Understanding of isoelectronic alloying induced energy gap variation for a large enhancement of thermoelectric power factor

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Band-structure engineering is an important strategy that can improve the properties of functional materials or even bring new features to existing systems. Band gap (or energy gap, Eg) plays a crucial role in deciding the electronic or optical properties of one material. Isoelectronic and isostructural alloys usually exhibit similar electronic band structures, but the related effect of Eg variation was found to be distinct and sometimes controversial. Herein, we provided a deep understanding of the origin of band tuning in isoelectronic alloys based on experimental characterizations and theoretical calculations. The prerequisites of an isoelectronic alloy system with an Eg that is sensitive to composition are thoroughly disclosed by studying (Sb, Bi)₂Te₃ and Pb(Se,Te). In the promising Mg₃(Sb, Bi)₂ thermoelectric materials, it is found that Bi isoelectronic substitution can significantly decrease the Eg, due to the combination of the higher energy of Bi 6p orbit than that of Sb 5p orbit and the varied bond strength induced by lattice expanding. A high room-temperature power factor (*PF*) value of 38.5 μ W cm⁻¹ K⁻² is obtained in nearly zero-gap Mg_{3.2}Sb_{0.3}Bi_{1.7} samples, which rationally guides the design of thermoelectric materials in the aspect of electronic transport.

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I. INTRODUCTION

Thermoelectric (TE) technology, which can convert electrical power to a temperature gradient and vice versa, has received renewed interest in the past two decades, which provides sustainable solutions for both solid-state refrigeration and waste-heat harvest [1–4]. TE performance is generally reflected by the TE figure of merit (ZT), which is expressed as $ZT = S^2 \sigma T / \kappa$, where S represents the Seebeck coefficient, σ the electrical conductivity, T the absolute temperature, and κ the thermal conductivity, which is composed of the electronic thermal conductivity (κ_e) and the lattice thermal conductivity (κ_{lat}) . The production of S square and σ is denoted as the power factor (PF). The underlying correlation between S and σ makes the optimization of *PF* a critical challenge compared with the minimization of κ , in which κ_{lat} is relatively independent and can be suppressed by defect engineering [5,6]. To comprehensively understand these correlations, multiple theoretical models have been constructed. From the perspective of the single parabolic band (SPB) model [7] (whose main formulas are listed in the Supplemental Material, SM [8]), the band degeneracy N_V , which dominates the density of state effective mass m_D^* through the relation $m_D^* = N_V^{2/3} m^*$, is the key factor which can decouple the trade-off relation between S and σ by keeping the Fermi level moderate, simultaneously realizing a high carrier concentration [9]. Numerous previous kinds of research have focused on promoting N_V by aligning multiple band edges to fulfill a high PF [10], but in reality, it

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is only effective in some specific TE systems, such as IV–VI semiconductors [11–14]. A general strategy for enhancing *PF* is the energy gap (*Eg*) tuning [15], which is confirmed in advanced TE materials such as PbTe and PbS [16,17]. The single Kane band (SKB) model is more precise when the shape of the band shows a great deviation from a parabola [18]. Since the primary objective of constructing a one-band model is to simplify the real electron dispersion relation, the *E-k* relations of the SPB model and the SKB model, which are given, respectively, reveal inherent difference:

$$E = \frac{\hbar^2 k^2}{2m^*},\tag{1}$$

$$E\left(1+\frac{E}{E_g}\right) = \frac{\hbar^2 k^2}{2m^*},\tag{2}$$

where m^* is the single-band effective mass, E the energy of the carrier, Eg the energy gap, k the wave vector, and \hbar the reduced Planck constant. As the value of the single-band effective mass of one carrier is defined by $1/(\partial^2 E/\partial k^2)$, it is easy to recognize that m^* is dependent on Eg and E in the SKB model. A small Eg will lead to a small m^* , which shows an inverse relation with carrier mobility [16]. Therefore, Eg narrowing can be an effective way to enhance the charge-carrier mobility, which provides an insight to achieve a high PF. When a compound is alloyed by its isoelectronic counterpart with heavier atoms, the Eg of the alloy system is expected to decrease and vice versa, enabling continuous manipulation of Eg is realized.

