Energetic Stability and Thermoelectric Property of Alkali-Metal-Encapsulated Type-I Silicon-Clathrate from First-Principles Calculation

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Possible combinations of alkali metal guest atoms and substitutional group-13 atoms in type-I Si clathrate and their thermoelectric properties were investigated using first-principles calculations. All alkali metals could be encapsulated as the guest element into a Si46 cage, and either Al or Ga was suitable for a substitutional atom. From the formation energy, possible clathrate compositions were selected as K8Al8Si38, K8Ga8Si38, Rb8Al8Si38, Rb8Ga8Si38, Cs8Al8Si38 and Cs8Ga8Si38. The thermoelectric properties of these compositions were calculated as functions of temperature and carrier density, using the Boltzmann transport equation and the calculated band energy. The obtained dependences of the Seebeck coefficient and electrical conductivity on the carrier density were discussed from the viewpoint of band structure. The thermoelectric properties were optimized to maximize $ZT$ for each composition by controlling the carrier density. $ZT \approx 0.75$ was predicted as the highest $ZT$ value for hole-doped Cs8Ga8Si38.

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1. Introduction

In recent years, reusable and clean energy generation technologies have been attracting much attention. Thermoelectric conversion is one of the promising clean energy sources because it enables the conversion of wasted heat into electric power.

In 1994, Slack proposed the concept of Phonon Glass Electron Crystal (PGEC). This hypothetical material can simultaneously behave as glass for phonons and as crystal for carriers. Filled skutterudite and clathrate compounds are nice examples of Slack’s PGEC concept. Such compounds are composed of a characteristic atomic structure. “Host atoms” form a cage network, and good electrical conductivity is exhibited because of the covalent bonding of the cage network. Cages are usually formed to encapsulate the additional element, which is frequently referred to as a “guest atom”. The guest atom is weakly bound in the cage and vibrates like an Einstein oscillator. The characteristic vibration of the guest atom can scatter the lattice vibration of the cage. This concept is referred to as “rattling”. Therefore, cage-networked materials such as glassy materials generally exhibit quite low thermal conductivities.

Thermoelectric materials can generate electric power through the Seebeck effect. Its conversion efficiency is determined from the dimensionless figure of merit ($ZT$), defined as follows:

$$ZT = s^2\sigma T/(k_e + k_l),$$

where $s$ is the Seebeck coefficient, $\sigma$ is electrical conductivity and $T$ is temperature. $k_e$ and $k_l$ are electrical and lattice thermal conductivities, respectively. Generally, $ZT > 1$ is regarded as a standard for actual application of thermoelectric conversion. It is crucial to increase both the Seebeck coefficient and the electrical conductivity while suppressing the thermal conductivity in order to achieve high thermoelectric performance. PGEC materials exhibit both high electrical and low thermal conductivities and have been extensively investigated for application as thermoelectric materials. In order to achieve high Seebeck coefficient, a low carrier density is desirable because the Seebeck coefficient is determined from the transport of entropy per carrier. On the contrary to the Seebeck coefficient, high electrical conductivity can be achieved with high carrier density. Thus, there is a tradeoff relation between the Seebeck coefficient and electric conductivity, and the optimal carrier density must be found to maximize $ZT$.

Carrier density is frequently optimized in semiconductor materials by adding a dopant. Clathrate compounds are thought to be one of the intermetallic compounds that exhibit a Zintl phase in which a guest atom supplies an electron while the substitution of an aliovalent element into a cage site can compensate for the supplied electron. If the number of guest and substitutional atoms is properly controlled, charge neutrality of the system is preserved. The carrier density of such an intrinsic semiconductor can thus be controlled through adjusting the composition of guest and substitutional atoms. Among the clathrate compounds, Ge-based clathrate has been widely investigated because its localized d-electrons give it favorable thermoelectric properties. Si-based clathrate, on the other hand, has not been investigated as compared with the Ge-based one for use in thermoelectric applications.

For example, reports on the $ZT$ of Si clathrate are quite limited. Kuznetsov et al. estimated the $ZT$ of Ba$_8$Ga$_{12}$Si$_{13}$ to be 0.87 at 870 K, and C. Candolfi et al. reported that a $ZT$ of approximately 0.2 had been achieved at 600 K for Ba$_6$Au$_x$, Si$_{46-x}$, where $x = 5.59$. It has not been established whether the maximum $ZT$ of Si-based clathrate exceeds 1. Si is a ubiquitous element that is cheaper than Ge and is nontoxic. Therefore, we believe that if a stable Si-based clathrate without harmful and rare-earth element will be obtained, its range of applications is significant, even if it only exhibited a moderate $ZT$. Experimental optimization of additional elements and the carrier density would require an enormous number of research trials, in general. On the other hand, a numerical method of predicting the thermoelectric properties of materials on the basis of theoretical calculations has been
developed. If such a simulation is used to optimize the composition of the compound and estimate the maximum $ZT$, it would help to develop effective thermoelectric materials.

