} cages, respectively. The framework Si vibrational bands are observed around 120–500 cm^{-1} . The characteristic properties of the lowest-frequency and the highest-frequency framework bands, and their pressure dependence are investigated in consideration of our recent high-pressure Raman study of Ba_8Si_{46} .¹⁴ The guest-host interactions are discussed by comparing them with the previous x-ray and neutron experiments of $I_8Si_{44}I_2$.^{11,12}

The sample of the iodine clathrate was synthesized at 5 GPa and 700 °C from Si powder and iodine,^{9,10} and its stoichiometry was determined to be $I_8Si_{44}I_2$ by x-ray Rietveld refinement. Our sample of pure $I_8Si_{44}I_2$ was fine powder with a blackish or metallic-like luster, but sometimes we found an orange-colored one due to the impurity contamination. We pressed the selected pure $I_8Si_{44}I_2$ powders into dense polycrystalline pellets for the Raman measurements.

High-pressure experiments were carried out by using a diamond anvil cell (DAC) with a metal gasket. The hole of

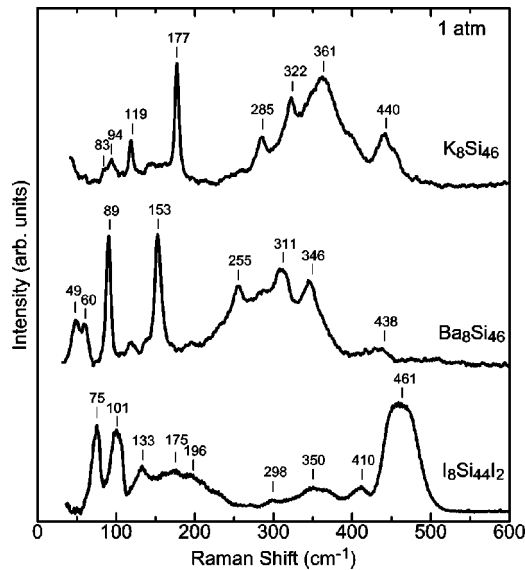


FIG. 1. Raman spectrum of $I_8Si_{44}I_2$ at 1 bar and 296 K with those of K_8Si_{46} (Ref. 16) and Ba_8Si_{46} (Ref. 14) clathrates for comparison.

the gasket serving as the sample chamber was set to about 100 μm in diameter and 100 μm in thickness. A few pieces of the pellet samples were placed into the chamber of DAC, and loaded with a ruby chip for pressure measurements. For fine measurements of $I_8Si_{44}I_2$ Raman signals which were very weak due to its semiconductor property, we used the dense argon as the pressure transmitting medium that is free from Raman signals.^{14,15} Raman spectra were measured in a backscattering geometry with a micro-Raman spectrometer (JASCO NR 1800) equipped with a triple monochromator and a charge-coupled-device (CCD) detector. The 514.5 nm line of an Ar-ion laser 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 vacuum cell to remove undesirable Raman lines of gaseous N_2 and O_2 rotation below 200 cm^{-1} . In order to avoid the stray light in high-pressure Raman measurements, we employed different laser lines of 488.0 and 532.0 nm, and carefully confirmed our Raman spectra to be intrinsic.

Raman scattering spectrum of $I_8Si_{44}I_2$ at ambient pressure and 296 K is shown in Fig. 1 with those of K_8Si_{46} (Ref. 16) and Ba_8Si_{46} (Ref. 14) clathrates for comparison. It can be clearly confirmed from K_8Si_{46} and Ba_8Si_{46} spectra that their Raman frequencies are sensitive to the guest atoms. For $I_8Si_{44}I_2$, just looking different from the others, we can find two sharp peaks at 75 and 101 cm^{-1} , a weak peak at 133 cm^{-1} , some broad structured bands around 150–420 cm^{-1} , and a strong and broad band centered at 461 cm^{-1} . Raman spectra at various pressures up to 28 GPa and their Raman frequencies as a function of pressure are shown in Figs. 2 and 3, respectively.

