Predicting high thermoelectric performance of ABX ternary compounds NaMgX (X = P, Sb, As) with weak electron–phonon coupling and strong bonding anharmonicity†

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The ABX ternary compounds have a variety of attractive physical properties. For example, some of the half-Heusler compounds as a class of ABX compounds exhibit high thermal power factors and thus promising thermoelectric performances. This motivates a search for potential thermoelectric candidates from the ABX compound family different from the half-Heusler structures. In this study, we investigate the electronic and phononic structures of tetragonal NaMgX (X = P, Sb, As) compounds, which belong to the ABX family using first-principles calculations based on density functional theory and density functional perturbation theory. The whole set of thermoelectric properties are thus evaluated from the semi-classical Boltzmann transport calculations. It is revealed that weak electron–phonon coupling and strong bonding anharmonicity are the critical physical ingredients for promising thermoelectric performance, giving rise to the optimized figure of merit factor $ZT$ of up to 1.38, 2.39, and 3.54 for NaMgX (X = P, Sb, As) compounds in the intermediate temperature range.

I. Introduction

Human being at present is facing two major problems: energy crisis and environment pollution. However, these problems are propelling explorations of new and clean energy sources.1–11 Thermoelectric (TE) devices, which can directly convert heat to electricity and vice versa, are considered to be one of the potential ways of addressing these problems. For a good TE material, a high figure of merit (FOM) factor $ZT = S^2 σkT/k_{tot}$ is required, where $k_{tot} = k_L + κ_s$, and $S$, $σ$, $κ_t$tot, $k_L$, and $κ_s$ represent, respectively, the Seebeck coefficient, absolute temperature, electrical conductivity, total thermal conductivity, and the lattice and electronic components of $κ_{tot}$. The electrical performance of a TE material is determined by the power factor ($PF = S^2 σ$). Conceptually, in order to possess a high $ZT$, the PF must be large, while the total thermal conductivity must be minimized. However, the challenge exists of how to simultaneously obtain a large PF and a low $k_{tot}$ due to the complex relationships between the physical parameters ($S$, $σ$, $k_L$, and $κ_s$), which have their respective electronic and phonon origins.

It is known that $κ_e$ is related with $σ$ via the Wiedemann–Franz law, suggesting that $κ_e$ may not be easily modulated without much modification of $σ$. One has to search for other possible opportunities to optimize the PF and $ZT$. In fact, substantial investigations on the relationship between $ZT$ and details of the electronic and phonon structures proposed that a high $ZT$ value can be obtained if the following TE dimensionless quality factor $B_{ZT}$ is maximized:12

$$B_{ZT} = \frac{2k_B h c_1 N_{v,e}}{3\pi m_e \lambda^2 k_L},$$

where $k_B$ is the Boltzmann constant, $h$ is the reduced Plank constant, $c_1$ is the average longitudinal elastic constant, $\lambda$ is the deformation potential constant, $m_e^*$ is the inertial effective mass for conduction electrons (holes), and $N_{v,e}$ is the number of degenerate hole or electron pockets. This equation suggests two schemes in terms of enhancing the $ZT$ by properly modulating the electronic and phonon structures. Obviously, a small $\lambda$ and a small $m_e^*$ in addition to a low $k_L$ benefit the enhancement of quality factor $B_{ZT}$. On one hand, parameter $\lambda$ describes the perturbation of electronic band energy against an elastic deformation and thus describes the electron–phonon coupling. Therefore, a small $\lambda$ represents a weak electron–phonon coupling, allowing a partially separated modulation of the electronic bands and phononic ones. On the other hand, strong bonding anharmonicity as an intrinsic character of some specific compounds has also been demonstrated to be effective in suppressing $k_L$ due to the...
strong phonon scattering, paving a road to manipulate the TE performance in parallel with the well-documented approaches via nanostructuring of a TE material.

Along these two lines, a number of trials from both theoretical and experimental explorations have been performed and indeed, some seminal progress has been achieved. For example, some ABX ternary compounds have been reported to have large PF and have other members that have lower structure symmetry than of the half-Heusler compounds, allowing enhanced bonding anharmonicity. Tetragonal MgAgSb is one example of a compound having \( ZT \approx 1 \) at room temperature and \( ZT \approx 1.4 \) at \( T = 1195 \) K. The p-type FeNbSb-based half-Heusler compounds were reported to have \( ZT \) values reaching up to \( \approx 1.1 \) at \( T = 1100 \) K.24 These materials are favored for their large PF and high thermal stability.

