Substitutional and interstitial impurity p-type doping of thermoelectric Mg$_2$Si: a theoretical study

Naomi Hirayama$^a$, Tsutomu Iida$^b$, Mariko Sakamoto, Keishi Nishio$^b$ and Noriaki Hamada$^{c,d}$

$^a$Graduate School of Science, Osaka University, Toyonaka, Osaka, Japan; $^b$Faculty of Industrial Science and Technology, Tokyo University of Science, Tokyo, Japan; $^c$Center for Spintronics Research Network, Osaka University, Toyonaka, Osaka, Japan; $^d$Faculty of Science and Technology, Tokyo University of Science, Noda, Chiba, Japan

ABSTRACT
The narrow-gap magnesium silicide semiconductor Mg$_2$Si is a promising mid-temperature (600–900 K) thermoelectric material. It intrinsically possesses n-type conductivity, and n-type dopants are generally used for improving its thermoelectric performance; however, the synthesis of p-type Mg$_2$Si is relatively difficult. In this work, the hole doping of Mg$_2$Si with various impurity atoms is investigated by performing first principles calculations. It is found that the Ag-doped systems exhibit comparable formation energies $\Delta E$ calculated for different impurity sites (Mg, Si, and interstitial 4b ones), which may explain the experimental instability of their p-type conductivity. A similar phenomenon is observed for the systems incorporating alkali metals (Li, Na, and K) since their $\Delta E$ values determined for Mg (p-type) and 4b (n-type) sites are very close. Among boron group elements (Ga and B), Ga is found to be favorable for hole doping because it exhibits relatively small $\Delta E$ values for Si (p-type) sites. Furthermore, the interstitial insertion of Cl and F atoms into the crystal lattice leads to hole doping because of their high electronegativity.

1. Introduction
Thermoelectric generators that directly convert thermal energy into electric energy through the Seebeck effect can be potentially used for recovering waste heat energy to improve the energy efficiency of multiple applications, thus providing a possible solution to various environmental problems, such as global warming and limited energy resources.
Thermoelectric silicide materials have attracted considerable attention over the last decade because of their potential applicability in renewable and sustainable energy technologies. Magnesium silicide (Mg$_2$Si) [1–3], a narrow-gap semiconductor with anti-fluorite crystal structure, is a promising candidate for medium-temperature (600–900 K) thermoelectric applications, owing to its non-toxicity, low production cost, and low weight. However, significant improvement of the thermoelectric conversion efficiency of Mg$_2$Si is required for its successful commercialization.

N-type dopants such as Sb [1], Al [4], Bi [4], and Sn [5] were previously utilized to tune the carrier concentration in the Mg$_2$Si crystal and improve its thermoelectric efficiency. However, despite the multiple attempts to locate suitable acceptors, the development of hole-doped Mg$_2$Si is currently hindered by the difficulties in achieving stable p-type conductivity. For example, according to the results of one experimental study [6], the Ag doping of Mg$_2$Si results in p-type conductivity; however, the obtained systems exhibit the change in conductivity from p-type to n-type at temperatures above 650 K. This instability of p-type conductivity represents one of the obstacles to the successful development of Mg$_2$Si-based thermoelectric power generators because the conventional thermoelectric modules have a π-shape structure consisting of both n-type and p-type semiconductors. Therefore, the realization of a stable p-type Mg$_2$Si semiconductor with high thermoelectric efficiency would significantly contribute to the development of thermoelectric power generators.

As indicated by the results of theoretical [7,8] and experimental [9] studies, the existence of native lattice defects strongly affects the carrier transport in the Mg$_2$Si structure. In particular, the Mg atoms interstitially inserted into the cell act as dopants, owing to the intrinsic n-type conductivity of Mg$_2$Si [7]. A previous theoretical study [10] suggested that in the systems containing both lattice defects and acceptors, the number of electrons generated by interstitial Mg doping could compensate for the number of holes produced by intentional impurity doping and even potentially exceed it if a system contained interstitial Mg defects with a comparable number of acceptors. Thus, the presence of interstitial Mg defects is one of the main reasons for the difficulty in achieving stable p-type conductivity of Mg$_2$Si.

In the present study, we focus on another possible origin of the observed instability of p-type Mg$_2$Si – the structural instability of impurity atoms. By today, many theoretical studies [11–17] have been performed to determine the electronic properties of impurity-doped Mg$_2$Si and select the most suitable acceptors for this system. However, detailed and comprehensive information regarding the site occupation and stability of impurities in a cell has not been obtained yet. According to the results of this work, Ag atoms can occupy not only p-type (Mg), but also n-type (Si and interstitial) sites because of the small differences in their formation energies. Furthermore, it is suggested that Ag atoms change their locations at operating temperatures (600–900 K), which is presumably related to the above-mentioned variation of the conduction type [6]. In addition, Li [15], Na [16], and K alkaline metals, as well as B and Ga [18] boron group elements are found to generate holes after doping the most stable sites; however, except for B, they can dope different sites simultaneously because of their close formation energies. Furthermore, the feasibility of achieving p-type conductivity through the interstitial insertion of impurities characterized by high electronegativity (F, Cl, and Br) has been evaluated.