Eg manipulation through alloying is not only a widely used strategy in the semiconductor industry but also a popular subject in condensed physics [19,20]. The intrinsic model based

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FIG. 1. The relationship between the electronegativity difference and E_g difference of 13 well-studied semiconductor systems [28–37]. The cases of Mg₂Si, GeTe, and their isoelectronic counterparts are discussed in detail in the SM (Fig. S1) [8].

on the chemical-bond theory indicates that a larger electronegativity difference between two isoelectronic atoms will result in a larger Eg variance [21]. Figure 1 displays a collection of 13 representative isoelectronic semiconductor systems. The x axis of the figure illustrates the electronegativity difference between two isoelectronic atoms. This difference is calculated by subtracting the electronegativity value of the lighter atom from that of the heavier atom. A plus sign is used for anion replacement, while a minus sign is employed for cation replacement. Similarly, the y axis is the Eg difference (ΔEg) between the heavy compound and the light compound but reversed for ease of interpretation. Herein, one can easily tell that in most systems the effect of alloying on the Eg variation is prominent. However, in systems such as (Sb, Bi)₂Te₃, (Ge,Pb)Te, and Pb(Se,Te) the changing of Eg is less significant, which is hard to explain merely by the electronegativity difference. Simultaneously, there exists Mg₃(Sb, Bi)₂ whose Eg changes the most dramatically with alloying among TE systems. The underlying difference is waiting to be uncovered. *n*-type Mg₃(Sb, Bi)₂-based alloys have been proven as the most potential TE material for next-generation TE cooling devices [22–24], whose performance for cooling applications, an upgrowing field of TE application, is optimized through isoelectronic alloying, i.e., Mg₃Bi₂ alloying. With Te as a regular but effective donor, TE performance of Mg₃(Sb, Bi)₂ in a wide component range keeps refreshing by several strategies, such as the grain-size tuning [25] and donor evolving [26,27]. More importantly, Eg narrowing in Mg₃(Sb, Bi)₂ holds great potential in cooling applications. Therefore, the fundamental mechanism of Eg narrowing needs to be addressed systematically and quantitatively.

In this study, we compare $Mg_3(Sb, Bi)_2$ with $(Sb, Bi)_2Te_3$ and Pb(Se,Te) to elucidate the reasons behind the distinct behavior of *Eg* in certain isoelectronic systems. Through our analysis, we identify two main factors that significantly influence *Eg*: the degree of spin-orbit coupling (SOC) and the lattice constants. We find that when these factors exhibit synergistic effects, it leads to notable variations in *Eg.* As a result, significant changes in *Eg* can be anticipated. Mg_{3.2}Sb_{0.3-0.5y}Bi_{1.7-0.5y}Te_y-based alloys with nearly zero *Eg* are synthesized and studied in detail. The critical role that an appropriate gap plays in the low-temperature TE application is highly emphasized by combining theoretical calculations and experimental results. By tuning the electron concentration, a high room-temperature power factor $PF_{rt} = 38.5 \,\mu\text{W cm}^{-1} \,\text{K}^{-2}$ is obtained, which is owing to a lifted Hall carrier mobility, $\mu_{\rm H} = 264.4 \,\text{cm}^2 \,\text{V}^{-1} \,\text{s}^{-1}$. This high *PF* demonstrates the potential of zero-gap materials for TE cooling applications, especially precise temperature control, in which a high cooling-energy density is necessary to be obtained. It is assumed that the *Eg* tuning strategy can pave the way for the discovery of TE systems by maximizing electrical performance.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

A. Sample preparation and characterization

High-purity Mg (99.95%), Sb (99.999%), Bi (99.999%), and Te (99.999%) were weighed according to the composition of Mg_{3.2}Sb_{0.3-0.5y}Bi_{1.7-0.5y}Te_y (y = 0, 0.002, 0.005, 0.0075, and 0.01), finally adding to 8 g and then the raw materials were loaded into a stainless-steel ball-milling jar in the glove box with argon atmosphere. The materials were ball milled for 5 h by a high-energy ball mill (SPEX 8000M). The obtained ball-milled powders were then loaded into a graphite die with an inner diameter of 12.7 mm, under the protection of an argon atmosphere, then immediately sintered by rapid hot pressing under the pressure of 50 MPa and at the temperature of 1073 K for 20 min. The hot-pressed disks are about 2 mm thick.

