Structural properties and thermodynamic stability of Ba-doped silicon type-I clathrates synthesized under high pressure

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We present a joint experimental and theoretical study of the stability and structural properties of Ba-doped silicon type-I clathrates Ba₈Si₄₆ synthesized under high pressures. The thermodynamic stability of Ba₈Si₄₆ under high pressure has been discussed from the total energy calculations of some barium silicides within the local density approximation (LDA). We have theoretically found that pressure favors the formation of the clathrate phase as experimentally observed. We have also performed a synchrotron x-ray-diffraction experiment of Ba₈Si₄₆ prepared under high pressures. Some of the missing endohedral Ba elements in the small cage of Si(20) have been observed by x-ray crystallography, while big cages of Si(24) are found to be completely occupied by Ba elements. The stabilization energies of Ba atoms in the endohedral sites estimated within the present LDA calculation suggest that this is presumably attributed to the energetical site preference of Ba atoms between d(6) and a(2) sites. In addition, the isothermal parameter of Ba in the big cage of Si(24) has been found to be larger than that in the small Si(20) unit, which is consistent with some theoretical predictions in earlier works.

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I. INTRODUCTION

Expanded-volume silicons and/or germaniums, called clathrates, have drawn considerable interest over the past few years. Clathrates are covalent-cage-like assembled crystals analogous to fullerene families. These structures form large polyhedral cavities that can accommodate guest elements allowing a wide variety of novel compounds. Though two forms of clathrates such as Si₄₆ (type I) and Si₃₄ (often referred to as Si₁₃₆, type II) have been known for many years, two experimental phenomena recently confirmed in clathrates have triggered intensive investigation. One is the discovery of superconductivity in the metal-doped clathrate Ba₈Na₅Si₄₆, and the other is the potential of clathrates for thermoelectric applications, where the figure of merit can be made arbitrarily large with the “phonon glass and electron crystal (PGEC)” mechanism. Clathrate structures are also considered as potential candidates for the band gap engineering based on group-IV elements. This is because the guest-free clathrate structures such as Si₃₄, Si₄₆, Ge₃₄, and Ge₄₆ have been theoretically predicted to have a much larger band gap than their ground state of cubic diamond phase. Recently, these theoretical predictions have been experimentally borne out by Gryko et al.

It has been shown that some metal-doped clathrate compounds could be synthesized in a controllable manner, resulting in a desired crystal structure and a chemical composition. For example, Yamanaka et al. have utilized high pressures to succeed in the synthesis of “bulk” barium-doped binary silicon clathrate compounds Ba₈Si₄₆ instead of “powder” compounds. The researchers involved have also observed type-II superconductivity with the critical temperature (T_c) of approximately 8 K in this silicon clathrate compound. In addition, in order to clarify a cause of the superconductive property in these Ba-doped silicon clathrates, we have also reported the electronic structure of Ba₈Si₄₆ and Na₈Si₄₆ using the first-principles calculation. Though the conventional x-ray-diffraction and the Rietveld refinement of Ba₈Si₄₆ synthesized under high pressures were presented in our previous work, the microstructural properties such as occupations and/or accurate isotropic thermal parameters of the endohedral Ba atoms in this clathrate compound have not been reported. This is because our previous experiment had a comparatively large signal/noise (S/N) ratio due to using the conventional x-ray-diffraction powder method. The thermal parameters, or atomic displacement parameters (ADP’s), of endohedral atoms are important aspects of clathrate compounds, when considering the PGEC mechanism for thermodynamic applications.

In this work, we present a joint experimental and theoretical study of the stability and structural properties of Ba-doped silicon type-I clathrates Ba₈Si₄₆ synthesized under high pressures. We have carried out total energy calculations of some barium silicides within the local density approximation (LDA), and discussed why the Ba-doped Si clathrate Ba₈Si₄₆ can be synthesized utilizing high pressures. In addition, we have performed a synchrotron x-ray-diffraction experiment of the Ba₈Si₄₆ prepared under high pressures, using...
the BL02B2 powder-diffraction beam line at SPring8 (Hyogo, Japan). We will report occupations and isotropic thermal parameters of the endohedral Ba atoms in this clathrate compound. We have found some of the missing endohedral Ba elements in the small cage of Si(20). The isothermal parameter of Ba in the big cage of Si(24) has been found to be larger than that in the small Si(20) unit, which is consistent with some theoretical predictions in earlier works.23–26