2. Computational method

2.1. Structural optimization of impurity-doped Mg$_2$Si crystals

Mg$_2$Si has the anti-fluorite crystal structure that belongs to the Fm-3m space group (No. 225). Its Si and Mg atoms occupy the 4a and 8c sites, respectively, and their atomic positions in the conventional unit cell (depicted in Figure 1) correspond to the following coordinates: Si (0, 0, 0), Mg (0.25, 0.25, 0.25), and Mg (0.75, 0.75, 0.75). Figure 1 describes the three impurity-doped systems examined in the present study: the substitution of an impurity atom for the Si and Mg atoms and its interstitial insertion into the 4b site (0.5, 0.5, 0.5).

![Figure 1](image-url) Figure 1. A Mg$_2$Si crystal unit cell (Fm-3m space group) consisting of the Si and Mg atoms denoted by the small and large spheres at the 4a and 8c sites, respectively. Possible impurity sites: (a) Mg atom, (b) Si atom, and (c) 4b site.
The impurity doping concentration \( x \) (at.%) is defined as its atomic fraction calculated with respect to the total number of atoms in the cell. As shown in Figure 1, the MgSi unit cell contains 12 (4 Si and 8 Mg) atoms; thus, assuming simple cubic (sc) periodicity for the atomic positions of impurities, their fraction in the cell \( x \) is equal to 8.333 at.% (1 impurity per 12 atoms). In order to examine the impurity-doped systems with \( x \) values close to the experimental ones (1 at.% or less), a \( 2 \times 2 \times 2 \) supercell that consists of eight unit cells with 96 (32 Si and 64 Mg) atoms must be utilized. When one atom (Mg or Si) in the \( 2 \times 2 \times 2 \) supercell is replaced by one (or two) impurity atoms with the sc periodicity, the value of \( x \) becomes equal to 1.042 at.% (or 2.083 at.%). Similarly, when the impurity distribution follows the fcc periodicity, a total of four impurity atoms are introduced into the supercell containing 96 atoms, which results in \( x = 4.167 \) at.%.

The obtained structures of the impurity-doped systems were optimized by taking into account the localized shifts of individual atoms from their regular positions in the perfect crystal caused by the presence of impurity atoms, as well as by optimizing the lattice constants using the cell-relaxation technique of the Quantum Espresso package [19] (which included a pseudopotential method based on the density functional theory). In all calculations, the norm-conserving pseudopotentials and generalized gradient approximation method (represented by the Perdew–Burke–Ernzerhof functional) were utilized. Wave functions, charge density, and potential were expanded into the plane waves with the cutoff parameters equal to 60 Ry for the wave functions and 240 Ry for the charge densities and potentials. Brillouin zone sampling was performed using the \( k \)-point grid with the \( 8 \times 8 \times 8 \) FCC mesh. For self-consistent field calculations, the convergence threshold of the total energy was equal to \( 10^{-8} \) Ry. A variable cell relaxation procedure was performed using the Broyden–Fletcher–Goldfarb–Shanno quasi-newton algorithm with the convergence thresholds for the total energy, all force components, and cell pressure equal to \( 10^{-5} \) Ry, \( 10^{-4} \) Ry/Bohr, and 0.5 kbar, respectively.

### 2.2. Formation energies and distributions of impurities

In order to identify the preferred occupation sites for various impurities in terms of energy, the following formation energies were calculated for the optimized structures:

\[
\Delta E^\text{Mg site} = E(\text{Mg}_2\text{Si}_3\text{SiA}_{3x}) + 3x E(\text{Si}) - E(\text{Mg}_2\text{Si}) - 3x E(A),
\]

(1)

\[
\Delta E^\text{Si site} = E(\text{Mg}_2\text{Si}_3\text{SiA}_{3x}) + 3x E(\text{Si}) - E(\text{Mg}_2\text{Si}) - 3x E(A),
\]

(2)

\[
\Delta E^\text{4b site} = E(\text{Mg}_2\text{SiF}_{3x}) + 3x E(\text{Ca}) - E(\text{Mg}_2\text{Si}) - 3x E(\text{CaF}_2).
\]

(3)

Equations (1)–(3) correspond to the Mg, Si, and 4b sites occupied by impurity atoms A (see Figure 1) (here \( E \) denotes the total energy values calculated assuming single-crystal structures for the studied systems). Although B can assume several crystal configurations, the crystallographic data for its rhombohedral lattice [20] were used to estimate the \( E(B) \) values. In addition, CaF\(_2\) [21] and crystalline Cl\(_2\) [22] were also considered precursors for doping the Mg\(_2\)Si system with F and Cl atoms at a temperature of 88.15 K, respectively, because they exist in the gaseous state at normal pressure and room temperature. Hence, Equations (1)–(3) for the CaF\(_2\) dopant can be expressed the following forms:

\[
\Delta E^\text{Mg site} = E(\text{Mg}_2\text{Si}_3\text{SiF}_{3x}) + 3x E(\text{Ca}) + 3x E(\text{Mg}) - E(\text{Mg}_2\text{Si}) - 3x E(\text{CaF}_2),
\]

(1')

\[
\Delta E^\text{Si site} = E(\text{Mg}_2\text{Si}_3\text{SiF}_{3x}) + 3x E(\text{Ca}) + 3x E(\text{Si}) - E(\text{Mg}_2\text{Si}) - 3x E(\text{CaF}_2),
\]

(2')

\[
\Delta E^\text{4b site} = E(\text{Mg}_2\text{SiF}_{3x}) + 3x E(\text{Ca}) - E(\text{Mg}_2\text{Si}) - 3x E(\text{CaF}_2).
\]

(3')