In fact, these half-Heusler compounds often have large \( m^* \), and the bonding anharmonicity is not very significant due to the relatively high structure symmetry. The high TE performance is mainly ascribed to the weak electron–phonon coupling. Nevertheless, the ABX ternary compound family does have other members that have lower structure symmetry than of the half-Heusler compounds, allowing enhanced bonding anharmonicity. Tetragonal MgAgSb is one example of a compound having \( ZT \approx 1 \) at room temperature and \( ZT \approx 1.4 \) at \( T = 475 \) K.15 Pure MgAgSb has a \( \kappa_L \) lower than 1.0 W K\(^{-1}\) m\(^{-1}\).15 These results suggest that there are additional possibilities of finding some ABX ternary compounds with low-symmetry structures and thus strong bonding anharmonicity. One set of candidates are NaMgX (X = P, As, Sb) as ABX compounds that have tetragonal structure. In addition, it is known that layered materials often have weak electron–phonon coupling such as graphene.25 The NaMgX compounds have a similar layered structure to that of BiCuSeO and LaFeAsO, and the only difference is that the layered structure of BiCuSeO and LaFeAsO is parallel to the (0 0 1) plane, while that of NaMgX is parallel to the (1 1 0) plane (see Fig. 1). Therefore, the tetragonal NaMgX (X = P, As, Sb) compounds are expected to have both weak electron–phonon coupling and strong bonding anharmonicity. The only unknown physical factor left is the carrier effective mass \( m^* \), which should also be related to the electron–phonon coupling.

Herein, we use first-principles calculations based on density functional theory (DFT)\(^{26} \) to obtain the electronic and phonon structures of NaMgX (X = P, As, Sb) compounds. Subsequently, the whole set of TE parameters of these compounds, given appropriate carrier doping, will be evaluated by means of a computational package based on the semi-classical Boltzmann transport theory and phonon transport approaches.\(^{27} \) We shall show that these compounds have weak electron–phonon coupling and strong bonding anharmonicity. The n-type NaMgX (X = P, As, Sb) compounds may obtain promising TE performances, such as the optimized \( ZT \) values of 1.38 for X = P at \( T = 1195 \) K, 2.39 for X = As at \( T = 965 \) K, and 3.54 for X = Sb at \( T = 1195 \) K. The similar \( ZT \) values for the p-type NaMgX compounds, i.e. 0.71 for X = P at \( T = 1195 \) K, 1.54 for X = As at \( T = 1195 \) K, and 1.59 for X = Sb at \( T = 1195 \) K are also predicted.

II. Approach and theory

In this study, we employ the DFT scheme with a plane-wave pseudopotential formulation to compute the electronic structures and physical parameters using the VASP code.\(^ {28,29} \) The exchange-correlated potential is treated using the Perdew–Burke–Ernzerhof (PBE) within the generalized gradient approximation (GGA).\(^ {10} \) The plane wave cutoff energy is set to 500 eV, and the first Brillouin zone is sampled with \( 30 \times 30 \times 18 \) Monkhorst–Pack \( k \) meshes. For the phonon calculation, we use the DFPT scheme as implemented in the VASP code under the GGA-PBE functional. A \( 5 \times 5 \times 3 \) mesh for the first Brillouin-zone sampling and 500 eV for cutoff of the plane-wave basis set are used.

According to the semi-classical Boltzmann transport equation (BTE),\(^ {34} \) the electrical conductivity tensors \( \sigma_{ab} \) and electronic thermal conductivity tensors \( \kappa_{0ab} \) at non-zero electric current are given as follows:

\[
\sigma_{ab}(T, E) = \frac{1}{\Omega} \int \sigma_{ab}(\epsilon) \left( \frac{\partial f}{\partial \epsilon} \right) d\epsilon, \quad (2)
\]

\[
\kappa_{0ab}(T, E) = \frac{1}{e^2 T \Omega} \int \sigma_{ab}(\epsilon)(\epsilon - E_i)^2 \left( \frac{\partial f}{\partial \epsilon} \right) d\epsilon, \quad (3)
\]

where \( e \), \( \Omega \), \( \epsilon \), and \( f \) represent the unit electron charge (e), unit cell volume (\( \Omega \)), carrier energy (\( \epsilon \)), and Fermi distribution function (\( f \)), respectively, and \( E_i \) is the Fermi energy level. The \( \sigma_{ab}(\epsilon) \) is given by the following formula:

\[
\sigma_{ab}(\epsilon) = \frac{e^2 \tau}{N_h} \sum_{ik} \nu_s \nu_p \frac{\partial (\epsilon - \epsilon_{ik})}{\partial \epsilon} \frac{1}{\hbar} \frac{\partial \delta_{ik}}{\partial k_x}, \quad (4)
\]

where \( \tau \), \( N_h \), and \( \nu_s \) (\( \nu_p \)) are the carrier relaxation time, total number of sampled \( k \)-points, and carrier group velocity along the \( \alpha(\beta) \) direction, respectively. The \( \nu_s \) can be calculated as follows:

\[
\nu_s(t, k) = \frac{1}{\hbar} \frac{\partial \epsilon_{ik}}{\partial k_x}. \quad (5)
\]

