Theoretical Study on Thermoelectric Properties and Doping Regulation of Mg$_3$X$_2$ (X = As, Sb, Bi)

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Abstract: For searching both high-performances and better fits for near-room temperature thermoelectric (TE) materials, we here carried out a theoretical study on thermoelectric properties and doping regulation of Mg$_3$X$_2$ (X = As, Sb, Bi) by the combined method of first principle calculations and semi-classical Boltzmann theory. The thermoelectric properties of n-type Mg$_3$As$_2$, Mg$_3$Sb$_2$, and Mg$_3$Bi$_2$ were studied, and it was found that the dimensionless figures of merit, $zT$, are 2.58, 1.38, 0.34, and the $p$-type ones are 1.39, 0.64, 0.32, respectively. Furthermore, we calculated the lattice thermal conductivity of doped structures and screened out the structures with a relatively low formation energy to study the phonon dispersion and thermal conductivity in Mg$_3$X$_2$ (X = As, Sb, Bi). Finally, high thermoelectric $zT$ and ultralow thermal conductivity of these doped structures was discussed.

Keywords: thermoelectric properties; doping; first principles calculation; Boltzmann theory

1. Introduction

Thermoelectric (TE) materials are non-polluted and can directly convert heat energy and electric energy to each other, and have a wide range of applications in areas such as waste heat recovery for power generation, car manufacturing and space probes. TE materials attract much attention. The TE efficiency can be measured by the dimensionless figure of merit, $zT$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, $\kappa_e$ and $\kappa_l$ are the electrical and lattice thermal conductivity, respectively. Power factor (PF) can be defined as the product of the square of Seebeck coefficient and the electrical conductivity, that is, $PF = S^2\sigma$. Therefore, it is essential to achieve a high power factor and a low thermal conductivity for a high $zT$ value. As a result, discovering TE materials with outstanding properties is of great practical significance for many applications. Recently, many thermoelectric materials have been explored for power generation applications, such as GeTe [1], PbTe [2], half-Heusler [3] and skutterudites [4]. Among the reported TE materials, the Zintl phase, a class of intermetallic compounds, has been paid attention to because they meet the character of phonon-glass electron-crystal (PGEC) [5]. As the typical Zintl phase, Mg$_3$Sb$_2$ have been investigated experimentally and theoretically. Condron et al. [6] prepared Mg$_3$Sb$_2$ by a direct reaction of the elements and obtained the maximum $zT$ value of 0.21 at 873 K. Chen et al. [7] got the maximum $zT$ value ~0.6 at 773 K in Mg$_3$Bi$_2$Li$_{0.025}$Sb$_2$ (p-type Li-doped Mg$_3$Sb$_2$). Wang et al. [8] carried out p-type Li-doping on Mg$_3$Sb$_2$ and got a higher $zT$ value of 0.59 at 723 K. Xu et al. [9] explored theoretically the relation between the electronic structure and the TE properties of Mg$_3$Sb$_2$. Meng et al. [10] studied anisotropic thermoelectric in Mg$_3$Sb$_2$ and confirmed anisotropic thermoelectric of $p$-type Mg$_3$Sb$_2$. The low thermoelectric properties of thermoelectric materials limit their further application under a medium–low temperature; even when the ultralow thermal conductivity in MgSb-based materials was reported, the search for high thermoelectric materials and great potential as candidates for near-room temperature thermoelectric generators seems still to be more urgent. As and Bi belongs to the same main V group as Sb, by contrast, few studies are conducted on Mg$_3$Bi$_2$ and Mg$_3$As$_2$. 
In this study, we investigated the thermoelectric properties of \( n \)-type and \( p \)-type \( \text{Mg}_3\text{X}_2 \) (\( \text{X} = \text{As}, \text{Sb}, \text{Bi} \)) systematically using the combined method of the first principles calculations and the semi-classical Boltzmann theory. A higher peak \( zT \) of 2.58 was obtained. In addition, we discussed the \( n \)-type and \( p \)-type doping effect in \( \text{Mg}_3\text{X}_2 \) (\( \text{X} = \text{As}, \text{Sb}, \text{Bi} \)), and the calculated doping formation energy and phonon dispersion curves proved that the doped structures are dynamically stable.