If an impurity-doped system exhibits close formation energies for different sites, both its n-type and p-type dopants quantitatively, the values of the occupation probability of an impurity atom \( p_1 \) were calculated for Mg, Si, and interstitial 4b sites. During calculations, it was assumed that impurity atoms were distributed across different sites as a canonical ensemble; therefore, the value of \( p_1 \) was proportional to the Boltzmann factor \( \exp(-\beta E_i) \), where \( E_i \) was the energy required for occupying site \( i \). Further, impurity atoms were also considered independent from each other; in this case, the formation energy per impurity atom \( \Delta e_i \) was equal to \( E_i \). Hence,

\[
p_{\text{Mg}} = 2 Z^{-1} \exp \left( -\frac{\Delta e_{\text{Mg site}}}{k_B T} \right),
\]

(4)
$p_i = Z^{-1} \exp \left( -\frac{\Delta \epsilon_i}{k_B T} \right), \quad i = \text{Si and 4b sites}$

where $k_B$ is the Boltzmann constant, and the partition function $Z$ is defined as:

$$Z = 2\exp \left( -\frac{\Delta \epsilon_{\text{Mg site}}}{k_B T} \right) + \exp \left( -\frac{\Delta \epsilon_{\text{Si site}}}{k_B T} \right) + \exp \left( -\frac{\Delta \epsilon_{\text{4b site}}}{k_B T} \right).$$

The temperature used in the synthesis by the vertical Bridgman technique (1378 K [23]) was substituted into $T$ of Equations (4)–(6). The obtained $p_i$ values were used to predict whether the added impurities would occupy not only the p-type sites, but also the n-type ones during synthesis.

3. Results and discussion

3.1. Site stability of conventional p-type Ag dopant

In this section, the stability of the sites occupied by Ag atoms in the Mg$_2$Si crystal lattice (which represent typical p-type dopants) is discussed in terms of the formation energies $\Delta E$ of the optimized Ag-doped structures.

Table 1 lists the changes in the lattice constant $a$ from that of pure Mg$_2$Si (6.354 Å) caused by doping with Ag atoms and the positions of its neighboring atoms determined via the variable cell relaxation calculations. Although this table contains only the data obtained for the $2 \times 2 \times 2$ cell incorporating an Ag atom, the values of $a$ determined at other doping concentrations $x$ are presented in Supplemental Material 1. These results show that the largest lattice constant was obtained for doping the 4b sites followed by the Si and Mg sites. In the first case, the insertion of an additional atom into the cell increased its lattice constant. In fact, the analysis of atomic positions revealed that when an Ag atom was inserted into the 4b site, the surrounding Mg atoms moved away from it by a relative distance of 2.6%. During substitutional doping, the crystal is expected to expand (or shrink) after the replacement of a Si (Mg) atom with Ag because the latter has a greater (lower) covalent radius (126 pm) compared to 116 pm for Si and 139 pm for Mg [24]. During the substitution of Si with Ag, the atomic positions remain mostly unchanged. In the case of Mg sites, the introduced Ag atom attracts the Mg atoms occupying the next-nearest neighbor sites causing them to move at a relative distance of 3.4%, which is larger than the displacement of the nearest Si atoms. Hence, it can be concluded that the observed shrinkage of the cell should be attributed to the interactions between the Ag species and their next-nearest Mg neighbors (in other words, the Ag atoms substituted for Mg ones occupy a smaller volume because of their smaller covalent radii; as a result, the next-neighboring Mg atoms move towards Ag ones).

The formation energies of the optimized structures $\Delta E_i (i = \text{Mg, Si, or 4b})$ were calculated using Equations (1)–(3). Figure 2 shows the dependences of $\Delta E$ on $x$. The numerical error of each data point was below $10^{-10}$ Ry in this and the subsequent figures, in which the error bars are not shown because they fall within the areas covered by the symbols. It should be noted that Figure 2 and the subsequent Figures 3–5 display the formation energies $\Delta E_i$ that have been converted to the values obtained for the conventional unit cell depicted in Figure 1. On the other hand, to calculate the occupational probabilities $p_i$ using Equations (4)–(6), the formation energies per impurity atom $\Delta \epsilon_i$ are used, which are explained in more detail in the Supplemental Material 2.

According to Figure 2, the studied systems exhibit close values of $\Delta \epsilon_i (i = \text{Mg, Si, or 4b})$; therefore, doping different sites with Ag can be achieved during the synthesis procedure. The densities of states (DOS) of the Mg$_2$Si crystals doped with Ag atoms at the concentration $x = 1.04$ at.% (1 impurity per 96 atoms in a cell) are also depicted in Figure 2. Their values indicate that for the Mg sites, the position of the Fermi energy level shifts towards the valence band leading to p-type conductivity, while for the other cases, it shifts towards the conduction band, leading to n-type conductivity.

The $p_i (i = \text{Mg, Si, or 4b})$ values calculated using Equations (4)–(6) are listed in Table 2; $\Delta \epsilon_i$ is obtained by fitting the $\Delta E_i(x)$ data plotted in Figure 2 using the method of least squares (here the values of $x$ do not exceed 4.17% because their experimental values are typically equal to 1% or less). The computational details are provided in Supplemental Material 2. As a result, the values $\Delta \epsilon_{\text{Mg site}} = 0.525$ eV, $\Delta \epsilon_{\text{Si site}} = 1.0$ eV, $\Delta \epsilon_{\text{4b site}} = 0.675$ eV, and accordingly, $p_{\text{Mg}} = 0.87$, $p_{\text{Si}} = 0.01$, and $p_{\text{4b}} = 0.12$ were obtained at a synthesis temperature of 1378 K, suggesting that the added Ag atoms mainly replaced Mg ones to generate holes; however, some of them occupied other sites (especially 4b ones) to produce electrons. Nevertheless, the resulting system should exhibit p-type conductivity because the majority of Ag atoms occupied the Mg sites.