In this study, several possible combinations of guest and substitutional atoms for the Type-I Si clathrate and their thermoelectric properties were systematically investigated using first-principles calculation. Alkali metals were considered as guest elements because thermoelectric properties in alkali metal encapsulated Si clathrates have not been revealed although their electronic structures were investigated.\textsuperscript{15)\textsuperscript{16)} Reducing the number of substitutional elements is expected to reduce the number of alloy scattering of the carriers more than using alkali earth elements for the guest elements would. On the basis of the calculated thermoelectric properties, we will discuss the optimal composition of guest and substitutional atoms that maximizes $ZT$ and whether $ZT > 1$ can be achieved for Si clathrate.

2. Computational Procedure

A plane-wave-basis projector augmented-wave (PAW) method implemented in Vienna \textit{ab initio} simulation package (VASP) code\textsuperscript{16)} was used for structural simulation. The Monkhorst–Pack scheme\textsuperscript{19)} was used for $k$-point sampling. The numerical error was estimated to be 1 meV/atom for a Si$_{46}$ unit cell on the basis of convergence tests of the cutoff energy and $k$-point mesh. A force of $<10^{-2}$ eV/Å and a total change in energy of $10^{-8}$ eV were selected as the convergence criteria for the structural optimization.

The formation energy ($E_f$) for guest atom encapsulation and host atom substitution was calculated using the following equation:

$$E_f = E_T(\text{dopant} \ g) - \left( E_T(\text{perfect}) + \Sigma n_A \mu_A - \Sigma n_B \mu_B \right) + q(\epsilon_F + E_{\text{VBM}}).$$

(2)

where $E_T(\text{dopant} \ g)$ and $E_T(\text{perfect})$ are the total energies obtained from the first-principles calculations for the dopant and the perfect cell, $q$ is the charge state of the dopant. In the whole cell, charge balance was maintained by adding/removing electrons. In eq. (2), $n_A$ and $n_B$ are the number and chemical potential of added dopant $A$, respectively. If the dopant is considered as a substitutional atom, $n_{\text{Si}}$ and $\mu_{\text{Si}}$ must be considered because they represent the number of removed host Si atoms and the chemical potential of Si in accordance with dopant substitution. $\epsilon_F$ is the Fermi energy, which corresponds to chemical potential of the electron. $E_{\text{VBM}}$ is the energy of the valence band maximum. Here, $E_{\text{VBM}}$ was determined using the following equations:

$$E_{\text{VBM}} = E_{\text{VBM(perfect)}} + V_{\text{av(defect) \ g}} - V_{\text{av(perfect)}}$$

(3)

and

$$E_{\text{VBM(perfect)}} = E_T(\text{perfect} \ g) - E_T(\text{perfect} \ g + 1).$$

(4)

where $V_{\text{av}}$ is the average electrostatic potential. When a dopant is introduced, $V_{\text{av(defect) \ g}}$ is defined as the average electrostatic potential at the farthest site from the dopant. This treatment can correct distortion of the band structure induced by long-range interaction of an ionized dopant. $E_{\text{VBM(perfect)}}$ and $E_{\text{VBM(perfect) \ g + 1}}$ are the total energy of the perfect cell when the charge is neutralized and when one electron is removed, respectively. The Fermi energy ($\epsilon_F$) in eq. (2) was measured from the $E_{\text{VBM}}$ determined in eq. (3), and it can vary within the band gap. Chemical potentials $\mu_i$ of element $i$ were calculated as per atom energy in each primitive cell. Si$_{46}$ unit was used for the perfect cell throughout the calculation. It was confirmed that the difference in the formation energy between the unit cell and the $2 \times 2 \times 2$ expanded supercell was about 0.1 eV. This difference does not affect our results and conclusion.

After the structural relaxation, the detailed band structure was further calculated using the all-electron method based on the Full potential Linearized Augmented Plane Wave + Local Orbital (FLAPW+lo) approach implemented in the WIEN2k code.\textsuperscript{20)} $R_{\text{max}}$ determines the size of the basis set, was set to 7, which assures convergence of total energy to less than 0.01 meV/atom for Si$_{46}$. A $12 \times 12 \times 12$ $k$-point mesh was used to sample the band energy within the Brillouin zone. The exchange-correlation functional was approximated using a GGA of Engel–Vosko formalism (EV-GGA),\textsuperscript{21)} which is known to reproduce the bandgap of Si and is previously used for the first-principles calculation of the Seebeck coefficient of the Zn-substituted Ge-clathrate.\textsuperscript{22)}