Two Raman peaks at 75 and 101 cm^{-1} can be identified to correspond to the low-frequency vibrational modes produced by the motions of I atoms accommodated in large and small cages, respectively, because of their sharp peaks, their good correspondence to those of Ba_8Si_{46} , and their pressure

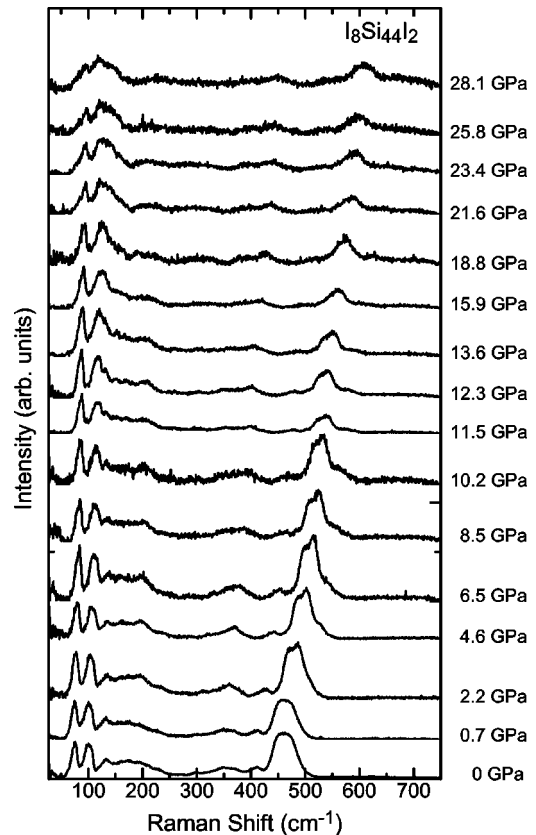


FIG. 2. Raman spectra of $I_8Si_{44}I_2$ at various pressures up to 28 GPa and 296 K.

dependence of Raman frequencies comparable with those of Ba_8Si_{46} ¹⁴ (see Raman peaks at 49, 60, and 89 cm^{-1} in Figs. 1 and 4). However, the PDOS of $I_8Si_{44}I_2$ measured by the neutron scattering¹² did not show a peak related to the vibration of engaged I atoms, in contrast to the present Raman spectra.

The peak at 133 cm^{-1} can be assigned to the lowest-frequency framework vibration, because it shows the softening with pressure (see Figs. 3 and 4), similar to the following two cases; a peak at 153 cm^{-1} of Ba_8Si_{46} clathrate¹⁴ (see Figs. 1 and 4) and a peak near 134 cm^{-1} in a type-II Si-136 clathrate studied by the theory¹⁷ and Raman measurement.¹⁸ These mode softenings seem to be the benchmark of Si clathrates and also of cubic-diamond Si,¹⁹ showing tetrahedral bonds.

As seen in Fig. 1, some broad structured bands of $I_8Si_{44}I_2$ around 120–420 cm^{-1} are remarkable in comparison with the corresponding spectra of K_8Si_{46} and Ba_8Si_{46} . This seems to be due to the considerable framework distortion induced by the presence of the larger I atoms on some of the host Si sites, which is mentioned later in details.

An outstanding band at 461 cm^{-1} of $I_8Si_{44}I_2$ in Figs. 1 and 2 can be assigned to the highest-frequency framework vibration. Here, at the beginning we checked the possible assignment of the iodine vibration²⁰ due to I-I bond formation, but there was no such confirmation. Let us investigate the origin of this strong and broad band. The Raman intensity is proportional to the square of the polarization change

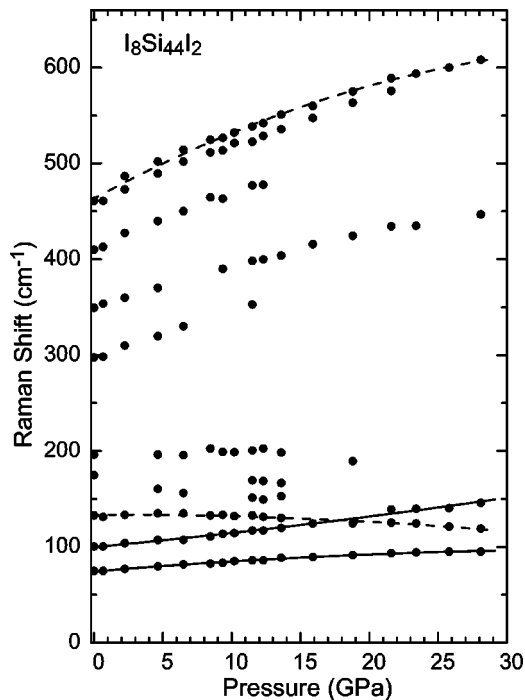


FIG. 3. Pressure dependence of Raman frequency shifts of $I_8Si_{44}I_2$ at 296 K. Solid lines show the low-frequency vibrations associated with guest I atoms inside the cages. Low- and high-frequency broken lines show the lowest- and the highest-frequency framework vibrations. This lowest framework vibration shows the softening with pressure.