In the discussion presented above, the multiple-site occupation with Ag atoms that occurs during synthesis was considered; however, a change in the type of the occupation site likely occurs when a thermoelectric generator is operated at elevated temperatures because of the very small energetic differences between the sites, as shown in Figure 2. The difference between $\Delta \epsilon_{\text{Mg site}}$ and $\Delta \epsilon_{\text{4b site}}$ is about 0.15 eV, which is relatively close to the heat energies.
of 0.05–0.08 eV corresponding to the temperature range of 600–900 K (note that Mg$_2$Si-based materials are expected to be used in this temperature range). Therefore, it may be possible that the Ag atoms occupying the Mg sites move to the 4b sites when the system is operated at high temperatures characterized by the dominant entropic contribution to the free energy. The heat-induced change in the type of occupation sites may explain the experimental findings [6] indicating that the conduction of Ag-doped Mg$_2$Si changes from p-type to n-type at temperatures above 650 K.

Additionally, if the Mg$_2$Si cell expands due to the applied heat, it can also increase the thermal instability of p-type conductivity because the optimized cell obtained for the p-type (Mg) site shrinks by doping with Ag, in contrast to the other sites. Thus, the Ag atoms substituted for Mg can become more unstable due to thermal expansion, which may further reduce the number of holes at elevated temperatures.
Furthermore, the site occupation of Ag may be controlled by applying an external pressure during synthesis. To estimate the pressure-induced shift of $\Delta \varepsilon_i$, we calculated the electronic state for systems containing Ag atoms at 1.04 at.%, which occupy the n-type (Si or 4b) sites, with the lattice constant of the Mg-site-occupation case ($a_{Mg} = 6.3477 \, \text{Å}$). The calculation method and the results are detailed in

Figure 2. (Top) Dependences of the formation energy of Ag-doped Mg$_2$Si on the doping concentration determined for Mg, Si, and 4b sites. Because the formation energies obtained at each concentration are relatively close, Mg doping may be interchanged with Si or 4b doping at a small difference in energy. (Bottom) The DOS of the crystals doped with Ag atoms occupying the Mg, Si, and 4b sites at $x = 1.04$ at.%. The Mg sites exhibit p-type conductivity, while the other two sites (Si and 4b) are characterized by n-type conductivity.
Figure 3. Formation energies and DOS values of (a) Li-, (b) Na-, and (c) K-doped Mg$_2$Si determined for Mg (circles), Si (triangles), and 4b (crosses) sites. Here, the results of $\Delta E(x)$ for Na-doped systems are almost identical to ones obtained in our previous study [25] where the different calculation conditions were used. The obtained results show that Mg and 4b sites are the two preferred sites for these impurities. The DOS of these systems at the concentration $x = 1.04$ at.% demonstrate that the substitution of Mg atoms with these impurities generated holes, whereas the occupation of 4b sites led to electron doping.
Supplemental Material 3 in detail. We here summarize the results briefly. The calculation results showed that a shift of the site occupation of Ag occurred due to the restriction of the lattice constant; the $p_{Mg}$ changed from 87% to 96% and the required pressure for inducing the shift was roughly estimated at 160 MPa. Although Mg$_2$Si is known to be brittle, it can withstand high pressure and maintain its semiconducting properties under pressures of several gigapascals (GPa). Considering that a pressure of the order of tens to hundreds of MPa is usually applied during the synthesis of Mg$_2$Si using the spark plasma sintering (SPS) method, it is presumably practical to apply additional pressure to shift the site occupation of dopants. Because of the page limitation, the calculation for other impurity species is described in Supplemental Material 3.

### 3.2. Substitutional impurities for hole doping

#### 3.2.1. Alkaline metals at Mg-site

Alkaline Li, Na, and K metals can serve as acceptors after replacing Mg atoms in the Mg$_2$Si lattice, owing to the difference in their valences. Table 1 shows the lattice constants $a$ of the optimized cells doped with Li, Na, and K atoms. Different changes in $a$ are observed for various impurity sites, which can be explained by the differences in their covalent radii. When a Li atom occupies a Mg site, the larger covalent radius of Mg (139 pm) with respect to that of Li (133 pm) leads to crystal shrinkage; on the other hand, the Mg$_2$Si crystal expands when Li replaces Si (116 pm). Similarly, doping with Na (155 pm) and K (196 pm) atoms results in larger lattice constants as compared to that of pure Mg$_2$Si for all types of impurity sites.