The Seebeck coefficient tensors \( S_{ab} \) and electronic thermal conductivity tensors \( \kappa_{0ab} \) at zero electric current are given as follows:

\[
S_{ab}(T, E) = (\sigma^{-1})_{ab} \nu_p, \quad (6)
\]
\[ \kappa_{ab}(T, E_t) = \kappa_{ab}^0 - T \eta_{abm}(\sigma^{-1})_{abm} \]  
where the coefficient tensor \( \eta_{abm} \) are written as follows:

\[ \eta_{abm}(T, E_t) = \frac{1}{cTQ} \sigma_{ab}(\varepsilon - E_t) \left[ -\frac{\partial^2 E}{\partial \varepsilon^2} \right] d\varepsilon, \]  
and \( E_t \) is determined from

\[ n(E_t, T) = n_0 - \int f(\varepsilon, E_t, T) d\varepsilon, \]  
where \( n, n_0 \) and \( D(\varepsilon) \) are the carrier density, valence electron number, and total density of states (DOS) as a function of \( \varepsilon \), respectively. The effective mass approximation based on Bardeen and Shockley's deformation potential (DP) theory is used to evaluate the carrier mobility \( \mu \) and relaxation time \( \tau \). In bulk systems, \( \mu \) and \( \tau \) along the \( \beta \) direction can be expressed as follows:\(^3^2\)

\[ \mu_\beta = \frac{2 \sqrt{2} \pi \hbar^3 c_ii}{3(k_B T)^{3/2} m_\beta^{3/2} \lambda_\beta}, \]  
\[ \tau_\beta = \frac{m_\beta}{e}, \]  
where \( c_{ii} \) is the lattice elastic constant \((i = 1, 2, 3)\) and \( \lambda_\beta \) is the DP constant defined as follows:

\[ \lambda_\beta \propto \frac{dE_{\text{edge}}}{d\delta_{\beta}}, \]  
\[ \delta_{\beta} = \frac{a - a_0}{a_0}, \]  
where \( \delta_{\beta} \) is the uniaxial strain along the \( \beta \) direction. For a tetragonal structure such as NaMgX (\( X = P, As, Sb \)) compounds, there are six independent elastic constants, i.e., \( c_{11z}, c_{22z}, c_{44}, c_{66}, c_{12}, \) and \( c_{13b} \), whose evaluation requires six independent homogenous distortion modes. According to Voigt's and Reuss's approximations,\(^3^3\) the bulk modulus \( B \) and shear modulus \( G \) can be evaluated by the following formulations:

\[ B_V = \frac{1}{2}(c_{11} + c_{12}) + 4c_{13} + c_{33} \]  
\[ G_V = \frac{1}{30}(c_{11} + 3c_{12} - 3c_{13} + 12c_{44} + 6c_{66}) \]  
\[ B_R = \frac{c N^2}{c M} \]  
\[ G_R = 15 \left[ \frac{B_V}{c N^2} + \frac{6}{c_{11} - c_{12}} + \frac{6}{c_{44}} + \frac{3}{c_{66}} \right]^{-1} \]  
\[ c_M = c_{11} + c_{12} + 2c_{33} - 4c_{13} \]  
\[ c_N^2 = (c_{11} + c_{12})c_{33} - 2c_{13}^2. \]  
from which the values of \( B \) and \( G \) are obtained by taking the mean arithmetic values of \( B_V \) and \( B_R \), \( G_V \) and \( G_R \), respectively:

\[ B = (B_V + B_R)/2 \]  
\[ G = (G_V + G_R)/2. \]  
In eqn (10) and (11), \( m_\beta \) is the effective carrier mass along the \( \beta \) direction at the conduction (valence) band edge:

\[ m_{\beta}^* = \frac{\sum a \delta (\varepsilon - E_{\text{edge}})}{\sum a \delta (\varepsilon - E_{\text{edge}})}, \]  
where \( m_{\beta}^* \) is the energy-dependent effective mass tensor and tensor \( m_{\beta} \) is given by

\[ m_{\beta}^{-1} = \frac{\partial^2 E}{\hbar^2 \partial k_\beta \partial k_\beta}. \]  
According to the Slack equation,\(^3^4\) parameter \( \kappa_L \) is governed by