On the basis of the band energies obtained at each $k$-point, the band energy was interpolated using a 6-dimesner grid method specialized in the original $k$-point mesh. The thermoelectric properties, including the Seebeck coefficient, electrical conductivity, and electronic thermal conductivity were calculated by numerically solving the Boltzmann transport equation using the BoltzTraP code.\textsuperscript{23)} A constant carrier relaxation time approximation was assumed so that the Seebeck coefficient could be obtained independent of the carrier relaxation time, while the electrical conductivity and electronic thermal conductivity could be obtained as carrier-relaxation-time dependent quantities. Carrier doping was treated as a shift in the Fermi level on the basis of the band structure of the $X_i Y_i S_i$.\textsuperscript{22)} Such a treatment is called a “rigid-band approximation”. However, as the band structure is expected to severely change in heavy doping, the rigid-band approximation would fail when Fermi-level is located more than 0.1 eV into the band edge.\textsuperscript{24)} We also checked the applicability of rigid-band approximation to the present Si-clathrate system, from the analysis on band structures of one electron and/or hole doped Si$_{46}$ and K$_8$Ga$_8$Si$_{38}$. It was confirmed that changes of band structure could be characterized only by shifting the Fermi level, which was moved about 0.1 eV inside bands. Therefore, the shift of the Fermi level was limited between the energy level of 0.1 eV inside each band edge. Thermal activation of the carrier was considered using the Fermi–Dirac distribution function.

Our research group had already investigated the lattice thermal conductivity of the Si clathrate with molecular dynamics simulation and the Green–Kubo method.\textsuperscript{25–27)} At 300, 600 and 900 K, a $4 \times 4 \times 4$ expanded clathrate supercell was equilibrated and then 12-ns simulation was performed within the NVE ensemble, and thermal flow was integrated.
The interatomic potential was constructed to reproduce the potential energy curve for the guest atom within a Si cage. (See details in Refs. 26 and 27.) The calculated lattice thermal conductivity was merged with the present first-principles-based results, and $ZT$ of each Si clathrate was then predicted.

3. Results and Discussion

3.1 Formation energy

3.1.1 Alkali metal and group 13 element in Si$_{46}$

A schematic illustration of the type-I Si clathrate, Si$_{46}$, is shown in Fig. 1. The atomic structure and charge density plot shown later were drawn using VESTA software. Si in the clathrate structure has the same 4-fold coordination similar to that in diamond. The primitive cell is cubic and is composed of two Si dodecahedra (12-Si-atom cage) and six Si tetrakaidecahedra (14-Si-atom cage). The Wyckoff representations of independent atomic positions of the cage site (6c, 16i and 24k) and the internal cage site occupied by the guest element (2a and 6d) are also shown in Fig. 1. The 2a and 6d sites are center of the 12- and 14-Si-atom cages, respectively. The calculated lattice constant of Si$_{46}$ was 10.225 Å, similar to the previously obtained theoretical value, 10.350 Å. The difference in energy between the Si$_{46}$ and diamond Si was 63 meV/atom, which is very consistent with the previously obtained theoretical value of 69 meV/atom. The tiny energetic difference is thought to originate in the strain of Si–Si bonds.

In the concept of the Zintl phase, one alkali metal supplies one electron when it is encapsulated in a Si cage. However, one group-13 element atom substituted at a Si-cage site compensates for the one electron because it has one fewer valence electron than Si. Therefore, the alkali metal X in Si$_{46}$ is thought to be X$^+$ in Si$_{46}$, while the substitutional group-13 element Y is thought to be Y$^-$ in Si$_{46}$. The calculated formation energies of alkali metals and group-13 elements are shown in Figs. 2(a) and 2(b), respectively. As the formation energy of the charged dopant is dependent on the chemical potential of the electrons, we assumed that the Fermi energy was located at the center of the band gap. This situation corresponds to the intrinsic semiconductor. All alkali metal dopants exhibit lower formation energies for the guest element than for substitution. This order did not change even though the Fermi level was located at the top of the valence band ($p$-type doping limit) or at the bottom of the conduction band ($n$-type doping limit). The formation energies of K, Rb and Cs at the 2a site gradually increased with increasing ionic radius. In the pristine Si$_{46}$, the theoretical size of the 12-Si cage is 3.32 Å, while that of 14-Si cage is 3.68 Å. Therefore, larger elements such as K, Rb and Cs are more comfortable at the 6d site than they are at 2a site. For group-13 elements, it seems that the interstitial formation energies at 2a and 6d site decrease as going down the periodic table. Especially for Al and Ga, the difference between interstitial (2a and 6d site) and substitutional (6c, 16i and 24k site) formation energies is fairly small. Figures 3(a) and 3(b) show the Fermi-level dependence of the Al and Ga formation energy in Si$_{46}$. The gradient of each line corresponds to the charge state, and the transition levels are represented as symbols. The previously mentioned formation energies in the discussion for Figs. 2(a) and 2(b) were calculated on the assumption that the Fermi level was located at the middle of the band gap. However, the Fermi level can vary within the band gap in accordance with dopant addition. Let us consider the situation in which the guest element is first encapsulated in Si$_{46}$ and then Al or Ga substitution occurs. As the clathrate structure is thought to be formed as Si encloses the guest element, the Fermi level should be located near the bottom of the conduction band. Obviously the substitutional formation energy is lower than the

Fig. 1 Crystal structure of type-I clathrate Si$_{46}$. Crystallographic sites are represented with Wyckoff notation.