II. METHODOLOGY

A. Theoretical

The main purpose of the present theoretical calculations is to examine equations of state of some barium silicides in order to discuss the thermodynamic stability of the clathrate phase under high pressures. We have calculated total energies versus volume for bcc-Ba, cd-Si (cubic diamond Si), BaSi, BaSi2, Si46, and Ba8Si46. Since a nonstoichiometric compound of Ba8Si46 has been experimentally prepared utilizing high pressures as will be described later, we have also calculated energetics and electronic states of Ba2Si24 and Ba8Si46, in which endohedral Ba atoms at d(6) or a(2) sites have been excluded from Ba8Si46. BaSi2 is known to have three crystallographic forms at ambient conditions orthorhombic, cubic, and trigonal.27 The orthorhombic BaSi2 is stable at ambient conditions, and the others are metastable.27 We have experimentally found that the arc-melted prepressured sample is a mixture of the orthorhombic BaSi2 and cd-Si,7 therefore, the orthorhombic BaSi2 has been adopted for the present calculation.

Our calculations are based on the ab initio pseudopotential theory within the LDA. We adopted the ultrasoft pseudopotential proposed by Vanderbilt.28 The Perdew-Zunger parametrization29 of the LDA was employed. We used the CASTEP code30 in order to self-consistently solve the pseudopotential Schrödinger equation. From the convergence tests of total energies, we chose the kinetic energy cutoff of 300 eV of plane-wave basis sets for all systems studied. For the Brillouin zone sampling, we adopted 84, 28, 27, 24, 10, and 20 special k points for bcc-Ba, cd-Si, BaSi, BaSi2, Si46, and Ba-doped type-I clathrates (Ba2Si146, Ba6Si146, and Ba8Si146), respectively. Optimized geometry and electronic structure of Ba8Si46 have already been reported in our previous work (see also in Table II).20 The bulk moduli were deduced by applying a fitting procedure of the total energies versus volume to the Murnaghan’s equation of state.

B. Experimental

The bulk samples of Ba8Si46 crystal were synthesized by a method utilizing high pressures reported in the previous work.7 The present sample was synthesized with the pressure applied by 3 GPa at 800 °C. Powder samples of Ba8Si46 for x-ray-diffraction experiments were prepared by the precipitation method and a fine powder was seeded in 0.3 mm {f} silica glass capillary. The x-ray-powder-diffraction data was measured by the synchrotron radiation powder method using the large Debye Scherrer Camera with Imaging Plate at BL02B2 in SPring8.31 The wavelength of the incident x-ray is 0.4979 Å. In order to correct data with high counting statistics, the exposure time was 25 min. The crystal structure was refined by the Rietveld method, which was carried out using the computer program RIETAN97 β.32 The initial crystal model for the Rietveld refinement was referred to the model in our previous work.7

III. RESULTS AND DISCUSSION

A. Theoretical energetics

We show schematic illustrations of crystal structures of barium silicides calculated in the present work in Fig. 1. The resulting equilibrium structures and inequivalent atomic positions are listed in Tables I and II. Though all of the lattice constants calculated here are slightly shorter than those of the experimental values, which is the well-known property using the LDA approximation,33–35 the calculated atomic positions for BaSi, BaSi2, and Ba8Si46 agree well with the experimental positions.7,36,37 In addition, the calculated lattice constant ratios a:b:c, for BaSi and BaSi2 are 1: 2.38: 0.81
TABLE I. Calculated equilibrium structures and inequivalent atomic positions for bcc-Ba, cd-Si, BaSi, and BaSi$_2$. The notation of atomic positions follows that of the International Tables for Crystallography. Experimental values of barium silicides (BaSi and BaSi$_2$) are also listed.

