Exploratory Study of Substitutional Elements in Mg$_2$Si for Inducing State of Negative Chemical Pressure

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First-principles calculations were used to investigate the effects of substituting a Mg atom in Mg$_2$Si with a foreign atom. The aim was to chemically induce a state of negative pressure for Mg$_2$Si, which would theoretically increase its thermoelectric power factor. First, density of states (DOS) calculations were performed for Mg$_2$Si with a Mg atom substituted with Group 3–12 elements (Sc to Zn). The results suggest that Group 3 and 4 elements are good candidates because the main features of the DOS curves for the substituted Mg$_2$Si were the same as that of the undoped semiconductor. Structural optimization and energy calculations were then performed for Mg$_2$Si substituted with Sc, Y, La, Ti, Z, and Hf. Only Sc and Y showed negative energy changes as a result of the substitutional reaction. The volume changes indicate that only Y is an appropriate substitutional element for inducing a state of negative pressure for Mg$_2$Si.

Keywords: Mg$_2$Si, thermoelectric performance, negative pressure, substitution

1. Introduction

There has been renewed interest in the use of thermoelectric (TE) energy conversion to address environmental and/or energy issues such as global warming, air pollution, and depletion or instability of fossil fuel energy resources. In addition to efforts to find new TE materials, many techniques have been devised for significantly improving the performances of traditional TE materials, including impurity doping to control the carrier density, changing the geometric parameters (nanostructures, amorphous structures, and low-dimensional structures), and pressure tuning of the relevant TE materials.

Although the last method has been intensively studied for Group IV–VI compounds (PbTe and PbSe),$^{1-3}$ Group V–VI compounds (Bi$_2$Te$_3$ and Sb$_2$Te$_3$),$^{4,5}$ Group II–VI compounds (CdTe, CdS, and ZnS),$^{6}$ clathrates,$^{7}$ and skutterudites,$^{8}$ there are apparently no reports of work on Mg$_2$Si, which is one of the most promising and environmentally friendly TE materials in the temperature range 600–900 K at ambient pressure, other than that by Mori et al.$^{8,9}$ They reported a disappointing result, namely that the Seebeck coefficient of Mg$_2$Si synthesized under high pressure is about one-fourth the value for Mg$_2$Si synthesized at ambient pressure.

In previous studies, we tried another approach, namely substituting Mg with the heavier elements Ca, Sr, or Ba. However, the solubilities of these elements in the Mg$_2$Si lattice are limited because they form half-silicides with different crystal structures from that of Mg$_2$Si. Our previous calculations showed a positive reaction energy for the assumed substitution of Mg by Ca,$^{10}$ and the introduction of Ca, Sr, or Ba would result in the formation of XMgSi (X = Ca, Sr, and Ba) or X$_2$Mg$_2$Si$_3$ (X = Ba and Sr).$^{11}$

In the present study, we considered another possible approach, namely substituting the Mg atoms in the Mg$_2$Si lattice with group 3–12 metal elements. The solid solubility of a substitutional element in a metallic system follows the Hume–Rothery rule, which states that the differences between the electronegativities and valences, and the atomic radius ratios of the constituent elements are important. However, it is unclear whether this empirical law is applicable to semiconducting Mg$_2$Si, which is somewhat ionic. In the present work, we performed first-principle calculations to determine the energetic possibility of substitution of Mg by group 3–12 metal elements in the Mg$_2$Si lattice to induce a state of negative pressure.
2. Calculation Details

2.1 Structures calculated

Mg2Si has the anti-fluorite structure, belongs to space group No. 225, and has a unit cell consisting of a simple cubic sublattice of eight Mg atoms and a face-centered sublattice of four Si atoms (Mg8Si4). In the Mg2Si unit cell, Mg occupies 8c sites [Wyckoff notation, (1/4 1/4 1/4)], and Si occupies 4a sites (0 0 0). The Mg2Si unit cell therefore contains four formula units (Mg8Si4). This unit cell can be reduced to the primitive rhombohedral Mg2Si cell by adopting a set of primitive vectors pointing from a corner site to any of the three types of face-centering points of the cubic lattice composed of Si atoms. Calculations were performed for a 2x2x2 supercell of the above rhombohedral primitive cell, which consisted of 24 atoms (Mg16Si8), and cells in which one of the 16 Mg sites of Mg16Si8 was substituted by one foreign atom X, i.e., the calculations were performed for X1Mg15Si8.