Fig. 2 Formation energies of (a) alkali metals and (b) group-13 elements at each crystallographic site in Si$_{46}$.
interstitial formation energy for both Al and Ga, and the fully ionized (Al$^{+}$Si and Ga$^{+}$Si) states are stable in $n$-doping. Therefore, when these elements are doped with alkali-metal elements, the group-13 element can be substituted into the Si-cage site.

3.1.2 Comparison with literature data on the synthesis

Except for Li, all alkali-metal-encapsulated Si clathrates experimentally synthesized exhibit the type-I clathrate structure: Na$_8$Si$_{46}$, K$_{7.62}$Si$_{46}$, Rb$_{6.15}$Si$_{46}$ and Cs$_{7.6}$Si$_{46}$. For Al and Ga, no report on the synthesis of single-doped clathrate is available, but there are reports of the substitutional element co-doped with guest element, such as Ba$_8$Al$_{16}$Si$_{30}$ and Ba$_8$Ga$_{16}$Si$_{30}$. For Li and Tl, there have been no report on experimental synthesis of Si-clathrate. Although Li exhibited a lower interstitial formation energy than substitutional formation energy, the phase diagram of Li-Si shows that phase separation of LiSi and Si occurs at 470 K. It has been reported for In that Ba$_9$In$_{16}$Ge$_{30}$ and K$_4$In$_{12}$Si$_{28}$ were synthesized. Although Tl is very toxic element, its calculated interstitial formation energy is lowest among all group-13 elements. The electronegativity of Tl is 2.04 (based on Pauling criterion), which is two-times larger than that of Si. Encapsulated Tl in the Si-cage is thought to be stably bonded with Si because its ionic radius is two-times larger than that of Si. Therefore, low thermal conductivity is not expected for encapsulated Tl because rattling effect arises from the loosely bound guest atom with the cage.

Present results for the formation energy indicate that cage size determines which guest elements are favorable. For example, Rb-doped Si clathrate has been synthesized as Rb$_6$Al$_{15}$Si$_{46}$ or Rb$_6$Ga$_{16}$Si$_{38}$. The former composition is consistent with the calculated formation energy for the 6d site being more stable than that for the 2a site by 0.5 eV. On the other hand, number of the encapsulated Cs in Si$_{46}$ cage was 7.6, which is larger than that of Rb. This difference should be originated in the synthesized condition, where Cs$_{7.6}$Si$_{46}$ was synthesized under high temperature and pressure. The order of elemental stability with regard to the substitutional formation energy can be understood by the ionic radius of dopant. From Figs. 2(a) and 2(b), the substitutional formation energy is the lowest at the 6c site for every element. Because the local strain at 6c site is largest, substitution of elements larger than Si at the 6c site can effectively relax the elastic strain. The substitutional formation energy of B, on the other hand, is the lowest at the 16i site. From the chemical bonding analysis, the 16i site exhibits the most covalent character because its bond angle and length are the closest to those of the Si-Si bond in diamond Si. Actually, B is only substituted at the 16i site in K$_3$B$_7$Si$_{39}$. For Li and Tl, there have been no report on experimental synthesis of Si-clathrate. Although Li exhibited a lower interstitial formation energy than substitutional formation energy, the phase diagram of Li-Si shows that phase separation of LiSi and Si occurs at 470 K. It has been reported for In that Ba$_9$In$_{16}$Ge$_{30}$ and K$_4$In$_{12}$Si$_{28}$ were synthesized. Although Tl is very toxic element, its calculated interstitial formation energy is lowest among all group-13 elements. The electronegativity of Tl is 2.04 (based on Pauling criterion), which is two-times larger than that of Si. Encapsulated Tl in the Si-cage is thought to be stably bonded with Si because its ionic radius is two-times larger than that of Si. Therefore, low thermal conductivity is not expected for encapsulated Tl because rattling effect arises from the loosely bound guest atom with the cage.

3.1.3 Codoping of guest and substitutional atom

It frequently occurs that the donor and acceptor are strongly bound that the formation energy is lower than that of each individual doped case. In Si$_{46}$, various configurations of the guest and the substitutional atom are possible. The configurations were systematically examined and the lowest formation energy of the combination of one guest atom X and one substitutional atom Y were obtained. The results are shown in Fig. 4, which can be interpreted as the superposition of the interstitial and substitutional formation energies, as shown in Figs. 2(a) and 2(b). Each guest and substitutional pair exhibited the lowest formation energy when Ga was substituted at the Si-cage site. It was also found that in the most stable configurations all the group-13 elements except for B was favorable to substitute at the 6c site. For the guest atom, Li and Na were positioned at the 2a site, while K, Rb and Cs were positioned at 6d site in the most stable guest-substitution configuration. It is noted that formation energy of B was significantly decreased by codoping with alkali metals because the electrons supplied by the guest atoms contributed to the B–Si covalent bonds.
The pair formation energy for Li and group-13 element, on the other hand, was the highest. Because the ionic radius of Li is the smallest among the alkali metals, Li moved near the substitutional atom during structural relaxation, which broke the charge balance within clathrate structure. This is the main reason that Li–Y pair is the most unstable. It must be mentioned here that the other alkali metals were most stable at the center of the Si cage.