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<th>Symmetry</th>
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<th>cd-Si</th>
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<tbody>
<tr>
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<td>Fd$ar{3}$m (227)</td>
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<td>Ba:</td>
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<th>Exp.: BaSi$_a^a$</th>
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<tbody>
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<td>Cmcm (63)</td>
</tr>
<tr>
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<td>c(4)</td>
<td>a = 4.951, b = 11.787, c = 4.019</td>
</tr>
<tr>
<td>Ba:</td>
<td>c(4)</td>
<td>x = 0; y = 0.858; z = 3/4</td>
</tr>
<tr>
<td>11.240</td>
<td>5.043</td>
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</tbody>
</table>

<table>
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<tr>
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<th>BaSi$_2$</th>
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<td>Pnma (62)</td>
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<td>Si:</td>
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<td>a = 8.710, b = 6.585, c = 11.240</td>
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<tr>
<td>Ba:</td>
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<tr>
<td>4.919</td>
<td>8.920</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reference 36.

$^b$Reference 37.

...and 1: 0.76: 1.29, which can be compared with the experimental values of 1: 2.37: 0.82 for BaSi and 1: 0.76: 1.30 for BaSi$_2$, respectively.36,37

Calculated lattice constants of Ba-doped type-I clathrates have been slightly increased with the contents of endohedral Ba atoms as shown in Table II. It has been found, however, that the elongation of lattice constant of Ba$_8$Si$_{46}$ is only 1.2% compared with guest-free Si$_{46}$. Thus, the lattice constants of these clathrate structures are assumed to be not so sensitive to the existence of endohedral metals in the cage structures. In Na-doped type-II Si clathrates, Ramachandran et al. have experimentally observed only a ~0.5% increase in the unit cell edge upon progressing from Na$_4$Si$_{136}$ to Na$_3$Si$_{136}$.38 These results suggest that the cage size in clathrate systems strongly depend on the framework atoms,23 but weakly on the “guest” atoms. This property is also experimentally pointed out in Ge clathrate compounds by Nolas et al.,10 in which they also suggest that appropriate “guest” atoms incorporated into the polyhedral cavities might change thermal conductivities for thermoelectric applications due to their dynamical “ rattling” modes.

The stabilization energy of the endohedral Ba atoms in the Ba-doped silicon clathrate is defined as the total energy of the clathrate subtracted from the sum of the total energies of the guest-free clathrate (Si$_{46}$) and isolated Ba atoms. In the present work, the total energy of the isolated Ba atom is estimated using the total energy of bcc-Ba and its experimental cohesive energy. The calculated stabilization energies of the endohedral Ba atoms are 3.3, 3.8, and 3.7 eV/atom for Ba$_4$Si$_{46}$, Ba$_8$Si$_{16}$, and Ba$_8$Si$_{16}$, respectively. Therefore, Ba[d(6)] in the large cage of Si(24) is energetically stabler than Ba[a(2)] in the small unit of Si(20) by about 0.5 eV/

*TABLE II. Calculated equilibrium structures and inequivalent atomic positions for clathrate phases of Si$_{46}$: Ba$_4$Si$_{46}$, Ba$_8$Si$_{16}$, and Ba$_8$Si$_{16}$. The notation of atomic positions follows that of the International Tables for Crystallography. Calculated values of Si$_{46}$ and Ba$_8$Si$_{16}$ listed here are from our previous work of Ref. 20.

<table>
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<th>Symmetry</th>
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<th>Ba$<em>8$Si$</em>{46}^a$</th>
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<td>Lattice constant (Å)</td>
<td>Pm$ar{3}$m (223)</td>
<td>Pm$ar{3}$m (223)</td>
<td>Pm$ar{3}$m (223)</td>
<td>Pm$ar{3}$m (223)</td>
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<tr>
<td>Si:</td>
<td>e(6)</td>
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<td>x = 1/4; y = 0; z = 1/2</td>
</tr>
<tr>
<td></td>
<td>i(16)</td>
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<td>x,y,z = 0.185</td>
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<tr>
<td></td>
<td>k(24)</td>
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<td>x = 0; y = 0.305</td>
<td>x = 0; y = 0.305</td>
</tr>
<tr>
<td></td>
<td></td>
<td>z = 0.117</td>
<td>z = 0.116</td>
<td>z = 0.120</td>
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<tr>
<td>Ba:</td>
<td>a(2)</td>
<td></td>
<td>x,y,z = 0</td>
<td>x,y,z = 0</td>
</tr>
<tr>
<td>Ba:</td>
<td>d(6)</td>
<td></td>
<td>x = 1/4; y = 1/2; z = 0</td>
<td>x = 1/4; y = 1/2; z = 0</td>
</tr>
</tbody>
</table>

$^a$Reference 20.
atom, and Ba atoms are predicted to prefer occupying the $d(6)$ sites to the $a(2)$ ones in the Si$_{46}$ crystal structure. As will be described in the next section, some of the missing endohedral Ba elements in the small cage of Si(20) have been actually observed by x-ray crystallography. The observed missing of Ba atoms in the Si(20) unit is presumably related to this site preference of Ba atoms.