\[ \kappa_L = A \left( \frac{V_{\text{par}}}{T^2} \right)^{1/3} \frac{\hbar}{n_{\text{tot}}}, \]  
where \( A \) is a dimensionless collection of physical constants \( (A \sim 3.1 \times 10^{-6}) \), \( \Theta_D \) is the Debye temperature, \( V_{\text{par}} \) is the volume per atom, \( n_{\text{tot}} \) is the number of atoms in the primitive unit cell, \( \bar{m} \) is the average mass of all the atoms in the crystal, and \( \gamma \) is the Grüneisen parameter\(^23^,2^6\) calculated by the DFPT combined with the quasi-harmonic approximation (QHA), which is defined as follows:\(^3^7\)

\[ \gamma = \frac{1}{C_V} \sum_{i, q} \gamma(i, q) C_V(i, q) \]  
\[ \gamma(i, q) = -\frac{V_0}{c_0(i, q) \hbar} \frac{\partial \omega(i, q)}{\partial V}, \]  
where \( i \) and \( q \) represent the band index and phonon wave vector, \( V_0 \) is the equilibrium volume, \( C_V \) is the isometric heat capacity, and \( C_V(i, q) \) and \( \gamma(i, q) \) are the mode heat capacity and mode Grüneisen parameter, respectively. The \( C_V(i, q) \) and then \( C_V \) are calculated from the phonon dispersions:

\[ C_V = \sum_{i, q} C_V(i, q) \]  
\[ = \sum_{i, q} k_B \left( \frac{\hbar \omega(i, q)}{k_B T} \right)^2 \exp \left( \frac{\hbar \omega(i, q)}{k_B T} \right) \]  
and then parameter \( \Theta_D \) is evaluated from the formula for \( C_V \):

\[ C_V = 9 N k_B \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^{-x}}{(e^x - 1)^2} dx \]  
where \( N \) is the number of atoms in the unit cell. It should be noted that we specify the volume changes in 3%, 2%, 1%, 0%, -1%, -2%, -3% for the QHA.

III. Results and discussion

A. Electronic structures

NaMgAs and NaMgSb were reported in the Inorganic Crystal Structural Database (ICSD) with the ZrCuSiAs type structure.
compared to that of X = P results in the change of localization of X = As and Sb. In fact, the reduced electronegativity at X = Sb and NaMgSb are an indirect gap. The calculated band gaps for NaMgP, NaMgAs and NaMgP upon substitution from P to Sb (see ESI, minimum has strong Na-s states, which become less localized X = P is attributed to the fact that the conduction band CBM and VBM, while the non-parabolic band has important effects in the TE properties of semiconductors.

The DOS data of the three compounds are presented in Fig. 2(b), (d), and (f). The total DOS increases more rapidly near the VBM than near the CBM. The X atoms contribute more than Na and Mg to the DOS near the VBM. It is implied that an appropriate doping at Na and Mg sites with either an anion or cation will only change the carrier density without seriously distorting the topology of the electronic structure. However, Na, Mg and X atoms have almost the same contributions to the DOS near the CBM.

B. Elastic properties

Subsequently, we list the calculated elastic parameters, including elastic constants $c_{ij}$ (nine components), bulk modulus $B$, and shear modulus $G$, in Table 2. All the elastic constants for NaMgP are larger than those of NaMgAs and NaMgSb, while NaMgSb has the smallest elastic constants. It is known that constants $c_{11}$, $c_{22}$, and $c_{33}$ represent the stiffness against principal strains, whereas $c_{44}$, $c_{55}$, and $c_{66}$ correspond to the resistance against shear deformations. Obviously, NaMgSb can easily undertake the shear elastic deformation, which may be roughly measured by the $G/B$ ratio. Namely, a big $G/B$ ratio implies a fragile material, which is unfavorable for TE devices. The $G/B$ ratio for NaMgP, NaMgAs, and NaMgSb is 0.58, 0.61, and 0.59, respectively, significantly

### Table 1

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<th>Compound</th>
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<th>$c$</th>
<th>$\Delta$</th>
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### Table 2

<table>
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<th>Elastic parameters</th>
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<th>NaMgSb</th>
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<td>$c_{13}$</td>
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<tr>
<td>$B$</td>
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<td>33.72</td>
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<td>$G$</td>
<td>22.65</td>
<td>20.48</td>
<td>16.38</td>
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Fig. 2 The calculated band structure of NaMgP (a), NaMgAs (c) and NaMgSb (e), and the total DOS spectra for NaMgP (b), NaMgAs (d), and NaMgSb (f), respectively.
lower than 1.06 for the reference fragile material $\alpha$-SiO$_2$, suggesting that the NaMgX materials possess low resistance against shear deformation and good machinability.