Disk samples whose diameters are 12.7 mm are polished for the thermal diffusivity measurements where a laser flash system (Netzsch LFA 457, Germany) is employed, with a pyroceram disk as the reference sample. The electronic performance measurements are conducted on a commercial system (ULVAC ZEM-3, Japan) using bar samples. The carrier concentration $(n_{\rm H})$ and mobility $(\mu_{\rm H})$ were calculated by the formula $n_{\rm H} = 1/(eR_{\rm H})$ and $\mu_{\rm H} = \sigma R_{\rm H}$, where $R_{\rm H}$ is the Hall coefficient acquired by the van der Pauw technique under a 1.5-T magnetic field. The room-temperature crystal structure was determined by x-ray diffraction (XRD) using X'Pert PRO-PANalytical, Netherlands with a Cu K_{α} radiation from 10° to 90°. Field-emission scanning electron microscopy (Quanta200FEG, FEI) is used to characterize the composition of each sample. The backscattering electron imaging mode was used to observe whether there was component segregation, and the elemental mapping in the same area was obtained by using the energy-dispersive x-ray spectrometer.

B. First-principles calculation

First-principles calculations have been constructed by VASP using the projector-augmented wave [38] method. For Mg_3Sb_2 , $Mg_3Sb_{0.25}Bi_{1.75}$ alloy, and PbSe, fully relaxed lattice structures are used to carry out the calculations. And, the Perdew-Burke-Ernzerhof [39] functional is used during the structure relaxations. The plane-wave cutoff energy is set as 600 eV unitedly. In the calculation process of $Mg_3Sb_{0.25}Bi_{1.75}$ the corresponding Brillouin zone was sampled by a $3 \times 3 \times 2$

k mesh, In the calculations of Mg₃Sb₂, PbSe, and Sb₂Te₃, the k mesh is chosen as $9 \times 9 \times 5$, $7 \times 7 \times 7$, and $12 \times 12 \times 1$, respectively, based on the specified lattice constants. The relaxations of these calculation processes were done until the total energy converged within 10^{-6} eV and the force on each atom was less than 10^{-4} eV/Å . The modified Becke-Johnson [40] (mBJ) meta-generalized-gradient approximation potential is used to calculate the band structure to obtain relative accurate band gaps. To obtain the effective band structure of the Mg₃Sb_{0.25}Bi_{1.75} alloy, the supercell band structure was unfolded to the first Brillouin zone of the pure compound using VASPKIT [41]. For Sb₂Te₃, the experimental lattice constants given by Fang et al. [42] are used in the calculations, and only the atomic positions are relaxed. The criteria to stop the calculation are set as in previous calculations in this study. The effect of SOC is always considered without any specific mention.

C. Cooling-performance simulation

The cooling power (Q_C) of a thermoelectric module can be expressed as [24]

$$Q_C = ST_C I - \frac{1}{2}I^2(R_0 + R_C) - K\Delta T,$$

where I, ΔT , T_C , S, R_0 , R_C , and K are the electrical current, the temperature difference between the hot side and cold side of legs, the cold-side temperature, the Seebeck coefficient of device, the resistances contributed by thermoelectric legs, the resistances from the contact layer, and the thermal conductance of thermoelectric legs, respectively, in which S, R_0 , R_C , and K can be expressed as

$$R_{0} = \frac{N}{\Delta T} \int_{T_{h}-\Delta T}^{T_{h}} \left(\frac{h}{A_{N}}\rho_{N}(T) + \frac{h}{A_{P}}\rho_{P}(T)\right) dT$$

$$R_{C} = 2N \left(\frac{\rho_{NC}}{A_{N}} + \frac{\rho_{PC}}{A_{P}}\right)$$

$$S = \frac{N}{\Delta T} \int_{T_{h}-\Delta T}^{T_{h}} (S_{P}(T) - S_{N}(T)) dT$$