The lineup of band structures and the density of states for Si$_{46}$, Ba$_2$Si$_{46}$, Ba$_6$Si$_{46}$, and Ba$_8$Si$_{46}$ is shown in Fig. 2. Four, twelve, and sixteen valence electrons from Ba atoms in Ba$_2$Si$_{46}$ [Fig. 2(b)], Ba$_6$Si$_{46}$ [Fig. 2(c)], and Ba$_8$Si$_{46}$ [Fig. 2(d)] contribute to form the conduction-band edge. In the Na-doped binary clathrate of Na$_{x}$Si$_{46}$, we have reported that Na state is weakly hybridized with the Si$_{46}$ conduction-band state and this weak hybridization results in almost rigid energy band modification of guest-free Si$_{46}$. Similar theoretical results have also been presented in the K-doped type-I Ge clathrate K$_{x}$Ge$_{46}$, by Zhao et al. In contrast, the conduction-band dispersion of Ba$_2$Si$_{46}$ ($x=2, 6, 8$) is strongly modified from that of the guest-free Si$_{46}$. This is caused by the strong hybridization between the Ba states and the Si$_{46}$ conduction-band as also suggested previously in Na$_{x}$Ba$_2$Si$_{46}$ by Saito and Oshiyama. It is interesting to note that the density of states (DOS) at the Fermi level in Ba$_2$Si$_{46}$ is strongly altered with the contents of endohedral Ba atoms. The Fermi levels of Ba$_6$Si$_{46}$ and Ba$_8$Si$_{46}$ are located closely to strong peaks of DOS as shown in Figs. 2(c) and 2(d), respectively, while the DOS at the Fermi level for Ba$_2$Si$_{46}$ is moderate. These results suggest that hybridizations of Ba[$d(6)$] in the large cage of Si(24) with the Si$_{46}$ conduction-band state play an important role to form a high-DOS peak at Fermi energy. These results are also reminiscent of the experimental work of Kawaji et al. They had prepared Ba containing ternary silicon clathrate compounds Na$_{x}$Ba$_2$Si$_{46}$ with various Na contents ($0.2 \leq x \leq 1.5$) by Na evaporation from Na$_2$Ba$_2$Si$_{46}$, and then reported that the critical temperature ($T_c$) of superconductivity increases with the decrease of Na content in a temperature range of 4.8–2.6 K. Though the exact reason why the $T_c$ depends on the Na content is yet uncertain, the clathrate compound with the smallest Na content Na$_{0.2}$Ba$_{0.6}$Si$_{46}$ in which $a(2)$ sites in the small cage of Si(20) are almost unoccupied, actually shows the superconductivity at $T_c=4.8$ K. We assume that the result by Kawaji et al. shows experimental evidence that Ba[$d(6)$] states play a crucial role for the superconductivity in Ba-doped silicon clathrates. Our present calculation results again demonstrate that the large density of states at the Fermi level $N(\epsilon_F)$ enhanced by the hybridization of Ba states with the clathrate frameworks plays a key role for the superconductivity of Ba-doped silicon clathrates as suggested in the previous works. Therefore, the analysis based on the conventional Bardeen-Cooper-Schrieffer (BCS) theory for phonon-mediated superconductivity is assumed to be quite effective for studying the superconductivity in silicon clathrate compounds.