Microscopically, moduli $B$ and $G$ reflect the magnitude of force between the atoms. The empirical rule also tells us that large $B$ and $G$ give rise to high melting point and high Debye temperature, leading to high lattice thermal conductivity. In comparison with the high-$T$ half-Heusler NbSbFe compound, which has $B = 163.62$ GPa and $G = 63.04$ GPa, the NaMgX compounds are lower in the two moduli, implying lower melting points and lower thermal conductivities.

C. Electro-transport behaviors

The carrier effective mass reflects the effect of a periodic crystal potential field on the carrier transport, and its values near the VBM and CBM are important for electrical transport. According to eqn (15), the $\varepsilon$-dependent effective mass $m$ can be calculated, and the data near the VBM and CBM along the different directions are listed in Table 3. In general, for the present compounds, the effective mass at the VBM along the $a$-axis is larger than that along the $c$-axis, but the opposite situations are observed at the CBM.

It is known that the deformation potential constant $\lambda$ scales the degree to which the carriers interact with phonons, namely, a low or high $|\lambda|$ corresponds to weak or strong electron–phonon coupling. It represents one of several key parameters for band engineering in the search for high performance TE materials. Considering that the carriers near the VBM and CBM are important for electrical transport, we calculate the deformation potential constant of the VBM for holes and CBM for electrons along the transport direction. The calculated $\lambda$ and $\tau$ are also summarized in Table 3. In fact, for n-type polycrystalline PbSe, the $|\lambda|$ is lower than 25 eV, characterizing the weak electron–phonon coupling and thus weak carrier scattering. It is noted that most half-Heusler materials have high TE performance mainly due to weak electron–phonon coupling. For example, HfNiSn has a $|\lambda|$ value of $\sim 5.0$ eV, which compensates the effect from the large carrier effective mass, beneficial to obtaining a high PF. As seen in Table 3, the deformation potential constant, effective mass, mobility, and relaxation time all indicate much weaker carrier scattering of the p-type compounds than the n-type compounds. The p-type NaMgAs has a very low $|\lambda|$ of $\sim 4.5$ eV along the $c$-axis.

An understanding of these low carrier scattering effects in these compounds is challenging, considering that the electron–phonon coupling in a solid is ubiquitous. The origin for the weak electron–phonon coupling can be complicated. It is shown that these compounds have the Mg layer on the $ab$-plane, benefiting carrier transport in a manner like that in metals. This may be the primary cause for the weak electron–phonon coupling, considering the fact that the electron–phonon coupling in metals is weak.

We then look at the relaxation time $\tau$. For the p-type carriers, the time along the $a$-axis is shorter than that along the $c$-axis. In contrast, for the n-type carrier, the time along the $a$-axis is longer than that along the $c$-axis. Along all the directions, the p-type carriers have much shorter $\tau$ values than those for the n-type. For instance, in NaMgAs with p-type carriers, the time along the $a$-axis is as short as 6.81 fs, but for the n-type carriers, it becomes 1112.15 fs.

Based on the whole set of data on the electronic structures, the electrical transport properties, including parameters $\sigma$, $S$, and $\kappa_e$, in the ($T,n$) plane for the p-type and n-type NaMgSb compounds as examples are plotted in Fig. 3. The data for the p-type and n-type NaMgP and NaMgAs compounds are presented in the ESI† (Fig. S2 and S3). In the general sense, the large $|S|$ corresponds to the low $\sigma$ and low $\kappa_e$, which appears in the region of low $n$ and intermediate $T$. The small $|S|$, high $\sigma$, and high $\kappa_e$ appear in the region of high $n$ and low $T$. The calculated data in the low-$n$ region do not support the

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<th>NaMgX</th>
<th>$\lambda_n$ (eV)</th>
<th>$\lambda_p$ (eV)</th>
<th>$m_h$ ($m_e$)</th>
<th>$m_h$ ($m_e$)</th>
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<th>$\mu_h$</th>
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<td>$a$</td>
<td>$c$</td>
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<td>NaMgSb</td>
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<td>$0.90$</td>
<td>$2.30$</td>
<td>$1.54$</td>
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Table 3 Calculated DP constant $\lambda$, carrier effective mass $m$ at zero temperature, carrier mobility $\mu$ (in units of cm$^2$ V$^{-1}$ s$^{-1}$), and relaxation time $\tau$ (in units of fs) at $T = 300$ K for NaMgX ($X = P, As, Sb$) compounds. The subscript n or p denotes the carrier type.
For evaluating the lattice thermal conductivity $k_L$, one needs to obtain the phonon spectrum. The calculated phonon dispersions for the three compounds along several representative symmetry lines within the first Brillouin zone of the primitive cell are plotted in Fig. 4(a), (c), and (e). Since each atom gives rise to three phonon branches containing one longitudinal branch and two transverse branches, there are in total eighteen branches for six atoms in this cell. They are one longitudinal acoustic (LA), two transverse acoustic (TA), five longitudinal optical (LO), and ten transverse optical (TO) modes. The highest optical frequencies for NaMgP, NaMgAs, and NaMgSb are 11.20 THz, 9.28 THz, and 8.28 THz, respectively, while the highest acoustic frequencies are only 4.08 THz, 3.16 THz, and 2.38 THz.