$$K = \frac{N}{\Delta T} \int_{T_{h}-\Delta T}^{T_{h}} \left(\frac{A_{N}}{h}\kappa_{N}(T) + \frac{A_{P}}{h}\kappa_{P}(T)\right) dT,$$

where N, h, ρN_c , ρP_c , T_h , A_N , and A_P are the number of the thermocouples, the leg length, the contact resistivity of *n*- and *p*-type legs, the hot-side temperature, and the cross-section area of *n*- and *p*-type legs, respectively. For pure simulation condition, the contact resistivity is neglected here.

The coefficient of cooling performance (COP) of a thermoelectric module can be calculated by

$$COP = \frac{ST_C I - \frac{R}{2}I^2 - K\Delta T}{I^2 R + SI\Delta T}$$

In the cooling-performance simulation study, the thermal radiation effect is neglected.

III. RESULTS AND DISCUSSION

Essential as the manipulation of Eg is in designing TE materials, there are also systems such as (Sb, Bi)₂Te₃, Pb(Se,Te),

and (Ge,Pb)Te, whose Eg is not sensitive to composition variation. Therefore, isoelectronic alloys can hardly optimize the electrical performance through band-structure manipulation in these systems (see Fig. S2 [8] for the intrinsic mobility of both alloy systems at different compositions [43,44]). The low sensitivity of their Eg is attributed to two main related factors: the lattice constants [45] and the degree of SOC [46] also including the competitive relationship between them. Take (Sb, Bi)₂Te₃ as an example, as the composition variates from Sb₂Te₃ to Bi₂Te₃, lattice constants will increase, and so will the degree of SOC effect. However, the former will cause a reduction of Eg, while the latter induces an opposite trend, finally leading to a moderate Eg variation. Band calculations of Sb₂Te₃ and PbSe under tensile strains ($\varepsilon \equiv$ $\Delta l/l$) are executed. In Sb₂Te₃, the variation trend shows no deviation from the regular situations: Eg decreases as the lattice expands. Under strains $\varepsilon_1 = 0.5\%$ and $\varepsilon_2 = 1\%$, Eg of Sb₂Te₃ decreases by 1.7 and 12.5%, respectively. However, in the calculation results of PbSe, Eg increased by 8.7 and 16.9%, respectively [Fig. 2(a)]. On the other hand, the effects on Eg of SOC are different according to different band features [47,48]. With an enhanced SOC effect, the value of Eg shows a nonmonotonic trend. An expected Eg shrinking will take place at first [Fig. 2(b)]. After the band-inversion phenomenon has emerged, an increasing SOC effect will lead to an opening between the valence band and the conduction band [Fig. 2(c)]. The projected band structures for Sb_2Te_3 and PbSe are given, respectively, in Figs. 2(d) and 2(e) and Figs. 2(f) and 2(g). It is illustrated that PbSe presents a directgap band structure, with no band-inversion feature. However, in the calculation result of Sb₂Te₃, a typical inversed band structure is observed since its valence-band edge located at Γ point is contributed by Sb 4p orbit and the conduction one by Sb 5s orbit. A similar band-inverse property can be seen in the contribution of Te. As PbSe features a band structure without band-inversion behavior, a strengthened SOC effect will lead to Eg narrowing, as the process illustrated in Fig. 2(b). However, in Sb₂Te₃, increasing the SOC effect will open the Eg, as shown in Fig. 2(c). Given the former discussion, in the composition variation process of both (Sb, Bi)₂Te₃ and Pb(Se,Te) systems, two effects of SOC degree changing and lattice constant changing on the Eg are contradicted. Significant Eg variation fails to be achieved in other similar systems, such as (Ge,Pb)Te, where cubic GeTe shows no inverted band structure with Eg increasing as the lattice expands [49,50] (see Fig. S1 [8] for the projected band structure of GeTe and the Eg of GeTe as a function of tensile strain [51]).