Increasing the occupancy of the guest atom encapsulated in the clathrate cage should effectively decrease thermal conductivity. In Type-I clathrate, eight guest atoms can be encapsulated at most per chemical formula. To preserve charge neutrality, the same number of Si site as that of guest atoms must be substituted by group-13 element. For this reason, the formation energies of X8Y8Si38 (X = Li, Na, K, Rb, and Cs, Y = B, Al, Ga, In and Tl) were calculated, and the energetically stable compositions were analyzed for further band structure calculation. In the Si46 clathrate, there are an enormous number of combinations of substitutional positions: more than 2 hundred billion. Previous theoretical works have suggested that substitutional atoms positioned at the nearest neighbor form anti-bonding, and the system becomes energetically unstable. On the basis of this insight, the energies of various configurations of eight substitutional Ga atoms were calculated while not only the atomic positions but also the cell shape and lattice constants were relaxed. The resulting tendencies for Ga configurations can be separated into two groups: 1) Li and Na (small ionic radii) encapsulated in a Si cage and 2) K, Rb and Cs (large ionic radii).

Figure 5(a) shows the relative formation energy (\(\Delta E_f\)) of Li8Ga8Si38 plotted as a function of the number of Ga atoms substituted at the 6c site. At each number of substituted Ga at the 6c site (horizontal axis), various combinations of Ga at the 16i and 24k site are possible. Relative energies of all examined configurations at the fixed number of Ga at the 6c site are also shown in Fig. 5. The clathrate structure apparently becomes more stable with the increasing number of Ga atoms substituted at the 6c site because Ga substitution most effectively relaxes the local elastic strain at the 6c site. When the occupancy of Ga atoms at the 6c site is 1.0, Ga–Ga bond formation can be prevented. Therefore, the most stable configuration within our trial was (6c, 16i, 24k) = (6, 2, 0) for Li8Ga8Si38 and Na8Ga8Si38. For the large ionic group, on the other hand, the most stable configuration within our trial was (6c, 16i, 24k) = (5, 0, 3) for K8Ga8Si38, Rb8Ga8Si38, and Cs8Ga8Si38, as shown in Fig. 5(b). The different stable Ga configurations for these two groups are suggested to originate in the different sizes of the guest elements.

Figure 6 shows the local strain at the Si sites in X8Si46 plotted as a function of the lattice constant. The strain at the 6c, 16i and 24k site was defined from change in average Si–Si bond length at each site compared with average Si–Si bond length at each site in diamond Si.
as the 6c site is bonded with the 24k site, further Ga substitution at 24k sites induces unfavorable Ga–Ga bonds when Ga is substituted at all 6c sites. Thus, the Ga configuration of (6c, 16i, 24k) = (6, 2, 0) was most stable for Li8Si46 and Na8Si46 because Ga–Ga bond formation can be prevented. However, for K8Si46, Rb8Si46, and Cs8Si46, not only the 6c sites but also the 24k sites can effectively release the strain by Ga substitution. Thus, Ga substitution at all 6c sites is not required for those compositions of Si clathrate.

The stable configuration of Ga found in the present study is not perfectly consistent with the experimentally determined Ga site occupancy in K8Ga8Si38,37,40 where the Ga substitutional configuration was found to be (6c, 16i, 24k) = (3, 0, 5) from the analysis of Ga occupancy. Recently, Imai et al. synthesized K8Ga3Si38 single crystal,41 and occupancy of Ga at the 6c, 16i and 24k sites were 0.607, 0.026 and 0.179, respectively,42 which is nearly equivalent to (6c, 16i, 24k) = (4, 0, 4). However, the present calculation is consistent with these experimental results in that Ga is difficult to substitute at the 16i site. In addition, as shown in next section, it was found that the effect of different configurations of the substitutional atom on the thermoelectric properties was negligible. Moreover, the lowest energy configuration obtained in the present study is more stable than the one calculated by Imai et al.15 by 0.21 eV/f.u., where the previous experimentally determined occupancy37,40 was used.

On the basis of the above result for the stable configurations of substitutional atoms, the formation energies of X8Y8Si38 per chemical formula were calculated and are shown in Fig. 7. The configurations of substitutional atoms used were (6c, 16i, 24k) = (6, 2, 0) for X = Li and Na, (6c, 16i, 24k) = (5, 0, 3) for X = K, Rb and Cs, and (6c, 16i, 24k) = (0, 8, 0) for Y = B because of the strongly covalent B–Si bond. The same as Fig. 4, resultant order of the energetic stability was obtained: K > Rb > Cs > Na > Li, independent of the substitutional atom. Although the site strain of Rb8Si46 and Cs8Si46 was larger than that of K8Si46, as shown in Fig. 6, the large tensile strain of former two compositions increase the energy by the stretching cage. This energy increase should exceed the energy gained from the strain released by substitutional atoms larger than Si. For this reason, formation energies of the former two compositions are higher than that of the K8Ga8Si38. In Fig. 7, the dotted line indicates the formation energy of K8B8Si38. Because a nearly identical composition, K1B7Si13g, was synthesized,38 formation energy of K8B8Si38 can be regarded as a criterion whether composition is formable as a clathrate or not. Therefore, X8Y8Si38 (X = K, Rb and Cs, Y = Al and Ga) was selected for further transport analysis because their formation energies were well lower than that of K8B8Si38.