The lattice thermal conductivity $k_L$ is mainly from the acoustic branches. In this sense, NaMgX should possess low $k_L$. The two TA modes along the highest symmetry lines are two-fold degenerate. Moreover, a small phononic band gap for NaMgSb is noted, and the phononic DOS data for these compounds are presented in Fig. 4(b), (d), and (f). Considering that the main contribution to $k_L$ is from the low-frequency branches, we focus our discussion on the phononic DOS only in the range of low frequency. For NaMgP, as shown in the phonon DOS (see Fig. 4(b)), the low-frequency branches up to 4.2 THz are mainly from Na vibration, while the Mg atoms and P atoms have relatively weak contributions to the DOS.

For NaMgSb, the low-frequency branches up to 2.1 THz are mainly from Sb atomic vibrations, while the frequency branches between 2.1 THz and 3.8 THz are mainly from Sb and Na atomic vibrations. Based on the electronic structure analysis, it is noted that the carrier doping at the Na site for NaMgX can not only reduce the lattice thermal conductivity but also change the carrier density $n$. However, a carrier doping at the Mg site changes the carrier density $n$, while the lattice thermal conductivity may only be weakly affected.

Subsequently, we calculate parameters $\gamma$ and $\theta_D$, which are related to the lattice thermal conductivity, as shown in Fig. 5(a)–(i). The remarkable $T$-dependences of both parameters apply mainly to the low-$T$ range, and they become nearly $T$-independent in the high-$T$ range. The values of $\gamma$ for NaMgP, NaMgAs, and NaMgSb at $T = 300$ K are 1.65, 1.64, and 1.61, respectively, but increase up to 1.71, 2.03, and 2.14 at $T = 1195$ K. It is known that a large $\gamma$ indicates strong anharmonic vibrations. The PbTe compound has a $\gamma \sim 1.45$ at 300 K, implying a strong anharmonic phonon scattering. Such large $\gamma$ values for NaMgX compounds also imply that these compounds may exhibit strong anharmonic phonon scattering. In general, it is approved that good TE materials often have $\gamma$ values larger than 1.0. For example, PbSe and PbS have $\gamma \sim 1.65$ and $\gamma \sim 2.0$ at room temperature, respectively. The layered BiCuSeO with $\gamma = 1.1$ at room temperature has a low $k_L$ below $\sim 0.7$ W K$^{-1}$ m$^{-1}$. The $\gamma$ value for AgSbTe$_2$ is $\sim 2.05$, while its $k_L$ at room temperature is only $\sim 0.68$ W K$^{-1}$ m$^{-1}$. In particular, the $\gamma$ values of SnSe along the three axes are $\sim 4.1$, $\sim 2.1$, and $\sim 2.3$, noting that its $k_L$ is lower than $\sim 1.0$ W K$^{-1}$ m$^{-1}$.

Microscopically, it is noted that the X atom in NaMgX compounds has some non-bonded s-valence electrons and p-valence electrons. These non-bonded valence electrons can form a shell of relatively large radius, which is the reason for strong bond anharmonicity in a compound of low lattice thermal conductivity. In lattice-driven thermal transport, atoms approach one another, which leads to an overlapping of the

![Fig. 4](image_url)  
**Fig. 4** The calculated phonon spectra of NaMgP (a), NaMgAs (c), and NaMgSb (e), and the total phononic DOS spectra for NaMgP (b), NaMgAs (d), and NaMgSb (f). The corresponding spectra and phononic DOS are plotted in (b), (d), and (f), respectively.

![Fig. 5](image_url)  
**Fig. 5** The calculated Grüneisen parameter $\gamma$, Debye temperature $\theta_D$, and intrinsic lattice thermal conductivity $k_L$ as a function of $T$ for NaMgP (a–c), NaMgP (d–f), and NaMgSb (h–j), respectively.
wave functions of these non-bonded electrons and offers a repulsive force or in other words an anharmonicity. This effect applies to the NaMgX compounds concerned here.