2. Computational Details

In this study, the structure of \( \text{Mg}_3\text{X}_2 \) (\( \text{X} = \text{As}, \text{Sb}, \text{Bi} \)) was built in VESTA (version 2.90.0b, Tohoku University, Sendai, Japan). The structure relaxations, the total density of states, projected density of states, and band structure were carried out in Vienna Ab-initio Simulation Package (VASP, vasp. 5.3.5.neb, University of Vienna, Vienna, Austria) based on density functional theory (DFT). The exchange-correlation functionals was described by the generalized gradient approximation (GGA) with Perdew, Burke, and Ernzerhof (PBE) functional [11]. The plane-wave cutoff energy was set to 400 eV and the energy convergence criterion was set up to \( 10^{-5} \) eV. The ionic relaxation was interrupted at \( -0.02 \) eV and was calculated by using \( 9 \times 9 \times 6 \) Monkhorst-Pack grid meshes in irreducible Brillouin Zone. To get the phonon dispersion curves of these structures, the primitive cell of \( \text{Mg}_3\text{X}_2 \) (\( \text{X} = \text{As}, \text{Sb}, \text{Bi} \)) was expanded to a \( 3 \times 3 \times 2 \) supercell in Phonopy package (version 1.9.6.1, National Institute for Material Science, Tsukuba, Japan) by the density functional perturbation theory (DFPT) [12]. The calculation of the TE transportation properties was based on the semi-classical Boltzmann theory and the rigid-band approach in the BoltzTrap code [13]. To verify the feasibility of doping on \( \text{Mg}_3\text{X}_2 \) (\( \text{X} = \text{As}, \text{Sb}, \text{Bi} \)), the formation energy of the doped structure was calculated using a \( 3 \times 3 \times 2 \) supercell of \( \text{Mg}_3\text{X}_2 \) (\( \text{X} = \text{As}, \text{Sb}, \text{Bi} \)). We replaced one Mg atom with one Hf (Sn, Zr) atom for \( n \)-type doping, and with one Ag (Li, Na) atom for \( p \)-type doping, respectively. The doping concentration was 5.56\%. The phonon dispersion curves, the total density of states, and projected density of states were calculated, where the K-Points were set as \( 3 \times 3 \times 3 \).

3. Results and Discussion

3.1. Atomic and Electronic Structure

Figure 1 shows the structure of \( \text{Mg}_3\text{X}_2 \) (\( \text{X} = \text{As}, \text{Sb}, \text{Bi} \)). As is shown, the structure of \( \text{Mg}_3\text{X}_2 \) (\( \text{X} = \text{As}, \text{Sb}, \text{Bi} \)) belongs to the hexagonal system with the space group P-3m1 [14,15]. The relaxed lattice constants of them are shown in Table 1. The parameter we obtained was not more than 1.5\% higher than that of the previous study and the parameter \( c \) we got was not more than 0.6\% higher than that of the early research, which agrees with those in the previous study [16–18].

Figure 1. The crystal structure of \( \text{Mg}_3\text{X}_2 \) (\( \text{X} = \text{As}, \text{Sb}, \text{Bi} \)). Brown spheres represent the Mg atom, and the green spheres represent the X (As, Sb, Bi) atom.
Table 1. The structure parameters of Mg\(_3\)X\(_2\) (X = As, Sb, Bi).

|       | a(Å)               | c(Å)               | Bond angle           |
|-------|--------------------|--------------------|----------------------|
| Mg\(_3\)As\(_2\) | 4.293 (4.264 [16]) | 6.763 (6.738 [16]) | \(\alpha = \beta = 90^\circ, \beta = 120^\circ\) |
| Mg\(_3\)Sb\(_2\) | 4.596 (4.53 [17])  | 7.280 (7.24 [17])  | \(\alpha = \beta = 90^\circ, \beta = 120^\circ\) |
| Mg\(_3\)Bi\(_2\) | 4.723 (4.67 [18])  | 7.44 (7.40 [18])   | \(\alpha = \beta = 90^\circ, \beta = 120^\circ\) |