From the optimized structures, the formation energies $\Delta E(x)$ were obtained (see Figure 3). The systems doped with Li for Mg and 4b sites exhibit relatively small values of $\Delta E$ (the substitution of its Si sites is very unlikely), which is in good agreement with the results of pseudopotential first-principles calculations that were performed by Kolezynski et al. using a different computational software (USPPACK90). The Na- and K-doped systems with occupied Mg sites demonstrated the lowest

![Figure 4](image-url)
Figure 5. Formation energies and DOS of (a) F-, (b) Cl-, and (c) Br-doped Mg$_2$Si determined for Mg (circles), Si (triangles), and 4b (crosses) sites. The F and Cl atoms occupying 4b sites exhibit the minimum formation energies. The DOS values of the Mg$_2$Si crystals doped with (g) F, (h) Cl, and (i) Br atoms at the concentration $x = 1.04$ at.% show that these systems exhibit p-type conductivity for the 4b sites.
Table 2. Formation energies per impurity atom $\Delta E_i$ ($i = \text{Mg, Si, or 4b}$), which were obtained using the procedure described in Supplemental Material 2, and the corresponding occupation probabilities of impurity sites $p_i$ determined by Equations (4)–(6) .

| Impurity | Occupation site | Conductivity type | Formation energy per atom $\Delta E$ (eV) | Site occupation probability* (%) |
|----------|-----------------|-------------------|------------------------------------------|----------------------------------|
| Ag       | Mg site         | p                 | 0.525                                    | 87                               |
| Si site  | n               |                   | 1.000                                    | 1                                |
| 4b site  | n               |                   | 0.675                                    | 12                               |
| Li       | Mg site         | p                 | $-0.008$                                  | 55                               |
| Si site  | n               |                   | 2.283                                    | 0                                |
| 4b site  | n               |                   | $-0.067$                                  | 45                               |
| Na       | Mg site         | p                 | 0.633                                    | 82                               |
| Si site  | n               |                   | 3.592                                    | 0                                |
| 4b site  | n               |                   | 0.733                                    | 18                               |
| K        | Mg site         | p                 | 1.400                                    | 88                               |
| Si site  | n               |                   | 4.992                                    | 0                                |
| 4b site  | n               |                   | 1.350                                    | 12                               |
| B        | Mg site         | n                 | 3.642                                    | 0                                |
| Si site  | p               |                   | 1.650                                    | 100                              |
| 4b site  | n               |                   | 3.442                                    | 0                                |
| Ga       | Mg site         | n                 | 0.719                                    | 30                               |
| Si site  | p               |                   | 0.540                                    | 68                               |
| 4b site  | n               |                   | 0.982                                    | 2                                |
| F        | Mg site         | p                 | 5.142                                    | 0                                |
| Si site  | n               |                   | 3.800                                    | 0                                |
| 4b site  | p               |                   | 2.508                                    | 100                              |
| Cl       | Mg site         | p                 | 1.733                                    | 0                                |
| Si site  | n               |                   | 0.125                                    | 14                               |
| 4b site  | p               |                   | $-0.092$                                  | 86                               |
| Br       | Mg site         | p                 | 2.350                                    | 0                                |
| Si site  | n               |                   | 0.660                                    | 98                               |
| 4b site  | p               |                   | 1.150                                    | 2                                |

*Site occupation probability is calculated at synthesis temperature (1378 K).

$\Delta E$; however, the interstitial insertion into 4b sites also resulted in small values of $\Delta E$ that were slightly higher than the values obtained for Mg sites. As indicated by the DOS depicted in Figure 3, the presence of these impurities causes hole doping in the case of Mg substitution, as was discussed earlier, whereas electron doping occurs when dopant atoms occupy 4b sites. Since the energies of Mg and 4b sites are almost the same, it can be suggested that doping with these impurities generates both holes and electrons.

The site-occupation probabilities of Li, Na, and K atoms are listed in Table 1. They exhibit finite values of $p_{4b}$, as well as $p_{\text{Mg}}$; in particular, the values of $p_{\text{Mg}}$ and $p_{4b}$ determined for Li insertion are comparable (55% and 45%, respectively). Although the obtained data do not support the stability of p-type conductivity, Li atoms can serve as potential acceptors in the Mg$_2$Si lattice because of the remarkably low $\Delta E$ of Mg sites (such as $-0.01$ eV at $x = 1.04$ at.%). Moreover, as shown in Figure 3(a), the Li-related impurity states were different for Mg and 4b sites (in the former case, Li formed few states at the edge of the valence band, whereas in the latter case, distinct impurity states were produced near the edge of the conduction band). Thus, at low doping levels that are generally used experimentally (0.1–1.0 at.%), Li atoms substituted for Mg create a shallow impurity state, whereas doping 4b sites results in the formation of a deep localized state. This suggests a possibility that the number of holes produced by the Li substitution of Mg sites will exceed the number of electrons generated by interstitial Li (even when comparable numbers of Li atoms occupy the Mg and 4b sites), ultimately leading to p-type conductivity. The described calculation results can explain the experimental findings reported by Koleynski et al. [15], who stated that Li-doped systems exhibited positive values of the Seebeck coefficient up to $x = 3.0$ corresponding to hole doping.

In addition, unusual behavior of the hole concentration was observed in the same work [15] (the Seebeck coefficient decreased with increasing Li content from $x = 0.5$ to 3.0), which could be attributed to the increase in the number of Li-occupied 4b sites, leading to electron doping. In fact, the X-ray diffraction data reported by this group revealed that the lattice constant $a$ increased linearly with $x$ according to the equation $a = 0.004 x + 0.6352$ with $R^2 = 0.98$ [15] and were in good agreement with the calculation results obtained for 4b sites in this work (see Fig. 6(b) of Supplemental Material 1), which demonstrated a similar linear dependence ($a = 0.0046 x + 0.6348$ with $R^2 = 1.0$) at $x$ values below 4.167 at%. Although Li is a potentially promising acceptor for Mg$_2$Si because of its negative formation energy, the simultaneous occupation of 4b (n-type), as well as Mg (p-type) sites due to nearly the same formation energies pose a challenge in achieving stable p-type conduction. Application of adequate pressure can likely improve the controllability of the p-type conduction by Li doping, because it should increase the occupation of the Mg site by Li and suppress the occupation of other sites. This idea is discussed in Supplemental Material 3 in detail.