The Debye temperature $\Theta_D$ reflects the magnitude of sound velocity determined by elastic moduli $B$ and $G$. Its values for NaMgP, NaMgAs, and NaMgSb compounds in the high-$T$ range are relatively low, e.g. 405 K, 338 K, and 292 K, respectively, at $T \sim 1195 K$. The relatively low $\Theta_D$ and large $\gamma$ for all these NaMgX compounds benefit the reduction of $k_B$. The evaluated intrinsic $k_B$ for these compounds are presented in Fig. 5(c), (f), and (i), reflecting the monotonous decreasing with increasing $T$, e.g. from 4.2 W K$^{-1}$ m$^{-1}$, 4.6 W K$^{-1}$ m$^{-1}$, and 4.4 W K$^{-1}$ m$^{-1}$ at $T = 300 K$ to 1.1 W K$^{-1}$ m$^{-1}$, 0.8 W K$^{-1}$ m$^{-1}$, and 0.7 W K$^{-1}$ m$^{-1}$ at $T = 1195 K$ for NaMgP, NaMgAs, and NaMgSb, respectively. Such low lattice thermal conductivities, due to the intrinsic weak bonding force and thus the small elastic constants, are impressive and less reported for available TE materials.

E. FOM factor $ZT$

Finally, one can evaluate the FOM factor $ZT$ for these NaMgX compounds, and the data in the $(n,T)$ plane for the p-type and n-type compounds are plotted in Fig. 6(a)-(f), where the red, green and blue colors represent the high, moderate, and low $ZT$ factors, respectively. Several prominent features deserve mention here. First, for all the three types of doped compounds, rather high $ZT$ values in the optimized states are predicted. At some optimized doping levels, the $ZT$ values may reach up to 2.0–3.0 at a relatively high $T$. Second, the n-type doped compounds have higher $ZT$ factors than the corresponding p-type doped ones due to the specific electronic and phonon structures. Third, one finds that the $ZT$ in the optimized region is not so sensitive to variation of either $n$ or $T$, suggesting that a practical control of the carrier doping in these compounds for a high $ZT$ value is not so challenging; moreover, high $ZT$ can be obtained in a relatively broad $T$-range. These issues are usually inevitable for many TE materials, leading to additional complexity in TE device design for broad-$T$ applications, but they are not so critical for the present NaMgX compounds.

For details, the optimized $ZT$ values and corresponding carrier density $n$ for NaMgP, NaMgAs, and NaMgSb compounds are summarized in Table 4. For NaMgP, the $ZT$ values at the optimized p- and n-type doping levels, corresponding to $n_{\text{opt}} \approx 9.12 \times 10^{20}$ cm$^{-3}$ and $7.24 \times 10^{18}$ cm$^{-3}$, reach 0.71 and 1.38 at $T \sim 1195$ K and 1155 K but rapidly decrease to 0.27 and 0.68 at $T \sim 600$ K, corresponding to $n_{\text{opt}} \approx 4.17 \times 10^{20}$ cm$^{-3}$ and $3.16 \times 10^{18}$ cm$^{-3}$. In comparison, the doped NaMgAs and NaMgSb have better TE performance than the doped NaMgP. For the doped NaMgAs, the $ZT$ values at the optimized p-type and n-type doping levels, corresponding to $n_{\text{opt}} \approx 4.79 \times 10^{20}$ cm$^{-3}$ and $2.76 \times 10^{18}$ cm$^{-3}$, reach 1.54 and 1.59 at $T = 1195$ K and 965 K. It is noted that the optimized $ZT$ for the n-type NaMgSb can reach as high as 3.54, while the p-type NaMgSb has $ZT = 1.59$ as the highest value, lower than the n-type doping cases.

F. Discussion

Up to this stage, one understands that the predicted electrical and thermal transport behaviors favored for good TE performance are substantially attributed to the weak electron–phonon coupling and strong bonding anharmonicity of these compounds. These compounds represent typical examples in which the control of the electrical and thermal transports can be partially separated so that the TE performance can be considerably optimized. Indeed, very large FOM factor $ZT$ values are obtained for all three compounds upon proper carrier doping.

It is also understood that a theoretically predicted high $ZT$ may not be reached experimentally due to some practical challenge or unforeseen factors of the theoretical calculations. First, these compounds are difficult to synthesize and may be unstable and easily oxidized due to the presence of sodium. Second, carrier doping may not be easy for many cases.