The band structures, total density of states (TDOS), and the projected density of states (PDOS) of Mg\(_3\)X\(_2\) (X = As, Sb, Bi) are calculated and displayed from left to right in Figure 2. From the figure of the band structures, it can be seen that Mg\(_3\)Bi\(_2\) may be a semimetal, which is consistent with the published researches [18,19]. Besides, Ferrier et al. [20,21] speculated that Mg\(_3\)Bi\(_2\) is a semimetal on the basis of the conductivity-composition result they obtained, whereas Mg\(_3\)As\(_2\) and Mg\(_3\)Sb\(_2\) are both semiconductors. Mg\(_3\)As\(_2\) has a direct band gap of 0.863 eV, and Mg\(_3\)Sb\(_2\) has an indirect band gap of 0.205 eV, which is close to the band gap of 0.303 eV of Mg\(_3\)Sb\(_2\) by Yu et al. [22] by a different interactive correlation function in PW91. Obviously, it is seen from the figure of TDOS and PDOS that Mg\(_s\)-orbital plays a major role in the total density of states at the conduction band minimum (CBM) of Mg\(_3\)As\(_2\) and Mg\(_3\)Sb\(_2\), while the peak of TDOS is mainly contributed by As\(_p\)-orbital in Mg\(_3\)As\(_2\) and Sb\(_p\)-orbital in Mg\(_3\)Sb\(_2\) at the valence band maximum (VBM), respectively. In Mg\(_3\)Bi\(_2\), the TDOS at CBM was mainly controlled by the hybrid orbital of Mg\(_s\)-orbital and Bi\(_p\)-orbital, while Bi\(_p\)-orbital contributes mainly at VBM.

Figure 2. Band structures, TDOS (total density of states) and PDOS (projected density of states) of Mg\(_3\)X\(_2\) (X = As, Sb, Bi). (a) Mg\(_3\)As\(_2\), (b) Mg\(_3\)Sb\(_2\), (c) Mg\(_3\)Bi\(_2\). The symbols \(\Gamma, A, H, K, M, L\) in x-axis are high symmetry points. DOS means density of states.
3.2. Dynamics Stability

Figure 3a,c,e are the phonon dispersion curves and Figure 3b,d,f are the phonon density of states. Clearly, there are no imaginary frequencies in the three phonon dispersion curves, demonstrating that the three structures are all dynamically stable. The mixing of low frequency optical and acoustic modes demonstrates their strong phonon scattering, which benefits low lattice thermal conductivity.

Figure 3. Phonon dispersion curves and phonon density of states of Mg₃X₂ (X = As, Sb, Bi), (a,b) Mg₃As₂; (c,d) Mg₃Sb₂; (e,f) Mg₃Bi₂.

The vibration of atoms at their equilibrium position can be described in as Debye temperature, which can be defined as, \( \Theta_D = \frac{h (\frac{3n}{4\pi\Omega})^{\frac{1}{3}} v_m}{k_B} \), in which \( h \) is Plank’s constant, \( k_B \) is Boltzmann constant, \( n \) is the number of the unit cell, \( \Omega \) is the volume of the unit cell, \( v_m \) is the average velocity of sound. Then \( v_m \) can be described by the transverse velocity of sound \( (v_t) \) and the longitudinal velocity of sound \( (v_l) \), the expression is as:

\[
 v_m = \left[ \frac{1}{3} \left( \frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-\frac{1}{3}}, \quad v_t = \sqrt{\frac{B}{\rho}}, \quad v_l = \sqrt{\frac{(B+4G)}{\rho}}, \]

where \( \rho \) is the density of materials, \( B \) and \( G \) are volume modulus and shear modulus. The elastic constants of \( c_{11}, c_{33}, c_{44}, c_{12}, c_{13} \) and \( B, G \) are calculated [14] of Mg₃As₂, Mg₃Sb₂, Mg₃Bi₂, respectively. According to the Debye theory, when the temperature is higher than the Debye temperature, the lattice thermal conductivity is proportional to \( 1/T \), which can be approximately equal to the minimum lattice thermal conductivity. The minimum lattice thermal conductivity is calculated by \( \kappa_{\text{min}} = \frac{1}{2} \left( \frac{\pi^2}{6} \right) k_B V^{-\frac{3}{2}} (2v_t + v_l) \), where \( V \) is the average volume of every atom in the unit cell. All the above results are shown in Table 2. The elastic constants we
calculated meet the Born stability criterion [23], demonstrating that the results are credible. The Debye temperature of Mg₃As₂, Mg₃Sb₂ and Mg₃Bi₂ is 332 K, 237 K and 175 K.