2.2 Calculation method

The calculation method is similar to that used in our previous study of the Ca3Si-Mg2Si system.2) Calculations were performed with the CASTEP code developed by Payne et al.14) This is a first-principles method based on DFT, with a pseudopotential description of the electron–core interaction and a plane-wave expansion of the wavefunctions. The ultrasoft pseudopotential generated by Vanderbilt’s scheme15) was used, in which the Mg 2p state is explicitly treated as a part of the valence. Perdew–Wang generalized gradient approximations (GGAs)16) were used to approximate the DFT exchange–correlation term. Self-consistent iteration convergence was assumed when the total energy difference between successive cycles was less than 0.001 eV per atom. The maximum error in the calculated energies was therefore approximately ±0.02 eV for Mg16Si8. The kinetic cutoff energy for the plane-wave expansion (Ecut) was set at 310 eV.

The Monkhorst–Pack (MP) scheme17) was used for k-point sampling with a spacing of 0.5 nm−1 in reciprocal space. To calculate the electronic energies, we performed geometric optimization with the total energy minimization algorithm and the Broyden–Fletcher–Goldfarb–Shannon optimization procedure. The DOS curves were obtained by broadening the discrete energy levels on a grid of MP k-points by using a Gaussian smearing function of 0.07 eV full-width at half-maximum. The energy was measured with respect to the Fermi level. In addition, all the angular momentum projections (s,p,d,...) on all the atoms were performed to give a partial density of states (PDOS) and determine the energy levels generated by doping. The units of the DOS are electrons/atom eV for the total DOSs and electrons/atom eV for the PDOSs.

The effects of the substitutional elements on the band structure (BS) of Mg2Si were determined by calculating the BS along several high-symmetry lines in the Brillouin zone. To draw the BS diagram, the middle value at the bottom of the conduction bands and that at the top of the valence bands was chosen as the energy zero.

3. Results and Discussion

3.1 DOSs of X1Mg15Si8 (X = Mg, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn)

First, we briefly describe the results of an exploratory study based on the calculated electronic DOSs of X1Mg15Si8 (X = group 3–12 elements: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn). Figure 1 shows the calculated DOSs of ScMg15Si8 and Ti1Mg15Si8, and that of Mg16Si8 for comparison. The contributions from the atomic orbitals of doped elements (Sc or Ti in this figure) are shown by broken curves in this and succeeding figures.

Mg2Si is a semiconductor with an indirect gap value of ca. 0.77 eV. The calculated Fermi level (0.0 eV) for the Mg16Si8 cell was located in the dent of the DOS curve, which indicates that Mg16Si8 is intrinsically semiconducting. The calculated gap value for the cell was 0.258 eV, which is only 34% of the observed value. The main features of the DOS curves of Sc1Mg15Si8 and Ti1Mg15Si8 are the same as those of the undoped Mg16Si8 curve. The partial DOSs of the doped elements (Sc or Ti) mainly contributed to the conduction band of the Mg2Si host material. The Fermi level (E_F) of Sc- or Ti-substituted Mg2Si was located just above the bottom of the conduction band, which implies n-type behavior for these materials.

Figure 2 shows the calculated DOSs of V1Mg15Si8, Cr1Mg15Si8, and Mn1Mg15Si8. In contrast to the above cases, the atomic orbitals of the substitutional elements (V, Cr, and Mn) were not resolved and were hybridized with the valence and conduction bands of the Mg2Si host material. Clear
energy gaps on the DOS curves disappeared, and the Fermi level shifted upward into the conduction band; this suggests metallic behavior of Mg$_2$Si with these substitutional elements.

Figure 3 shows that for substitution with Group 8–10 elements, clear energy gaps in the DOS curves appeared again. However, the $E_F$ values for Fe- or Co-doped Mg$_2$Si were located far below the top of the valence band. This suggests that Mg$_2$Si partly substituted with Fe, Co, or Ni may behave as a metal.