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**Table 4 Optimized $ZT$ values ($ZT_{\text{opt}}$) and the corresponding optimal carrier density ($n_{\text{opt}}$) for NaMgX ($X = P$, As, Sb) compounds. The evaluated PF values at ($n_{\text{opt}}$ and $ZT_{\text{opt}}$) are also listed, which may not be optimized.**

<table>
<thead>
<tr>
<th>NaMgX</th>
<th>Carrier</th>
<th>$n_{\text{opt}}$ (cm$^{-3}$)</th>
<th>PF (mW m$^{-1}$ K$^{-2}$)</th>
<th>$ZT_{\text{opt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = P</td>
<td>Hole</td>
<td>$9.12 \times 10^{20}$</td>
<td>0.98 (1195 K)</td>
<td>0.71 (1195 K)</td>
</tr>
<tr>
<td></td>
<td>Electron</td>
<td>$7.24 \times 10^{18}$</td>
<td>3.58 (1155 K)</td>
<td>1.38 (1155 K)</td>
</tr>
<tr>
<td></td>
<td>Hole</td>
<td>$4.79 \times 10^{20}$</td>
<td>1.75 (1195 K)</td>
<td>1.54 (1195 K)</td>
</tr>
<tr>
<td></td>
<td>Electron</td>
<td>$2.88 \times 10^{20}$</td>
<td>2.57 (600 K)</td>
<td>0.57 (600 K)</td>
</tr>
<tr>
<td>X = As</td>
<td>Hole</td>
<td>$1.74 \times 10^{18}$</td>
<td>8.54 (600 K)</td>
<td>1.48 (600 K)</td>
</tr>
<tr>
<td></td>
<td>Electron</td>
<td>$3.31 \times 10^{18}$</td>
<td>1.46 (1195 K)</td>
<td>1.59 (1195 K)</td>
</tr>
<tr>
<td>X = Sb</td>
<td>Hole</td>
<td>$2.19 \times 10^{20}$</td>
<td>2.39 (600 K)</td>
<td>0.58 (600 K)</td>
</tr>
<tr>
<td></td>
<td>Electron</td>
<td>$6.31 \times 10^{19}$</td>
<td>6.90 (1195 K)</td>
<td>3.54 (1195 K)</td>
</tr>
<tr>
<td></td>
<td>$4.17 \times 10^{19}$</td>
<td>9.33 (600 K)</td>
<td>1.67 (600 K)</td>
<td></td>
</tr>
</tbody>
</table>

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![Fig. 6](image-url) The calculated $ZT$ map as a function of $T$ and carrier density $n$ for NaMgP (a and b), NaMgAs (c and d), and NaMgSb (e and f), respectively.
A favored carrier doping should impose an impact as weak as possible on the electronic and phononic band structures although an increase of $\kappa_e$ is inevitable. For the three compounds, one may propose a doping at the Na site with some transition metals, such as Ti, V, Nb, Ta, Fe, Co, Ni, Cu, and Zn, in order to obtain the n-type systems, given a consideration of atomic radius and valence. A challenge exists for the p-type doping, and it may be feasible to optimize the electron density by introducing a Na or Mg vacancy by C or Si doping at the Sb site. In these two cases, the impact on the electronic structure may be remarkable.

On the other hand, the high operating temperature may not be reachable due to the degraded mechanical properties of these NaMgSb compounds in such high temperatures. In addition, the charge polarity for a specific compound may not be easily modulated when some materials prefer one polarity and the other becomes difficult. However, the experimental testing of our calculation predictions is appealing.

IV. Summary

In summary, we investigated in detail the electronic, phonon, and elastic properties of ABX ternary NaMgX ($X = P, As, Sb$) compounds and predicted the whole set of TE parameters using first-principles calculations. First, we used the DFT combined with semi-classical BTE and DP theories to calculate the electrical parameters. Second, we calculated the lattice thermal conductivity using the DFPT combined with the QHA scheme and found that the lattice thermal conductivity for NaMgX at $\sim 600$ K is lower than $2.0\, \text{W m}^{-1}\, \text{K}^{-1}$, which is ascribed to the strong bonding anharmonicity. For all three compounds, a doping at the Na site with either an anion or cation will not only reduce the lattice thermal conductivity but also enhance the carrier density $n$. Finally, we also predicted that the optimized $ZT$ values for the p-type NaMgX ($X = P, As, Sb$) compounds can reach up to 0.71, 1.54, and 1.59, respectively, while the $ZT$ values for the n-type doping can be as high as 1.38, 2.39, and 3.54. The main physics underlying such large $ZT$ values originates from the weak electron–phonon coupling and strong bonding anharmonicity. The present study not only approves the two physical ingredients as effective schemes for enhancing the TE performance of a TE material but also suggests the possibility of more ABX ternary compounds with promising TE properties.

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Notes and references

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