Table 2. Calculated elastic constants ($c_{ij}$), bulk modulus ($B$), shear modulus ($G$), density ($ρ$), volume ($V$), the transverse velocity of sound ($v_t$) and the longitudinal velocity of sound ($v_l$), the average velocity of sound ($v_m$), Debye temperature ($Θ_D$) and the minimum lattice thermal conductivity ($κ_{\text{min}}$).

|          | Mg₃As₂ | Mg₃Sb₂ | Mg₃Bi₂ |
|----------|--------|--------|--------|
| $c_{11}$ (GPa) | 96.63  | 71.73  | 58.77  |
| $c_{33}$ (GPa) | 90.89  | 75.91  | 65.52  |
| $c_{44}$ (GPa) | 23.71  | 13.79  | 12.48  |
| $c_{12}$ (GPa) | 45.84  | 36.78  | 32.06  |
| $c_{13}$ (GPa) | 26.63  | 21.06  | 20.13  |
| $ρ$ (g/cm$^3$) | 3.43   | 3.95   | 5.67   |
| $V$ (Å$^3$) | 21.59  | 26.64  | 28.75  |
| $B$ (GPa) | 53.28  | 41.83  | 36.39  |
| $G$ (GPa) | 26.54  | 17.70  | 14.62  |
| $Θ_D$ (K) | 332    | 237    | 175    |
| $v_t$ (m/s) | 2782.50 | 2117.95 | 1605.26 |
| $v_l$ (m/s) | 5085.97 | 4071.74 | 3138.67 |
| $v_m$ (m/s) | 3102.70 | 2370.11 | 1798.33 |
| $κ_{\text{min}}$ (W/K) | 0.76   | 0.52   | 0.38   |

3.3. Thermoelectric Transport Properties

Using the formula of $zT = \frac{z^2 e^2 T}{2k_B(κ_0 + κ_0)}$ and $κ_e = LσT$, where $L$ is the standard Lorenz number, $L = 2.45 \times 10^{8} W \, Ω \, K^{-2}$, we calculated the thermoelectric transport properties of Mg₃As₂, Mg₃Sb₂ and Mg₃Bi₂ by semi-classical Boltzmann theory and the rigid-band approach in the BoltzTrap code. Figure 4 presents the electrical conductivity of the $n$-type and $p$-type Mg₃X₂ ($X = \text{As, Sb, Bi}$). The carrier concentration of Mg₃X₂ is adopted. At the same time, $κ$ can be defined as $κ = neμ$, where $n$, $e$ and $μ$ are the carrier concentrations, the charge of an electron and the carrier mobility, respectively. As shown in Figure 4, the $κ$ of $n$-type materials increases with the carrier concentration, whereas the $κ$ of $p$-type ones have the same change trend.

Figure 4. The electrical conductivity of the $n$-type and the $p$-type Mg₃X₂ ($X = \text{As, Sb, Bi}$) with carrier concentration. (a) $n$-Mg₃As₂, (b) $n$-Mg₃Sb₂, (c) $n$-Mg₃Bi₂, (d) $p$-Mg₃As₂, (e) $p$-Mg₃Sb₂, (f) $p$-Mg₃Bi₂.
Figure 5 is the electrical thermal conductivity of the n-type and p-type Mg$_3$X$_2$ (X = As, Sb, Bi) with carrier concentration. As can be seen, the electrical thermal conductivity increases with the temperature at the same carrier concentration for all the n-type or p-type Mg$_3$X$_2$ (X = As, Sb, Bi), and increases when the carrier concentration rises at the same temperature. It is noted that the electrical thermal conductivity value of n-type in the same material is generally larger than that of the p-type. Figure 6 displays the Seebeck coefficient of the n-type and p-type Mg$_3$X$_2$ (X = As, Sb, Bi). As shown, the S of n-type Mg$_3$X$_2$ (X = As, Sb, Bi) is negative, while that of most p-type material curves is positive. For Mg$_3$As$_2$ and n-type Mg$_3$Bi$_2$, the absolute value of S increases when the temperature increases. For Mg$_3$Sb$_2$ and p-type Mg$_3$Bi$_2$ at a low carrier concentration, the absolute value of the Seebeck coefficient decreases with the temperature increases, which is due to the influence of the bipolar effect. The bipolar effect usually occurs in wide band gap semiconductors at high temperatures and narrow band gap semiconductors at room temperature. With the higher carrier concentration, the absolute value of Mg$_3$Sb$_2$ and p-type Mg$_3$Bi$_2$’ s S increases with the temperature increases.
Figure 7 is the power factor performance with the carrier concentration of the \( n \)-type and \( p \)-type \( \text{Mg}_3\text{X}_2 \) (\( \text{X} = \text{As}, \text{Sb}, \text{Bi} \)). For \( n \)-type one, PF increases first and then decreases when the carrier concentration increases. In addition, it can be found that, with the same carrier concentration, the power factor of \( n \)-type material and \( p \)-type \( \text{Mg}_3\text{As}_2 \) increases with the temperature gradually. However, it is an exception to that of \( p \)-type \( \text{Mg}_3\text{Sb}_2 \) and \( p \)-type \( \text{Mg}_3\text{Bi}_2 \) at a low concentration due to the influence of the negative Seebeck coefficient.