Figure 4 shows the calculated DOSs of Cu$_1$Mg$_{15}$Si$_8$ and Zn$_1$Mg$_{15}$Si$_8$. The energy gaps in the DOS curves were clearer than those in the curves for Fe-, Co-, or Ni-substituted Mg$_2$Si. The $E_F$ of Cu-substituted Mg$_2$Si was located just below the top of the valence band, which suggests $p$-type semi-conducting behavior rather than the expected moderate $n$-doping. However, Sakamoto et al. reported that Cu-doped Mg$_2$Si has negative Seebeck coefficients at 300–800 K, in contrast to the above speculation. This inconsistency between the experimental results and prediction can be understood from the energetic point of view on the basis of our previous study, which predicted Cu insertion at the 4$b$ site of the Mg$_2$Si lattice rather than substitution of Mg (or Si) atoms in the lattice. The solubility limit of Cu in Mg$_2$Si is considered to be less than the concentration needed to compensate for all the $n$-type carriers in the undoped Mg$_2$Si, which is supposed to be caused by unintentional deviation from the stoichiometric ratio of Mg to Si.

We previously showed that substituting Ag for Mg is accompanied by almost the same energy gain as (1) insertion into the 4$b$ sites of Mg$_2$Si and (2) substitution of Si.

However, Ag incorporation into the Mg$_2$Si lattice causes a downward shift of the conduction bands, which are mainly composed of the Mg 3s atomic orbital, with respect to the top of the valence bands, which are mainly composed of Si 3s and 3p orbitals. This effect causes the bandgap to narrow, which counteracts the expected bandgap widening caused by negative pressure.

For Zn substitution of Mg$_2$Si, the DOS also had a clear energy gap, and $E_F$ was located in that gap because both Mg and Zn have two valence electrons. Although, to our
knowledge, no experimental study has been conducted on Zn doping, bandgap widening by Zn substitution is less likely than in the case of Y substitution described above because the ionic diameter of Zn$^{2+}$ is 74 pm on Pauling’s scale, which is much smaller than that of Y$^{3+}$, i.e., 93 pm. The ionic diameter of Mg$^{2+}$ is 65 pm. Although Cd and Hg belong to the same group as Zn and have larger ionic diameters (Cd$^{2+}$: 97 pm, Hg$^{2+}$: 110 pm), they are toxic and should not be used as dopants. We therefore decided not to conduct further research on Group 3 and 4 elements but not when substituted with elements from any other groups.

To summarize the results of our DOS calculations, Mg$_8$Si maintains its n-type semiconducting nature when substituted with Group 3 and 4 elements but not when substituted with elements from any other groups.

### 3.2 Formation energies of X$_1$Mg$_{15}$Si$_8$ (X = Sc, Y, La, Ti, Zr, and Hf)

The DOS calculations discussed in section 3.1 suggest that the n-type semiconducting nature of Mg$_8$Si would be maintained even if Mg atoms are substituted by Sc or Ti. This is also the case when Y and La (Group 3) or Zr and Hf (Group 4) substitute the Mg atom (their DOSs are not shown here). However, the energy changes for the substitutional reactions need to be examined to judge whether or not the substitution is possible. We therefore calculated the energies of the following reactions:

\[
\text{Mg}_{16}\text{Si}_8 + X \rightarrow \text{X}_1\text{Mg}_{15}\text{Si}_8 + \text{Mg}
\]

where X = Sc, Y, La, Ti, Zr, or Hf.

First, we briefly describe the results for the pure metallic (semiconducting) states of Mg and Si and binary compounds of undoped Mg$_2$Si. Although we previously performed similar calculations for the Mg$_2$Si$_2$Ni system, we performed them again because the size of the Mg$_2$Si cell used in the previous calculation differed from that in the previous work. Table 1 gives the results for the present study. One lattice constant of Mg metal (a) and the lattice constants of Si were slightly underestimated, and the other lattice constant of Mg (c) was overestimated. The lattice constant of Mg$_{16}$Si$_8$ (= 0.8980 nm) was well reproduced by the present calculations (= 0.9003 nm). The degree of underestimation or overestimation therefore depended on the substrate. However, we used this approximation because the GGA is known to give relatively good results for qualitatively evaluating the energy differences among different types of structures.