Finally, we discuss the solid solubility of these dopants. In the experimental work [16], it was reported that the solid solubility of Na in Mg$_2$Si reaches a limit at $y = 1$ for Mg$_{66.7-y}$Si$_{33.3}$Na$_y$, which corresponds to $x = 1.04$% (i.e. Mg$_{66.7}$Si$_{33.3}$Na$_1$) in the present paper. As shown in Table 2, the formation energy per Na atom, substituted for Mg, is given as 0.633 eV. Based on this result, it is assumed that the solubility limit of K is less than 1%, since it has a higher formation energy $\Delta E$, whereas the Li is expected to be substituted for Mg at $x = 1$% or more. We are not aware of comparative studies on the solubility limit of the Alkaline metals; however, an experimental work on MgSi$_{1-x}$Sn$_x$ [26] revealed that Li is a far more effective acceptor in comparison to Na or K because it exhibits better carrier activation and brings about a significant increase in the hole.
density. This experimental result is consistent with the foregoing prediction.

### 3.2.2. Boron group elements at Si-site

The boron group elements B and Ga with a valence of 3 are expected to generate holes after their substitution for Si atoms characterized by a valence of 4.

The changes in $a$ caused by incorporating these impurities are mostly consistent with the produced variations of atomic positions (see Table 1). For instance, the substitution of Mg and Si atoms with B decreases the value of $a$, owing to their attraction of the nearest-neighbor atoms. On the other hand, both the value of $a$ and atomic positions remain nearly unchanged after the interstitial insertion of B into 4b sites.

The lowest formation energies were obtained for the doping of Si sites with B and Ga atoms (Figure 4). The B-doped systems exhibited relatively high formation energy, such as $\Delta E_{Si \text{site}} = 1.65$ eV, which was one order of magnitude higher than the energy corresponding to the synthesis temperature of 1378 K equal to 0.119 eV (see Table 2). This result is unfavorable for B doping during the conventional synthesis process (especially when rhombohedral B crystals are used as the starting material, which was assumed when calculating the formation energies in Equations (1)–(3)). Selecting a suitable precursor with small formation energy is required for the successful fabrication of p-type B-doped MgSi. Here, we recall that the experimental solubility limit of Li at the Si site is approximately 1% [16], and in this case, our calculated formation energy per atom $\Delta e$ is 0.633 eV. In contrast, B doping for the Si site exhibits a substantially higher $\Delta e$ value of 1.650 eV, as shown in Table 2. Therefore, the solubility limit of B is likely to be less than 1 at.%. As shown in Table 2, the Ga-doped system exhibits a value of $\Delta E_{Si \text{site}}$ (0.067 eV) that is lower than the thermal energy corresponding to the synthesis temperature (0.119 eV); moreover, it is much lower compared with the B-doped system, which allows us to expect that the solid solubility limit of Ga is greater than that of B. The DOS obtained for this system (Figure 4(b)) is in good agreement with the results of a previous theoretical work conducted by Ihou-Mouko et al. [18], suggesting that its p-type conductivity could be successfully achieved via Ga doping. Indeed, their experimental measurements revealed that hole concentrations of $1.62 \times 10^{19}$ cm$^{-3}$ were achieved by the 0.8 at.% Ga doping [18]. Although close values of $\Delta E$ were determined for the Mg and Si sites, it would be difficult for Ga atoms to move from Si sites to other sites due to thermal fluctuations as they have a relatively large atomic mass. Consequently, it is expected that stable p-type conductivity can be maintained at elevated temperatures.

### 3.3. Acceptor candidates with high electronegativity

This section is devoted to the impurities with high electronegativity, such as F (3.98), Cl (3.16), and Br (2.96) [27], which can be potentially used as acceptors (for comparison, the electronegativities of Mg and Si atoms are equal to 1.31 and 1.90, respectively).

The lattice constants $a$ of the MgSi$_2$ systems doped with these impurities are listed in Table 1. According to the obtained results, doping with F atoms leads to lattice shrinkage; in contrast, doping with Cl and Br atoms expands it regardless of the type of occupied sites. The largest value of $a$ was obtained for the Br-doped systems followed by the Cl- and F-doped ones, which was consistent with the order of their corresponding atomic radii Br $> \text{Cl} > \text{F}$.

As shown in Figure 5, the F- and Cl-doped systems exhibit the smallest values of $\Delta E$ for 4b sites. Their corresponding DOS plots contain the Fermi levels in the valence bands, indicating that these impurities act as acceptors. In particular, the $\Delta E_{4b \text{site}}$ values obtained for the systems doped with Cl atoms at doping concentrations $x$ below 2.08 at.% were almost zero, suggesting that Cl species easily occupied 4b sites. Although $\Delta E_{Si \text{site}}$ also exhibits a low value at $x = 1.04$ at.%, it increases with $x$ more rapidly than $\Delta E_{4b \text{site}}$. Therefore, the formation energy per Cl atom calculated from the slope of the $x - \Delta E$ graph is different for the Si and 4b sites (according to Table 2, $\Delta E_{4b} = -0.092$ eV and $\Delta E_{Si} = 0.125$ eV), suggesting that the occupation of 4b sites is more energetically favorable. For the Br-doped system, the lowest $\Delta E$ value was obtained for Si sites followed by 4b and Mg sites. Since n-type conductivity is observed for the most stable Si sites (see the DOS depicted in Figure 5(c)), it is hard to achieve stable hole doping with Br atoms.