![Figure 7](image)

Figure 7. The power factor of the \( n \)-type and the \( p \)-type \( \text{Mg}_3\text{X}_2 \) (\( \text{X} = \text{As}, \text{Sb}, \text{Bi} \)) with carrier concentration. (a) \( n \)-\( \text{Mg}_3\text{As}_2 \), (b) \( n \)-\( \text{Mg}_3\text{Sb}_2 \), (c) \( n \)-\( \text{Mg}_3\text{Bi}_2 \), (d) \( p \)-\( \text{Mg}_3\text{As}_2 \), (e) \( p \)-\( \text{Mg}_3\text{Sb}_2 \), (f) \( p \)-\( \text{Mg}_3\text{Bi}_2 \).

Figure 8 demonstrates the \( zT \) values of the \( n \)-type and \( p \)-type \( \text{Mg}_3\text{X}_2 \) (\( \text{X} = \text{As}, \text{Sb}, \text{Bi} \)). The \( zT \) increases with temperature ranging from 300 K to 800 K. The \( n \)-type and \( p \)-type \( \text{Mg}_3\text{Bi}_2 \) have the maximum \( zT \) values of 0.34 and 0.32, respectively, and that of the \( n \)-type and \( p \)-type \( \text{Mg}_3\text{Sb}_2 \) can reach 1.38 and 0.64, respectively. It is noted that the maximum \( zT \) value of \( n \)-type and \( p \)-type \( \text{Mg}_3\text{As}_2 \) can achieve 2.58 and 1.39, which is competitive among most published results, indicating that \( \text{Mg}_3\text{As}_2 \) is a promising candidate for TE materials.

![Figure 8](image)

Figure 8. The \( zT \) values of the \( n \)-type and the \( p \)-type \( \text{Mg}_3\text{X}_2 \) (\( \text{X} = \text{As}, \text{Sb}, \text{Bi} \)) with carrier concentration. (a) \( n \)-\( \text{Mg}_3\text{As}_2 \), (b) \( n \)-\( \text{Mg}_3\text{Sb}_2 \), (c) \( n \)-\( \text{Mg}_3\text{Bi}_2 \), (d) \( p \)-\( \text{Mg}_3\text{As}_2 \), (e) \( p \)-\( \text{Mg}_3\text{Sb}_2 \), (f) \( p \)-\( \text{Mg}_3\text{Bi}_2 \).