Table 2 gives the optimization results for X$_1$Mg$_{15}$Si$_8$ with X = Sc, Y, and La, and Table 3 gives the results for X = Ti, Zr, and Hf.

The electronic energies listed in Tables 1–3 can be used to obtain the energy changes for the substitutional reactions; e.g., for Sc:

\[
\text{Mg}_{16}\text{Si}_8 + \text{Sc} \rightarrow \text{Sc}_1\text{Mg}_{15}\text{Si}_8 + \text{Mg}
\]
The energy change is given by
\[ \frac{\Delta E}{C_0} = (\frac{\Delta E}{C_0} + \frac{\Delta E}{C_0}) + (\frac{\Delta E}{C_0} + \frac{\Delta E}{C_0}) \]
This reaction is therefore energetically possible.

Table 4 summarizes the results for similar reactions of Y, La, Ti, Zr, and Hf. The calculated energy changes were positive for elements other than Sc and Y. The reactions for substitution of Mg atoms in the Mg2Si lattice by Group 3 or 4 elements are therefore energetically unfavorable, except in the cases of Sc and Y.

The cell volume change caused by the substitution of Mg atoms in the Mg2Si lattice with the above elements can be predicted by comparing the optimized cell volumes of Mg16Si8 (= 515.9444 ± 10⁻³ nm³) and X1Mg15Si8. As expected, the volume increase caused by Sc substitution is less than that caused by Y substitution. La substitution would result in a much greater volume increase, but this reaction is energetically impossible because the La atom is too large to occupy the Mg site of the Mg2Si lattice, as predicted by the present energetic calculations.

To conclude, we performed DOS and energetic calculations to identify possible substitutional elements for Mg in the Mg2Si lattice to induce a negative chemical pressure, which would enhance the TE performance. Y substitution was predicted to be energetically possible and would increase the cell volume and induce a negative chemical pressure without changing the main features of the DOS curve of Mg2Si.

Before concluding this section, we would like to briefly discuss the electronegativity, atomic radius, and ionic valence in relation to the Hume–Rothery rule. The electronegativity difference between Mg and Y is not large compared with those between Mg and other candidate substitutional elements in Groups 4–12. Although there is a great difference between the radii of Mg²⁺ and Y⁺ ions, and it exceeds the limit (= 15%) for making solid-substitutional alloys prescribed by the Hume–Rothery rule, this difference will be tolerated in the case of the Mg2Si lattice because Mg2Si has a loose structure compared with those usually found in metals. Y has the lowest valence among the transition metals; this is favorable in terms of the valence electron concentration rule, which states that the smaller the valence number of the solute atom is, the more advantageous solid-solution formation is.

3.3 Band structures of X1Mg15Si8 (X = Y and Zr)
We compared the calculated BS of Y-substituted Mg2Si with those of undoped and Zr-substituted Mg2Si. Figure 5(a)–(c) show the BS diagrams of Mg16Si8, Y1Mg15Si8, and Zr1Mg15Si8, respectively.24) To draw the BS diagrams, the energy origin was set to the middle values of the bottom of the conduction bands and top of the valence bands.

Undoped Mg16Si8 has 64 valence electrons (two electrons from each Mg atom and four electrons from each Si atom) and 32 bands will be fully occupied. The bandgap \( E_g \) between the valence bands and conduction bands was 0.258 eV, and its Fermi level \( E_F \) coincided with the middle of the energy gap when the effective masses of the electrons and holes were the same.

When Mg was substituted by Y, \( E_F \) shifted upward into the conduction band. The \( E_g \) value of this system was calculated to be 0.498 eV, which is much wider than the value expected from the volume expansion by Y substitution. The optimized volume of Y1Mg15Si8 was 0.524 ± 10⁻³ nm³, which corresponds to an applied negative pressure of ca. −0.7 GPa. This volume expansion produces \( E_g = 0.263 \) eV if applied to undoped Mg2Si. The difference between these values must reflect the effect of the chemical natures of the elements. The electronegativity of Y is 1.22, which means

![Fig. 5 Calculated band structures (BSs) of X1Mg15Si8, where X = Mg, Y, or Zr. The numbers plotted in the BS diagrams express the order counted from the bottom of the valence bands. Note that bands mainly composed of Si 2p, Mg 2p, and Y 4p atomic orbitals are omitted from the numbering, although they are explicitly treated as part of the valence bands.](image-url)
that Y is more positive than Mg, which has an electro-negativity of 1.31 on Pauling’s scale. Substitution of Mg by a more positive atom causes an upward shift of the conduction band mainly composed of Mg atomic orbitals, and this widens the bandgap between the conduction bands and valence bands.