3.2 Thermoelectric properties

3.2.1 Seebeck coefficient

As explained previously, optimization of the carrier density is crucial to obtain high ZT because there is a tradeoff dependence on carrier density between the Seebeck coefficient and the electrical conductivity. The Seebeck coefficient was calculated for each composition, and the results for hole- and electron-doping at 900 K are plotted in Figs. 8(a) and 8(b), respectively, as a function of the carrier density. The selected temperature, 900 K, is almost comparable to the temperature of the steam temperature generated by fossil power plants. As derived from the Wiedemann–Franz law, a Seebeck coefficient of at least ~160 μV/K is required in order to achieve ZT > 1. This value is represented as the dotted line in Fig. 8. Within the wide range of carrier densities, all compositions can achieve |s| > 160 μV/K. The Seebeck coefficient reached a maximum at the carrier density of ~10¹⁸–10¹⁹ cm⁻³. A carrier density of ~10²⁰ cm⁻³ was needed to maximize the Seebeck coefficient for pristine Si46. This is consistent with the change in the band gap. Introducing guest atoms into pristine Si46 decreases the band gap of pristine Si46 because the guest atom forms an additional s-orbital energy band at the bottom of the conduction band. The lattice constant increases as the size of the guest atom. In accordance with this volume relaxation effect, the degree of band dispersion is decreased, and the band gap also decreases. Actually, calculated band gaps were 0.98, 1.53, 0.76, 0.80, 0.82, 0.88, 0.91 and 0.97 eV for the diamond Si, Si46, K8Al8Si38, K8Ga8Si38, Rb8Al8Si38, Rb8Ga8Si38, Cs8Al8Si38 and Cs8Ga8Si38, respectively, at the EV-GGA level. Although a systematic difference was found between the present band gaps and those obtained by Imai et al.15 using different functional, the present band gaps are consistent with those in the previous theoretical work. The order of carrier densities where the Seebeck coefficient reaches a maximum is consistent with the previously mentioned order of band gaps for each composition.

It must be noted that the configurations of the substitutional atoms did not alter the order of the Seebeck coefficients shown in Fig. 8. Absolute value of the Seebeck coefficients did not change very much. For example, the maximum Seebeck coefficients for K8Ga8Si38 with the Ga configuration of (6c, 16i, 24k) = (6, 2, 0) were 439 and ~425 μV/K at 900 K, respectively, for the hole- and electron-doped clathrates, while those for the configuration (6c, 16i, 24k) = (5, 0, 3) were 403 and ~400 μV/K at 900 K, respectively. In addition to this difference, the required carrier density to maximize the Seebeck coefficient was slightly changed. This difference can be explained by the different band gaps of 0.80 eV for the Ga configuration of (6c, 16i, 24k) = (6, 2, 0)
and 0.73 eV for that of (6c, 16i, 24k) = (5, 0, 3). This result suggests that those different configurations of the substitutional atom did not change the order of the resulting thermoelectric properties, and the change in the resulting ZT was <0.01.

3.2.2 Power factor and band structure

Figures 9(a) and 9(b) show the optimized power factor for the hole- and electron-doped clathrates plotted as a function of temperature. The carrier relaxation time, 2.0 × 10⁻¹⁴ s, was assumed to be constant for all compositions, according to the estimation of Blake et al. for Ba₈Ga₁₆Si₃₈ single crystal.⁴³) Because of the balance between the Seebeck coefficient and the electrical conductivity, the optimized carrier density required for maximizing the power factor was ~5 × 10⁻²⁰ cm⁻³, which is higher than that for the Seebeck coefficient. For the hole-doped clathrate, the power factor exhibits the same temperature dependence for all compositions.

Figure 10 shows band structure of (a) K₈Ga₈Si₃₈, (b) Rb₈Ga₈Si₃₈, and (c) Cs₈Ga₈Si₃₈. Although the configuration of the substituted Ga breaks symmetry of the pristine Si₄₆, the same k-point path of pristine Si₄₆ was used for each composition. The Fermi level was set at the middle of the band gap. The band structures of those compositions looked all similar especially near the valence band edge because the tops of the valence bands are mainly composed of hybridized Ga–Si, and their configuration is the same for each composition. This should be the reason of the above mentioned temperature dependence of power factor.