We have also calculated total energies as a function of atomic volume near the equilibrium volume for each system. In these calculations for each system, we have fixed the atomic positions listed in Tables I and II. In addition, the lattice constant ratio of $a:b:c$ for BaSi and BaSi$_2$ has been fixed at the ratio of the equilibrium structure. In order to examine the numerical accuracy of equations of states of BaSi$_2$ and Ba$_2$Si$_{46}$ for the approximation fixing atomic positions, we have compared the energies calculated for (i) the fractional coordinates at the LDA equilibrium unit volume given in Tables I and II and (ii) the structures with the fractional coordinates optimized at a certain unit volume. These comparisons have been performed at the unit volumes compressed by 7.5% from the LDA equilibrium volumes, in which the lattice constant for Ba$_2$Si$_{46}$ is $a=9.918$ Å and the lattice constants for BaSi$_2$ are $a=8.485$ Å, $b=6.415$ Å, and $c=10.949$ Å. The total energy differences for BaSi$_2$ and Ba$_2$Si$_{46}$ within the present scheme are found to be 9.3 and 3.1 meV/atom, respectively. From the present calculations,
the cell volume compressed by 7.5% is estimated to correspond to the equilibrium pressure of 4.8 and 7.8 GPa for BaSi$_2$ and Ba$_8$Si$_{46}$, respectively. Therefore, we presume that the relative enthalpy of Ba$_8$Si$_{46}$ to the coexisting phase of cd-Si and BaSi$_2$, which will be described later, is accurate within less than 10–20 meV/atom at about 5 GPa.

The equation of state for each system is depicted in Fig. 3(a) and the summary of calculated values are listed in Table III. In Fig. 3(a), the calculated total energies are shifted so that the energies of bcc-Ba and cd-Si are equal to the experimental negative cohesive energies. Since the bulk modulus deduced using the Murnaghan’s equation of state is known to be strongly sensitive to its pressure derivative ($B'$), bulk moduli assuming $B' = 3.7$ of Si$_{46}$ are also listed in parentheses in Table III for Ba$_2$Si$_{16}$, Ba$_6$Si$_{46}$, and Ba$_8$Si$_{46}$.

The bulk moduli of type-I clathrate phases are predicted to be 83–89 GPa, which are about 9–13% smaller than that of cd-Si. The reduction of the bulk modulus for clathrates has been pointed out theoretically. In addition, San-Miguel et al. and Ramachandran et al. have experimentally reported bulk moduli of Si$_{136}$-based (type-II) clathrate phases along with the theoretical results. Our calculated results of clathrates are in good agreement with their experiments. The calculated bulk moduli of Ba-doped type-I clathrates were increased slightly in comparison with that of the “guest”-free silicon clathrate of Si$_{46}$, but not so sensitive to the existence of Ba atoms in the endohedral sites. This indicates that the hardness in clathrate systems essentially depends on the framework atoms.

We show the pressure dependence of the unit volume in Ba$_8$Si$_{46}$ from LDA calculations in Fig 3(b). To the authors’ best knowledge, the experimental results of the pressure dependence of the unit volume in Si$_{46}$ (type-I clathrates) have not yet been reported. In addition, the equation of state of guest-free Si$_{136}$ (Si$_{34}$) is theoretically known to be almost identical with that of Si$_{46}$. Therefore, the experimental variation of cell volume with pressure for Si$_{136}$ from Ref. 44, which is scaled to the Si$_{46}$ unit volume, is also shown in Fig 3(b) for comparison. In their experiment, the “guest”-free silicon clathrate Si$_{136}$ is used for measurements of pressure dependence of the unit volume. Over the pressure range from 0 to 8 GPa, Ba$_8$Si$_{46}$ is predicted to undergo ~7.5% volume change, which corresponds with the change in Si$_{136}$ experimentally observed by Ramachandran et al. On pressurization above 8 GPa, Ramachandran et al. have observed the structural transition from Si$_{136}$ to $\beta$-tin phase. Similar transition has been also observed in Na$_{18}$Si$_{136}$ at a slightly higher transition pressure (11 GPa) by San-Miguel et al. In contrast, transition properties of type-I clathrate compounds under high pressures have not been experimentally reported yet, as far as we know.