with atomic displacement, and is also dominated by Raman selection rules. Therefore, we will first consider the structural details of the $I_8Si_{44}I_2$ clathrate. As mentioned above, large I atoms are selectively sited at 11% of Si (2) sites in the framework. Recently, Tse²¹ has calculated the optimized structure of $I_8Si_{44}I_2$ at ambient conditions. From its result the distances of Si-Si and Si-I of the framework were estimated as follows: the Si-Si distance ranges from 2.26 to 2.38 Å, but the Si-I distance does from 2.68 to 3.02 Å. These Si-I bond lengths are surprisingly large. Therefore, there should be the considerable framework distortion, which can significantly induce the electronic polarization. As a result, we can expect the increase in Raman intensity for the framework mode associated with their bond stretchings between a pair of Si (I) atoms in the framework. And, the breakdown of Raman selection rules induced by this distortion of crystal lattice leads possibly to the strong and broad band. At the same times, various Si-Si (I) bond lengths ranging from 2.26 to 3.02 Å result in the wide-frequency distribution of stretching lines.

As for the pressure-induced phase transition in $I_8Si_{44}I_2$, we could not clearly confirm it up to 28 GPa. However, as seen in Fig. 2, Raman bands around 120 cm^{-1} show the broadening above 18 GPa, which may be corresponding to the slight change in the cell parameter at 17 GPa found by Miguel *et al.*¹¹ The present result supports that the $I_8Si_{44}I_2$ clathrate is more stable than Ba_8Si_{46} at high pressures.¹¹

Mélinon *et al.*²² measured the PDOS of Na_8Si_{46} and K_8Si_{46} clathrates by inelastic neutron scattering, and reported that the low-frequency acoustic mode [AM] shows a blue-

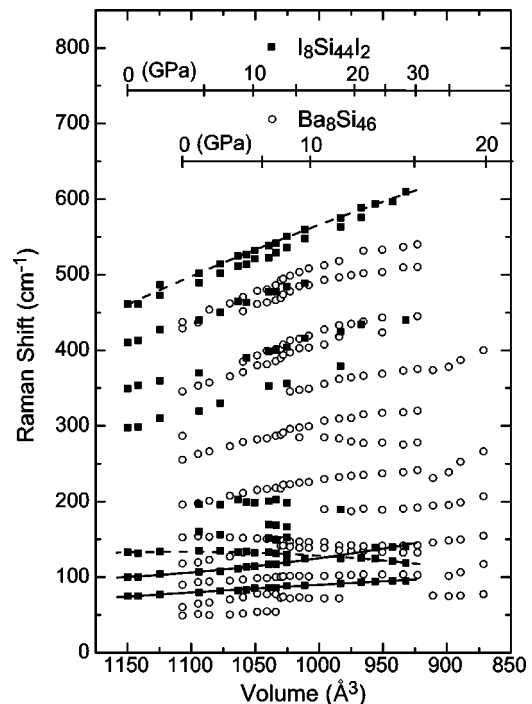


FIG. 4. Volume dependence of Raman frequency shifts of $I_8Si_{44}I_2$ and Ba_8Si_{46} (Ref. 14) at 296 K. Solid squares and open circles represent the data of $I_8Si_{44}I_2$ and Ba_8Si_{46} , respectively. Solid lines show the low-frequency modes associated with guest I atoms inside the cages of $I_8Si_{44}I_2$. Low- and high-frequency broken lines show the lowest- and the highest-frequency framework vibrations of $I_8Si_{44}I_2$. Each scale of applied pressure is shown at the upper part in this figure.