The electrical conductivity exhibited a similar value when the hole-carrier density was higher than ~10¹⁹ cm⁻³ for each composition. This result indicates that the electrical conductivity is mainly attributed to the cage structure of Si and to the substituted Al or Ga when the carrier is a hole. The electrical conductivity of the electron-doped clathrate, on the other hand, exhibited the order of Cs > Rb > K, when the electron carrier density was higher than ~10¹⁹ cm⁻³. For the electron-doped clathrate, band dispersion near the bottom of the conduction band should be noted. For each composition, the bottom of the conduction band is located at the M-point. From compositions K₈Ga₈Si₃₈ to Cs₈Ga₈Si₃₈, the effective mass at the M-point became lighter (Fig. 10). For the Al-substituted clathrates, such tendency did not change. Therefore, the order of the electrical conductivity was Cs > Rb > K for the electron-doped clathrates, and the reverse order was exhibited for the Seebeck coefficient at the carrier electron density ~10¹⁰ cm⁻³ (Fig. 8(b)).

3.2.3 Implication for recent experimental investigation

Recently, Imai et al. synthesized K₈Ga₈Si₃₈ single crystal, and showed that it exhibits an indirect band gap of 0.10 eV and semiconducting behavior.⁴¹) They suggested that the discrepancy between the observed band gap and their calculated one (0.798 eV)⁴²) may be due to random substitutional positioning of Ga, vacancies, nonstoichiometry, and so on.⁴²)
It can be considered that random Ga configuration does not significantly narrow the band gap because the change in the band gap was found to be at most 0.1 eV, as demonstrated by changing the Ga configuration in the present work. Although a number of investigated configurations was small, the band gap should not become drastically narrower as far as the stoichiometric composition is preserved. As for the non-stoichiometry, a possible scenario is that different Ga substitutional contents from 8. When the Ga substitution content was changed from 8 to 7 or 9, the band structures were characterized as a shift of the Fermi level inside the band, and significant changes in the band gap did not occur. This behavior was the same for K deficiency. As for the vacancy, the calculated formation energies were 1.99 eV for the Si vacancy at the 6c site. The lowest formation energy of the Ga vacancy was 2.96 eV, which is higher than that of the above Si vacancy. The lowest vacancy formation energy in pristine Si$_{46}$ was 3.69 eV at the 6c site. The difference between formation energies of these Si vacancies should originate in the strain induced by the K encapsulation and the Ga substitution. Therefore, Si vacancy should be dominant in K$_8$Ga$_8$Si$_{38}$.

Band structure of K$_8$Ga$_8$Si$_{37}$ is shown in Fig. 11(a). The dispersion relations at the band edges are different from those in the pristine K$_8$Ga$_8$Si$_{38}$. In the K$_8$Ga$_8$Si$_{38}$, there are three nearly degenerated states at the top of the valence band at the R-point. However, because of the Si vacancy, such degenerated states are released, and the top of the valence band moves to a higher energy level. Figure 11(b) shows the contour of charge densities of the top of the valence band, cut in the plane including the Si vacancy and its nearest neighbor site. The contours are drawn within the range of 0.001 to 0.1 eV. The distance between successive contour lines corresponds to a factor of 1/10. The localized charge density around Si vacancy shown in Fig. 11(b) belongs to the surrounding dangling bond. Along with the formation of the dangling bond, the band gap becomes narrower: about 0.54 eV. Introducing further Si vacancies is expected to reduce the band gap much more. As evidence of this, the discrepancy between the calculated and experimentally determined band gaps can be explained by the formation of the Si vacancy.

### 3.2.4 Estimation of ZT values

By merging the calculated thermoelectric properties and the previously reported lattice thermal conductivity of X$_8$Si$_{46}$ (X = K, Rb or Cs), the ZT values were predicted as a function of temperature for all compositions. The results are represented as solid lines in Figs. 12(a) and 12(b), for hole- and electron-doping, respectively. The ZT values for all compositions continuously increased with temperature. The ZT of Cs$_8$Ga$_8$Si$_{38}$ exhibits the highest value for hole-doping, while that of Cs$_8$Al$_8$Si$_{38}$ exhibits the highest value for electron-doping, although the difference between the ZT values for Cs$_8$Al$_8$Si$_{38}$ and Cs$_8$Ga$_8$Si$_{38}$ is small for electron-doping.

In order to verify the present prediction, the same calculation was conducted for Ba$_8$Ga$_{16}$Si$_{30}$. The predicted ZT value at 300 K was 0.06 for hole-doping and 0.05 for electron-doping. Blake et al., on the other hand, estimated the ZT for electron-doped Ba$_8$Ga$_{16}$Si$_{30}$ at room temperature...
from experimental transport properties. They obtained a ZT value 0.185 for the single crystal,\textsuperscript{43} which is not consistent with our prediction. However, the experimental lattice thermal conductivity of Ba\textsubscript{8}Ga\textsubscript{16}Si\textsubscript{30} was about 1 W/mK at room temperature,\textsuperscript{44} while that of Ba\textsubscript{8}Si\textsubscript{30} we used was 9.5 W/mK. When we used the experimental lattice thermal conductivity,\textsuperscript{44} our predicted ZT value increased to 0.28. Note that the experimental condition was not necessarily optimized for carrier density. The Seebeck coefficient was $-42 \mu$V, and the electrical conductivity was 3500 S/cm according to the estimation of Blake et al.\textsuperscript{43} When the carrier density was properly selected in our calculation, the above quantities could be reproduced, and the resulting ZT value was 0.174, where the thermal conductivity was assumed to be 1 W/mK. This ZT value is close to the above estimated value of 0.185.\textsuperscript{43}