In order to discuss thermodynamic stability in a given chemical composition, we consider the following relative free energy:

$$
\Delta G(P) = G_{Ba_8Si_{46}}(P) - \frac{(8 \times 3) G_{BaSi_2}(P) + (30 \times 1) G_{cd-Si}(P)}{54},
$$

where $G_{Ba_8Si_{46}}(P)$, $G_{BaSi_2}(P)$, and $G_{cd-Si}(P)$ are Gibbs free energies per atom at a pressure, $P$, for Ba$_8$Si$_{46}$, BaSi$_2$, and cd-Si, respectively. $G(P)$ can be evaluated using the simple Legendre transformation of associated equation of state. Using Eq. (1), we can judge relative thermodynamic stability between Ba$_8$Si$_{46}$ and the coexisting phase of BaSi$_2$ and cd-Si for the chemical composition of Ba$_3$Si$_{8:46}$. In Fig. 3(c), we
show the variation of relative Gibbs free energy (relative enthalpy) of Ba$_8$Si$_{46}$ to the coexisting phase of cd-Si and BaSi$_2$ in the case of atomic composition of Ba:Si = 8:46 with pressure. Though these two phases are almost degenerate in energetics under relatively low pressures, the energetic degeneracy is noticeably broken under higher pressures. That is, the driving force for the conversion to Ba$_8$Si$_{46}$ from the mixture of BaSi$_2$ and cd-Si becomes larger with an increase of pressure. We have experimentally reported that the arc-melted prepressed sample is a mixture of BaSi$_2$ and cd-Si.\textsuperscript{7} In addition, the conversion to Ba$_8$Si$_{46}$ from this mixture has been found to be not completed, if the applied pressure is lower than 2 GPa.\textsuperscript{7} Therefore, the enhancement of the driving force for the conversion to Ba$_8$Si$_{46}$ is assumed to play an important role in the success of synthesizing this Ba-doped clathrate compound under high pressures. Using the equilibrium volumes listed in Table III, the atomic volume of the mixture of BaSi$_2$ and cd-Si in the case of atomic composition of Ba:Si = 8:46 is calculated by 22.751 Å$^3$/atom. In contrast, the atomic volume of Ba$_8$Si$_{46}$ is 19.606 Å$^3$/atom, which is about 14% smaller than the reactant mixture. Therefore, high-pressure conditions should favor the formation of Ba$_8$Si$_{46}$, though the clathrate structure has appeared to be loosely packed compared with cd-Si. A point to notice here is that the structural transition from type-II clathrates (Si$_{24}$) to β-tin phase has been experimentally observed on pressurization above 8 GPa, as mentioned above.\textsuperscript{43,44} While transition properties of type-I clathrate compounds under high pressures have not been experimentally reported, such transitions will affect the form of the high pressure phase relations in these Ba-doped Si$_{46}$ clathrate compounds. More experiments are needed to understand this point more clearly.

Recently, Fukuoka \textit{et al.}\textsuperscript{45} have successfully synthesized a new silicon clathrate compound of Ba$_3$Si$_{106}$ from a mixture of BaSi$_2$ and cd-Si utilizing high pressures, in which they have also found that the synthesis using a pressure higher than 3 GPa at 800°C gives a mixture of Ba$_8$Si$_{46}$ and cd-Si. While the equation of state of this new clathrate compound, Ba$_{32}$Si$_{100}$, has not been calculated, high pressure synthesis of silicon compounds will be a promising method for developing new silicon-based materials.

B. Experimental structural properties

The Rietveld refinement pattern of Ba$_5$Si$_{46}$ is shown in Fig. 4 along with the experimental pattern. The crystallographic data of this compound determined by the Rietveld refinement are summarized in Table IV. The clathrate compound of Ba$_8$Si$_{46}$ is isomorphous with Na$_8$Si$_{46}$ (a = 10.19 Å).\textsuperscript{1} All of the peaks of the diffraction pattern can be indexed on the basis of a cubic unit cell (Pm$ar{3}$m, No. 223) of a = 10.3279 Å. The lattice constant and the atomic coordinates given in this table are in good agreement with those in the previous work.\textsuperscript{7}