3.4. Doping Effect

The studies above show that \( \text{Mg}_3\text{X}_2 \) (\( \text{X} = \text{As}, \text{Sb}, \text{Bi} \)) have good TE properties and potential application prospects. The doping strategy is considered as an effective approach for improving TE performance; therefore, further investigations into doping were carried...
out in this work. To verify the feasibility of doping on Mg$_3$X$_2$ (X = As, Sb, Bi), elements of Hf (or Sn, Zr, Ag, Li and Na) atom substituting to the Mg atom are investigated. The formation energy of each doped structure is calculated by $E_f = E(Mg_{53}XY_{36}) - E(Mg_{53}X_{36}) - E(Y) + E(Mg)$, where X can be As, Sb or Bi. Y can be Hf, Sn, Zr, Ag, Li and Na. The results are shown in Table 3. The formation energies of Mg$_{53}$ZrAs$_{36}$, Mg$_{53}$ZrSb$_{36}$, Mg$_{53}$ZrBi$_{36}$ and Mg$_{53}$SnBi$_{36}$ are relatively lower of $n$-type doping, while those of Mg$_{53}$LiAs$_{36}$, Mg$_{53}$LiSb$_{36}$, Mg$_{53}$NaSb$_{36}$, Mg$_{53}$LiBi$_{36}$ and Mg$_{53}$NaBi$_{36}$ are relatively lower of $p$-type doping, wherein the negative formation energy indicates the stability of the structure. The phonon dispersion curves are calculated (shown in Figure 9) and the corresponding density of states are shown in Figure 10. Figure 9 presents that all doped structures have no imaginary frequencies, indicating that all the doped structures are dynamically stable. Compared with the phonon dispersion curve of the un-doped structure, the slope of the acoustic mode of the doped one decreases, which proves that the doped structure has a lower phonon group velocity. The mixing amplitude of the dominant contribution orbitals to the density of states, but the band gaps move to the lower of $p$-type doped ones. In addition, we calculated the lattice thermal conductivity of doped structures shown in Table 4. As is shown, the lattice thermal conductivity and Debye temperature was reduced by doping except Mg$_{53}$ZrBi$_{36}$ and Mg$_{53}$SnBi$_{36}$. Therefore, it can be safely concluded that implementing $n$-type and $p$-type doping on Mg$_3$X$_2$ (X = As, Sb, Bi) by replacing an Mg atom can improve the thermoelectric properties.

| Y  | E$_f$ (eV) | $\Theta$ (K) | $\kappa$ (W/mK) | $\kappa_{\text{min}}$ (W/mK) |
|----|-----------|--------------|-----------------|-----------------|
| Ag | -0.54     | 1000         | 1.0             | 0.7             |
| Li | -0.55     | 1100         | 1.5             | 1.1             |
| Na | -0.54     | 1200         | 2.0             | 1.5             |

| X  | Y  | Mg$_{53}$X$_{36}$ | Mg$_{53}$YX$_{36}$ | Mg$_{53}$X$_{36}$ | Mg$_{53}$YX$_{36}$ | Mg$_{53}$X$_{36}$ | Mg$_{53}$YX$_{36}$ | Mg$_{53}$X$_{36}$ | Mg$_{53}$YX$_{36}$ |
|----|----|------------------|-------------------|------------------|-------------------|------------------|-------------------|------------------|-------------------|
| As | Hf | 53 | 53 | 36 | 36 | 36 | 36 | 36 | 36 |
| Sb | Sn | 53 | 53 | 36 | 36 | 36 | 36 | 36 | 36 |
| Bi | Zr | 53 | 53 | 36 | 36 | 36 | 36 | 36 | 36 |

Figure 9. Phonon dispersion curves of doped $3 \times 3 \times 2$ Mg$_3$X$_2$ (X = As, Sb, Bi). (a) Mg$_{53}$ZrAs$_{36}$, (b) Mg$_{53}$LiAs$_{36}$, (c) Mg$_{53}$ZrSb$_{36}$, (d) Mg$_{53}$LiSb$_{36}$, (e) Mg$_{53}$NaSb$_{36}$, (f) Mg$_{53}$ZrBi$_{36}$, (g) Mg$_{53}$SnBi$_{36}$, (h) Mg$_{53}$LiBi$_{36}$, (i) Mg$_{53}$NaBi$_{36}$.
Figure 10. TDOS and PDOS of doped $3 \times 3 \times 2 \text{Mg}_3X_2$ ($X = \text{As, Sb, Bi}$). (a) $\text{Mg}_5\text{ZrAs}_{36}$, (b) $\text{Mg}_5\text{LiAs}_{36}$, (c) $\text{Mg}_5\text{ZrSb}_{36}$, (d) $\text{Mg}_5\text{LiSb}_{36}$, (e) $\text{Mg}_5\text{NaSb}_{36}$, (f) $\text{Mg}_5\text{ZrBi}_{36}$, (g) $\text{Mg}_5\text{SnBi}_{36}$, (h) $\text{Mg}_5\text{LiBi}_{36}$, (i) $\text{Mg}_5\text{NaBi}_{36}$.