Now, we will assume that the lattice thermal conductivity of all compositions was 1 W/mK by the phonon scattering of the Ga substitution, independent of temperature. This assumption can be justified because of weak temperature dependence of lattice thermal conductivity of clathrate material.\textsuperscript{5} Then, optimal carrier density can be determined to maximize ZT because not only the electrical conductivity but also the electrical thermal conductivity are carrier-relaxation-time dependent. The ZT values of each composition after the re-optimization are represented as dotted lines in Fig. 11. The predicted ZT values are similar in electron-doped case, and about 0.66 at 900 K. On the other hand, clear distinction can be seen between X\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38} and X\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38} (X = K, Rb, Cs) in hole-doped case. Various configurations of Ga substitutional sites were evaluated, and the (6c, 16i, 24k) configuration was the most stable for Li\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38} and Na\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38}, while the (6c, 16i, 24k) configuration was the most stable for K\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38}, Rb\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38} and Cs\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38}. The different stable configurations of those two groups are suggested to originate in the degree of strain of the Si site in each cage. From the formation energy, possible clathrate compositions were investigated using first-principles calculations. The optimal carrier density for the Seebeck coefficient was dependent on 900 K should be lower than 1.0. The predicted ZT value of 0.75 for K\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38}, Rb\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38} and Cs\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38} might be the reasonable upper limit for ZT at 900 K.

However, present theoretical prediction does not exclude the possibility that ZT > 1 will be achieved in polycrystalline Si clathrate. Because the present calculation was performed for single crystal, only the optimal chemical composition for achieving a high ZT value can be predicted. Maximizing the ZT of the polycrystalline form, on the other hand, should be more beneficial for real application. If the grain size is smaller than the mean free path of a heat carrying phonon and carrier, the scattering of them is dependent on the grain size. At that small grain size limit, optimization of only the power factor is required, and ZT is expected to exhibit a maximum value.\textsuperscript{46} In order to verify this idea and our prediction, further studies on the experimental evaluation of the thermoelectric properties and analysis of the carrier and phonon scattering mechanisms must be needed.

![Fig. 12 Predicted dimensionless figures of merit (ZT) for ternary Si clathrate. ZT for each composition was calculated using $k_i$ predicted from MD simulation.\textsuperscript{26,27}](image)

4. Conclusion

In this study, possible combinations of alkali metal guest atoms and substitutional atoms in Type-I Si-clathrate were investigated using first-principles calculations. From the formation energy, it was found that all alkali metals were encapsulated as the guest element into a Si\textsubscript{46} cage, and either Al or Ga was suitable as the substitutional atom. Various configurations of Ga substitutional sites were evaluated, and the (6c, 16i, 24k) = (6, 2, 0) configuration was the most stable for Li\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38} and Na\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38}, while the (6c, 16i, 24k) = (5, 0, 3) configuration was the most stable for K\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38}, Rb\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38} and Cs\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38}. The different stable configurations of those two groups are suggested to originate in the degree of strain of the Si site in each cage. From the formation energy, possible clathrate compositions were proposed as K\textsubscript{8}Al\textsubscript{8}Si\textsubscript{38}, K\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38}, Rb\textsubscript{8}Al\textsubscript{8}Si\textsubscript{38}, Rb\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38}, Cs\textsubscript{8}Al\textsubscript{8}Si\textsubscript{38} and Cs\textsubscript{8}Ga\textsubscript{8}Si\textsubscript{38}.

The thermoelectric properties were calculated from the Boltzmann transport equation using the band energies obtained by the first-principles calculations. The optimal carrier density for the Seebeck coefficient was dependent on
the band gap. Hole-doping gave similar electrical conductiv-

ities for all clathrate compositions because the tops of the
valence bands are mainly composed of hybridized Ga–Si,
and this was the same for all compositions. However, the
order of the electrical conductivity for electron-doping was
Cs > Rb > K because of the changes in effective mass of
electron. In addition, the large discrepancy between the
theoretically and experimentally determined band gaps of
0.8 and 0.1 eV, respectively, for K$_2$Ga$_8$Si$_{13}$B$_2$ possibly originate in Si vacancy formation. The dimensionless figure of merit (ZT) for each composition was systematically predicted by combining the Seebeck coefficient, electrical conductivity, and electronic thermal conductivity calculated in the present study and the previously reported lattice thermal conduc-
tivity. ZT $\approx 0.75$ was predicted as the highest ZT value for hole-doped Cs$_3$Ga$_8$Si$_{13}$.

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REFERENCES

27) Table S2 in supplementary material of Ref. 41) for the site occupancy of K$_2$Ga$_8$Si$_{13}$B$_2$.