Ba$_8$Si$_{46}$ is composed of two types of silicon cages of Si(20) and Si(24) linked by sharing a pentagonal face with each other. Ba atoms in the ideal Ba$_8$Si$_{46}$ should occupy endohedrally in all of these silicon cages. We have, however, found the missing 12% of some endohedral Ba atoms in the small cage of Si(20) in the present analysis (see Table IV), while the big cages of Si(24) are found to be completely occupied by Ba elements. The observed missing of the Ba atoms in the small unit of Si(20) is presumably due to the site preference of Ba atoms between the d(6) and a(2) sites, as theoretically mentioned in the previous section. In the NMR study of metal-doped Si$_{46}$ clathrate compounds such as Na$_{8}$Ba$_{1-x}$Si$_{46}$ and Na$_{10}$Si$_{46}$, Shimizu \textit{et al.}\textsuperscript{46} and Ramachandran \textit{et al.}\textsuperscript{47} have observed three distinct $^{29}$Si signals with a different Knight shift. In these two experimental reports, the main three peaks of $^{29}$Si NMR spectra of the clathrate compounds can be assigned by using the integrated intensities, which correspond to the ideal stoichiometry of three in-

![FIG. 4. Rietveld refinement patterns for Ba$_5$Si$_{46}$. X-ray-diffraction patterns between 40° and 65° are magnified in the inset. Observed, simulation, and difference patterns are indicated by plus marks (+), and solid, and solid bottom lines, respectively. The experiment pattern is in good agreement with the simulated one in all 2θ region.](image)
TABLE IV. Crystallographic data for Ba$_8$Si$_{46}$ obtained by Rietveld refinement. Lattice parameters, occupations, isotropic thermal parameters ($B_0$), and atomic coordinates are listed. The previous results using the conventional x-ray-diffraction experiment in Ref. 7 are also listed for comparison.

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<th>Site</th>
<th>Occupation</th>
<th>$B_0$ (Å$^2$)</th>
<th>Atomic coordinates</th>
<th>$B_0$ (Å$^2$)</th>
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<td>0.26(32)</td>
<td>$x = 1/4; y = 0; z = 1/2$</td>
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<td>Si: $i(16)$</td>
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<td>0.66</td>
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<td>0.38(25)</td>
<td>$x, y, z = 0.1864(6)$</td>
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<td>Si: $k(24)$</td>
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<td>0.80</td>
<td>$x = 0; y = 0.3066; z = 0.1215$</td>
<td>0.35(21)</td>
<td>$x = 0; y = 0.3055(9); z = 0.1199(10)$</td>
</tr>
<tr>
<td>Ba: $a(2)$</td>
<td>0.88</td>
<td>0.78</td>
<td>$x, y, z = 0$</td>
<td>2.05(19)</td>
<td>$x, y, z = 0$</td>
</tr>
<tr>
<td>Ba: $d(6)$</td>
<td>1.00</td>
<td>1.22</td>
<td>$x = 1/4; y = 1/2; z = 0$</td>
<td>0.71(10)</td>
<td>$x = 1/4; y = 1/2; z = 0$</td>
</tr>
</tbody>
</table>

Reliability factors$^a$ (%)

Table: $R_{WP} = 1.69$, $R_e = 1.47$, $R_f = 1.44$, $R_I = 1.59$

Goodness of fit: $S = R_{WP} / R_e = 1.15$

$^aR_{WP}$: $R$-weighted pattern, $R_e$: $R$ expected, $R_f$: $R$ structure, and $R_I$: $R$ integrated intensity.

IV. CONCLUSIVE REMARKS

We have presented a joint experimental and theoretical study of the stability and structural properties of Ba-doped...
x-ray crystallography, while the big cages of Si
d to energetical site preference of Ba atoms between
oms in endohedral sites suggests that this is presumably due
present LDA calculation for stabilization energies of Ba at-
founds to be completely occupied by Ba elements. The
periment of the Ba$_8$Si$_{46}$ prepared under high pressures, using
BL02B2 powder-diffraction beam line at the SPring8
Hyogo, Japan). Some of the missing endohedral Ba ele-
ments in the small cage of Si(20) have been observed by
x-ray crystallography, while the big cages of Si(24) are
found to be completely occupied by Ba elements. The
present LDA calculation for stabilization energies of Ba at-
oms in endohedral sites suggests that this is presumably due
to energetical site preference of Ba atoms between $d(6)$ and $a(2)$ sites. The isothermal parameter of Ba in the big cage of
Si(24) has been found to be larger than that in the small
Si(20) unit, which is consistent with some theoretical predic-
tions in earlier works.

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diffraction experiments at the SPring8. We would like to
the encouragement and power generation applications
material, which is consistent with some theoretical predic-
tion in earlier works.

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