shift, while the high-frequency optical mode [OM] indicates a redshift with respect to the diamond silicon structure.²³ They also suggested that the redshift of this OM frequency is responsible for the degree of guest-host coupling. Here, they used the terms of acoustic and optical modes as a matter of convenience.^{12,22} Recently, Reny *et al.*¹² estimated the degree of guest-host coupling in Si clathrates from the following two results of their PDOS measurements: (1) Softening of the framework stretching mode; the guest-host coupling diminishes the restoring stretch force and reduces the vibrational frequency.²⁴ (2) Intensity of the vibrations of guest atoms inside the cages; with an increasing coupling, these vibrational bands broaden progressively, to finally disappear in the PDOS, i.e., the amplitude of these modes is inversely proportional to the guest-host coupling. They concluded the highest guest-host coupling in $I_8Si_{44}I_2$ among Na-, K-, Ba-, and I-doped Si clathrates, which is based upon no signal of the low-frequency mode¹² corresponding to the vibration of engaged I atoms.

Raman spectra do not necessarily coincide with the PDOS determined by the neutron scattering, because the selection rules exist in Raman scattering while the absence of such rules in the neutron experiment, allowing the total view of the PDOS. Furthermore, Raman experiments probe vibrational modes only near the Brillouin zone-center Γ . The following three key signals as (1) the vibrational bands associated with guest atoms, (2) the lowest-frequency framework

band (showing the softening in frequency), and (3) the highest-frequency framework band are clearly observed to investigate the guest-host interactions in these Si clathrates (see Fig. 1). As for the first case of the vibrations of guest atoms inside the cages, their frequencies are mainly determined by their masses of guest atoms (K; 39.1, I; 126.9, and Ba; 137.4). Therefore, the iodine frequencies of $I_8Si_{44}I_2$ (i.e., 75 and 101 cm^{-1}) seem to be reasonable by considering their frequencies of K_8Si_{46} (83, 94, and 119 cm^{-1}) and Ba_8Si_{46} (49, 60, and 89 cm^{-1}). Furthermore, the existence of their sharp and strong iodine peaks in $I_8Si_{44}I_2$ may suggest that the motion of guest I atoms is not substantially suppressed by the effect of guest-host interaction, that is, unlikely the highest iodine-framework interaction. Next, as seen in Figs. 1 and 4, high-frequency framework vibrations of Ba_8Si_{46} (346–430 cm^{-1}) show the redshift with respect to those of $I_8Si_{44}I_2$ (410–461 cm^{-1}) but the volume dependences of their frequencies are almost the same, which imply that the guest-host interaction may be stronger in Ba_8Si_{46} than in $I_8Si_{44}I_2$. The superconductivity was found in Ba_8Si_{46} ⁴ and $Ba_8Ag_xSi_{46-x}$ ($x < 4$)²⁵ clathrates, but the absence in $I_8Si_{44}I_2$ down to $T = 2$ K.⁹ If the strong hybridization between the guest atoms and Si framework plays an important role in its appearance of superconductivity,¹² more detailed studies about the guest-host interactions are required for $I_8Si_{44}I_2$ and “ideal” I_8Si_{46} clathrates with the careful investigation of the effect of stoichiometry.²⁶

In conclusion, we present the vibrational properties of the iodine doped $I_8Si_{44}I_2$ up to 28 GPa and 296 K. Two sharp Raman peaks were clearly observed at 75 and 101 cm^{-1} , which were assigned to the vibrations of engaged I atoms. The lowest framework vibration at 133 cm^{-1} shows the softening with pressure, which seems to be the common feature of Si clathrates. The strong and broad Raman band centered at 461 cm^{-1} was understood as the highest-frequency framework mode, which was characterized by the substantial lattice distortions due to I atoms replaced in the Si framework. No obvious pressure-induced phase transition was found, which supports the previous conclusion of the stable cage-structured iodine clathrate. The vibrational properties imply that the guest-host interaction is likely stronger in Ba_8Si_{46} than in $I_8Si_{44}I_2$, which was discussed with the recent investigation by the PDOS of neutron study. More studies about the guest-host interactions in $I_8Si_{44}I_2$ and “ideal” I_8Si_{46} clathrates are needed to understand the appearance of the superconductivity in Si clathrates.

We would like to thank Dr. John S. Tse of NRC of Canada and Dr. A. San-Miguel of University of Lyon for their valuable discussions. This work was partially supported by the KAKENHI (Contract No. 15340095) and the COE Research (Contract No. 13CE2002) of the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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