Y substitution did not have a great effect on the energy dispersion, as shown in Fig. 5(a) and (b). The effective mass of the electrons of Y₁Mg₁₅Si₈ would therefore be similar to that in the case of undoped Mg₂Si. In contrast, Zr substitution significantly affected the energy dispersion. As shown in Fig. 5(c), the electronic energy of Zr₁Mg₁₅Si₈ was much less dispersed than those shown in Fig. 5(a) and (b). This means that the effective mass of electrons would be much greater than that in the case of undoped Mg₂Si, and this would help to increase the TE PF. However, the concentration of the Zr substituent must be small because dissolution of Zr in Mg₂Si is energetically unfavorable and may only be possible by increasing the configurational entropy term.

Before concluding the present discussion, we should point out that two problems remain for future studies. First, the TE performance of a doped material is determined not only by the modified BS of the matrix material but also by the change in carrier density caused by doping. Y substitution increases the electron density, which is necessary for enhancement of the TE performance of doped Mg₂Si. In addition, the proportion of substituted Mg atoms changes the bandgap, which must also be considered. Calculations of the effect of the concentration of substituted Mg atoms are underway, and the results will be reported in the near future. Secondly, the substitution of Mg atoms by a third element X might cause formation of (1) X silicides (XₛSiₓ), (2) binary Mg–X alloys (MgₓXᵧ), and/or (3) ternary compounds (MgₓXᵧSiₜ). The formation of these compounds and alloys could affect Mg substitution by X, and this will be addressed in future studies and experimentally confirmed.

4. Conclusions

In the present work, we examined the possibility of substituting Mg atoms in the Mg₂Si lattice with foreign atoms to increase the TE PF. On the basis of Balout et al.’s work, which suggests that a state of negative pressure enhances the TE performance, we performed first-principles calculations to select candidate substitutional elements that could induce a state of negative pressure. First, DOS calculations were performed for Mg₂Si, in which a Mg atom was substituted by Group 3–12 elements (Sc to Zn). Group 3 and 4 elements were chosen as candidates because the main features of the DOS curves of X₁Mg₁₅Si₈ (X = Sc or Ti) were the same as those of undoped semiconducting Mg₂Si. Next, structural optimization and energy calculations were performed for X₁Mg₁₅Si₈ (X = Sc, Y, La, Ti, Zr, and Hf). Only Sc and Y had negative energy changes for these substitutional reactions. The calculated volume changes suggest that only substitution with Y would induce a state of negative pressure for Mg₂Si. Zr substitution could increase the TE PF by increasing the effective mass of electrons, but the solubility of Zr in the Mg₂Si lattice is low.

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20) To introduce another related example, alkali-metal substitution of Ba in the semiconducting Ba₃Si₂ was predicted to cause bandgap widening for Ba₅Si₈. This is caused by the upward shift of the conduction bands from substitution with a more positive element. This is the opposite case to the present case, where the less positive Ag substitution of Mg would cause a downward shift of the conduction bands and thus narrow the bandgap.
23) Compared to our previous work, the reproducibility of the optimized lattice constant of Si was quite good, but that of Mg was not so good. This may have been caused by the insufficient cutoff energy used in the present calculations so that the optimized lattice constants and energy would converge with respect to the cutoff energy. However, because of our limited computational resources, we were obliged to use an insufficiently large cutoff energy of 310 eV for the larger cells calculated here, compared to the previous work.
24) MgₓSiₘ may appear to be a direct semiconductor at first glance, though Mg₂Si is known to be an indirect semiconductor. This is merely appearance caused by the fact that both I(000) and X(1/2,0,1/2) of the reciprocal space of Mg₂Si correspond to I(000) of the reciprocal space of MgₓSiₘ. See, for details, Appendix 2 of Ref. 25.