Table 3. The formation energy ($E_f$) of $n$-type (Hf, Sn, Zr) and $p$-type (Ag, Li, Na) doping on $3 \times 3 \times 2$ supercell of Mg$_3$X$_2$ ($X = \text{As, Sb, Bi}$).

| $Y$ | $E_f$ (Mg$_5$YA$_{36}$) | $E_f$ (Mg$_5$YSb$_{36}$) | $E_f$ (Mg$_5$YBi$_{36}$) |
|-----|------------------------|------------------------|------------------------|
| Hf  | 0.97                   | 2.41                   | 0.98                   |
| Sn  | 1.22                   | 2.62                   | 0.50                   |
| Zr  | 0.55                   | 2.09                   | 0.50                   |
| Ag  | 1.89                   | 1.32                   | 1.05                   |
| Li  | 0.26                   | $-0.14$                | $-0.35$                |
| Na  | 0.36                   | $-0.14$                | $-0.39$                |

Table 4. Calculated transverse velocity of sound ($v_t$) and longitudinal velocity of sound ($v_l$), Debye temperature ($\Theta_D$) and the minimum lattice thermal conductivity ($\kappa_{\text{min}}$) of doped $3 \times 3 \times 2 \text{Mg}_3X_2$ ($X = \text{As, Sb, Bi}$).

| Material | $v_t$ (m/s) | $v_l$ (m/s) | $\Theta_D$ (K) | $\kappa_{\text{min}}$ (W/mK) |
|----------|-------------|-------------|----------------|-----------------------------|
| Mg$_5$As$_2$ | 5085.97    | 2782.52     | 332            | 0.76                        |
| Mg$_5$ZrAs$_{36}$ (n) | 5036.81    | 2735.55     | 326            | 0.75                        |
| Mg$_5$LiAs$_{36}$ (p) | 4841.40    | 2462.41     | 295            | 0.70                        |
| Mg$_5$Sb$_2$       | 4071.74    | 2117.95     | 237            | 0.52                        |
| Mg$_5$ZrSb$_{36}$ (n) | 3998.69    | 2051.21     | 229            | 0.50                        |
| Mg$_5$LiSb$_{36}$ (p) | 4014.01    | 2051.68     | 229            | 0.51                        |
| Mg$_5$NaSb$_{36}$ (p) | 4009.55    | 2045.79     | 228            | 0.50                        |
| Mg$_5$Bi$_2$        | 3138.67    | 1605.26     | 175            | 0.38                        |
| Mg$_5$ZrBi$_{36}$ (n) | 3134.87    | 1613.38     | 176            | 0.38                        |
| Mg$_5$SnBi$_{36}$ (n) | 3149.64    | 1608.67     | 175            | 0.38                        |
| Mg$_5$LiBi$_{36}$ (p) | 3053.87    | 1503.96     | 164            | 0.36                        |
| Mg$_5$NaBi$_{36}$ (p) | 3050.20    | 1493.58     | 163            | 0.36                        |
4. Conclusions

In summary, the thermoelectric properties of Mg₃X₂ (X = As, Sb, Bi) were studied by first principles and semi-classical Boltzmann theory. The calculated results show that the maximum $zT$ values of n-type Mg₃Sb₂ and p-type Mg₃Sb₂ are 1.38 and 0.64, respectively. The maximum $zT$ values of n-type Mg₃Bi₂ and p-type Mg₃Bi₂ are 0.34 and 0.32 respectively, and these maximum values were obtained at a temperature of 800 K. It is noted that Mg₃As₂ is a direct bandgap semiconductor with a band gap of 0.8626 eV, and the maximum $zT$ of n-type and p-type Mg₃As₂ can reach 2.58 and 1.39, respectively. Based on the calculation results, the element of Hf (or Sn, Zr, Ag, Li and Na) substituting to Mg atoms in doped Mg₃X₂ (X = As, Sb, Bi) is investigated, and the formation energy and stability of the p-type doping of Li for Mg₃As₂, p-type doping of Li and Na for Mg₃Sb₂, and p-type doping of Li and Na for Mg₃Bi₂ was discussed.

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