For doping with F, the lowest formation energy was obtained for the 4b site, as mentioned above, which suggests F insertion into the interstitial site. However, to elucidate the microscopic structure of the crystal doped with F, it may be necessary to examine the interaction between F and self-vacancies in Mg$_2$Si. Experimental [28,29] and theoretical [30] studies have revealed that interstitial F in Si has a tendency to form complexes with vacancies. According to Ref. [30], the vacancy-F complexes have two ground-state configurations and they are negative-$U$ systems that accompany lattice distortion. Therefore, in future studies, it is important to clarify whether F in Mg$_2$Si also exhibits such behavior.
Finally, the structural changes observed after the addition of F, Cl, and Br atoms into the interstitial 4b sites must be discussed. First, we examine the opposite effects produced by F and Cl additions because they may provide important information on the volume of the interstitial region. As shown in Table 1 and Fig. 6 in Supplemental Material 1, the value of $a$ decreased and increased with F and Cl doping, respectively. The atomic positions listed in Table 1 also demonstrate that the nearest-neighbor Mg atoms move towards interstitial F atoms and become repelled by the interstitial Cl species, which is consistent with the trends previously observed for the $a$ values of these systems. Therefore, it can be concluded that the volume of the interstitial region around 4b sites is between the volumes occupied by F (the ionic radius: 136 pm) and Cl (0 < $r_e$ < 181 pm) species. As shown in Table 1, moreover, the addition of Br atoms to 4b sites drives the nearest-neighbor Mg atoms away. As a result, the increase in $a$ is larger than that obtained via Cl doping. Thus, the relatively high value of $AE_{4b\text{ site}}$ obtained for Br doping should be attributed to the structural instability of the produced system (in other words, it was difficult to dope 4b sites with Br due to its larger ionic radius of 195 pm).

4. Conclusions

Variable cell relaxation calculations were performed for the Mg$_2$Si systems doped with several elements using the first-principles pseudo-potential method. As a result, the Ag-doped systems exhibited close values of formation energies and finite occupation probabilities for both 4b (n-type) and Mg (p-type) sites. The obtained results suggest a possibility of the simultaneous doping of holes and electrons during synthesis; moreover, the Ag atoms occupying Mg sites would be driven towards 4b sites at elevated temperatures. The same problem may be encountered for the systems incorporating alkali metals (Li, Na, and K) and Ga. However, Li needs small energy to occupy Mg sites; in addition, it forms shallow impurity levels adjacent to the valence band, which can be easily activated to dope holes. The possibility of using interstitial p-type dopants is also suggested in this work; it was found that Cl and F atoms tended to occupy the interstitial 4b sites leading to hole doping.

The obtained calculation results revealed that the lattice constant and atomic positions depended on the type of the sites occupied by an impurity atom, whose occupation characteristics could be controlled by varying the structural properties of the crystal. For instance, conducting the synthesis procedure at a relatively high pressure may prevent the insertion of Li and Ag atoms into 4b sites; in contrast, it would be favorable for the substitution of Mg sites with these atoms because the most stable structure obtained for 4b (Mg) sites has a larger (lesser) lattice constant as compared to that determined for pure Mg$_2$Si.

In the present study, we limited our investigation to the three cases, namely, the substitutional Mg- and Si-site occupation and the interstitial insertion, as structures of a system incorporating impurities and estimated the occupation probabilities for these cases. However, to estimate the realization probability of these phases rigorously, more realistic simulations of the actual growth process are required; in particular, other side phases that can form from the Mg, Si, and dopant atoms need to be considered. If such side phases have a formation energy that is comparable to or lower than that of the impurity-doped Mg$_2$Si, they will hinder the hole doping in the matrix. Furthermore, our calculation does not consider the anisotropic deformation of the cell through uniaxial pressing, which is generally used in SPS and other compaction methods. In order to consider the uniaxial pressing of a polycrystalline sample theoretically, various directions in which the pressure is applied to the crystal lattice should be taken into account. Although we have estimated the pressure necessary to realize a shift in the impurity occupation by assuming equiaxial deformation of the cell, further calculations for a uniaxially contracted cell are required to obtain a realistic guideline for actual material development. In addition, there are few experimental reports on Mg$_2$Si doped with acceptors; in contrast, several experimental groups realized successful p-type doping for Mg$_2$Si$_{1-x}$Sn$_x$ (0 < $x$ < 1) (e.g. Ref. [31]), where Si atoms were partly replaced with Sn in the same crystallographic structure with Mg$_2$Si. Therefore, more experimental studies on p-type Mg$_2$Si are desired; further, comparisons of their doping ability with that of Mg$_2$Si$_{1-x}$Sn$_x$ from the viewpoint of electronic and structural properties will enhance our understanding as well.

Acknowledgments

The authors would like to thank Prof. Hiroshi Katayama-Yoshida (The University of Tokyo), who suggested that the insertion of elements with high electronegativity into a cell can dope holes into Mg$_2$Si.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This research was partially supported by JSPS KAKENHI Grant Numbers [17K14922 and 18K03550].
References

[1] Oto Y, Iida T, Sakamoto T, et al. Thermoelectric properties and durability at elevated temperatures of impurity doped n-type Mg2Si. Phys Status Solidi C. 2013;10:1857–1861.

[2] Borisenko VF. Semiconducting silicides. Berlin: Springer; 2000.

[3] Morris RG, Redin RD, Danielson GC. Semiconducting properties of MgSi single crystals. Phys Rev. 1958;109:1909–1915.

[4] Sakamoto T, Iida T, Matsumoto A, et al. Thermoelectric characteristics of a commercialized MgSi source doped with Al, Bi, Ag, and Cu. J Electron Mater. 2010;39:1708–1713.

[5] Zaitsev VK, Fedorov MI, Gurieva EA, et al. Highly effective Mg2Si1−xSnx thermoelectrics. Phys Rev B. 2006;74:045207.

[6] Akasaka M, Iida T, Matsumoto A, et al. The thermoelectric properties of bulk crystalline n- and p-type MgSi prepared by the vertical Bridgman method. J Appl Phys. 2008;104:013703.

[7] Kato A, Yagi T, Fukusako N. First-principles studies of intrinsic point defects in magnesium silicide. J Phys Condens Matter. 2009;21:205801.

[8] Jund P, Viennois R, Colinet C, et al. Lattice stability and formation energies of intrinsic defects in MgSi and MgGe via first principles simulations. J Phys Condens Matter. 2013;25:035403.

[9] Kubouchi M, Hayashi K, Miyazaki Y. Quantitative analysis of interstitial Mg in MgSi studied by single crystal X-ray diffraction. J Alloy Compd. 2014;617:389–392.

[10] Hirayama N, Iida T, Nishio K, et al. Influence of native defects on structural and electronic properties of magnesium silicide. Jpn J Appl Phys. 2017;56:05DC05.

[11] Mars K, Ihou-Mouko H, Pont G, et al. Thermoelectric properties and electronic structure of Bi- and Ag-Doped Mg2Si1−xSnx compounds. J Electron Mater. 2011;40:889–897.

[12] Zwoleński P, Tobola J, Kaprzyk S. A theoretical search for efficient dopants in Mg2X (X = Si, Ge, Sn) thermoelectric materials. J Electron Mater. 2013;42:1855–1863.

[13] Bourgeois J, Tobola J, Wiendlocha B, et al. Study of electron, phonon and crystal stability versus thermoelectric properties in Mg2X (X = Si, Sn) compounds and their alloys. Funct Mater Lett. 2013;6:1340005.

[14] Kajitani T, Kubouchi M, Kikuchi S. High-performance p-type magnesium silicon thermoelectrics. J Electron Mater. 2013;42:1855–1863.

[15] Koleżynski A, Nieroła P, Wojciechowski KT. Li doped Mg2Si p-type thermoelectric material: theoretical and experimental study. Comp Mater Sci. 2015;100:84–88.

[16] Niwa Y, Todaka Y, Umemoto M, et al. Thermoelectric property of Na-doped Mg2Si. Jpn Inst Met. 2008;72:693–697, in Japanese.

[17] Tani J, Kido H. Thermoelectric properties of p-doped Mg2Si semiconductors. Jpn J Appl Phys. 2007;46:3309–3314.

[18] Ihou-Mouko H, Mercier C, Tobola J, et al. Thermoelectric properties and electronic structure of p-type Mg2Si and Mg2Si0.4Ge0.6 compounds doped with Ga. J Alloy Compd. 2011;509:6503–6508.

[19] Giannozzi P, Baroni S, Bonini N, et al. Quantum Espresso: a modular and open-source software project for quantum simulations of materials. J Phys Condens Matter. 2009;21:395502.

[20] McCarty LV, Kasper JS, Horn FH, et al. A new crystalline modification of boron. J Am Chem Soc. 1958;80:2592.

[21] Gerward L, Olsen JS, Steenstrup S, et al. X-ray diffraction investigations of CaF2 at high pressure. J Appl Crystallogr. 1992;25:578–581.

[22] Keesom WH, Taconis KW. On the crystal structure of chlorine. Physica. 1936;3:237–242.

[23] Akasaka M, Iida T, Nemoto T, et al. Non-wetting crystal growth of MgSi by vertical Bridgman method and thermoelectric characteristics. J Cryst Growth. 2007;304:196–201.

[24] Pyykko P, Atsumi M. Molecular single-bond covalent radii for elements. Chem Eur J. 2009;15:186–197.

[25] Hirayama N, Iida T, Morioka S, et al. First-principles investigation of structural, electronic, and thermoelectric properties of n- and p-type Mg2Si. J Mater Res. 2015;30:2567–2577.

[26] Zhang Q, Cheng L, Liu W, et al. Low effective mass and carrier concentration optimization for high performance p-type Mg2Si1−xLi2xSn1−ySn2y solid solutions. Phys Chem Chem Phys. 2014;16:23576–23583.

[27] Huheey JE. Inorganic chemistry: principles of structure and reactivity. New York (NY): Harper & Row; 1983.

[28] Simpson PJ, Jenei Z, Asoka-Kumar P, et al. Observation of fluorine-vacancy complexes in silicon. Appl Phys Lett. 2004;85:1538–1540.

[29] Uedono A, Inumiya S, Matsuki T, et al. Vacancy-fluorine complexes and their impact on the properties of metal-oxide transistors with high- gate dielectrics studied using monoeenergetic positron beams. J Appl Phys. 2007;102:054511.

[30] Lopez MG, Fiorentini V, Impellizzeri G, et al. Fluorine in Si: native-defect complexes and the suppression of impurity diffusion. Phys Rev B. 2005;72:045219.

[31] Isoda Y, Tada S, Nagai T, et al. Thermoelectric performance of p-Type Mg2Si0.4Ge0.6 with Li and Ag double doping. Mat Trans. 2010;51:868–871.