Alloying as an Eg manipulation strategy is remarkably effective for Mg₃(Sb, Bi)₂. Mg₃(Sb, Bi)₂ is the TE alloy system whose Eg is the most sensitive to the alloy composition as illustrated in Fig. 1. The Eg narrowing effect also leads to the band-sharpening effect, which promotes high carrier mobility [52,53]. So, it is worth understanding how these two mentioned factors affect Eg variation in the Mg₃(Sb, Bi)₂ system. Furthermore, density of states (DOS) and partial crystal-orbital Hamiltonian population (COHP) results of Mg₃Sb₂ elucidating bonding states in detail are displayed in Fig. 3. Considering the similarity between Mg₃Sb₂ and Mg₃Bi₂, Mg₃Sb₂ is taken as an example when analyzing band-edge states from the covalent bond perspective. As shown in the



FIG. 2. Critical factors induce the band-gap variation process. (a) The ratios of the energy gap change of Sb_2Te_3 and PbSe after and before 0.5 and 1% strains. (b), (c). The schematic illustration of SOC-driven band narrowing (b) and band inversion (c). (d), (e) Orbital projected band structure of PbSe and (f), (g) Sb_2Te_3 , Fermi level is set at 0 eV.

structure schematic Fig. 3(f), there exist two types of Mg cations with different chemical environments in Mg₃Sb₂. One participates in the construction of the cation layer, labeled as Mg1, and the other belongs to the Mg₂Sb₂²⁻ covalent network, labeled as Mg2 [52].

Taking the process of substituting Sb with Bi as an example, this substitution leads to lattice expansion and a strengthening of the SOC effect. First, we studied the electronic structure of Mg₃Sb₂ under tensile strains ($\varepsilon \equiv \Delta l/l = 0.5, 1\%$) to abstract lattice constants changing from real circumstances. Considering the anisotropic crystal structure of Mg₃Sb₂, tensile strains along the *a* axis and the *c* axis are applied, respectively, during calculation. ε_a and ε_c are used to denote tensile strain along the *a* axis, and *c* axis, respectively. As shown in Fig. 4, when the primitive cell is subjected to a tensile strain along the *a* axis, the value of Eg tends to go downhill [Fig. 4(a)], while an opposite tendency is observed under the ε_c condition [Fig. 4(c)]. The former effect is more significant, finally leading to a decreased Eg ($\Delta Eg = -0.033 \, \text{eV}$) when an isotropic tensile

strain ($\varepsilon = 1\%$) was applied to the primitive cell based on our first-principles calculation results. The crystal-orbital Hamiltonian population result and integrated COHP (ICOHP) of both original and strained primitive cells are also displayed in Fig. 4(b) and Fig. 4(d). The COHP method, which manipulates DOS by the corresponding element of the Hamiltonian, is a widely used tool to reflect the bonding information. A negative COHP is a sign of bonding states, while a positive value means antibonding states and zero means no bonding [54]. ICOHP can describe the strength of a covalent bond quantitatively. A more negative ICOHP means a stronger covalent bonding that will lead to a wider band. Under the a-axis strain, -ICOHP of both the Sb-Mg1 bond and the Sb-Mg2 bond increase, compared with the results of the unstrained cell, while their corresponding -ICOHP values in the ε_c case are both decreased [Fig. 4(b) and Fig. 4(d)]. If the lattice constant affects Eg independently, a decrease of Eg will be observed by calculating the mBJ band of Mg₃Sb₂ using the lattice constants of Mg₃Bi₂ (from 0.44 to 0.35 eV).



FIG. 3. Calculation results of DOS and pCOHP of Mg_3Sb_2 . (a) Partial density of states of selected atoms in Mg_3Sb_2 . (b)–(e) pCOHP of Sb-Mg1, Sb-Mg2, Mg1-Mg1, and Mg1-Mg2 interaction. (f) The structure schematic of Mg_3Sb_2 : one Sb atom and its ligand in the perspective of ligand-field theory.



FIG. 4. Eg calculation and chemical bonds analyzing for strained Mg₃Sb₂. For (a) and (c), Mg₃Sb₂ Eg as a function of uniaxial tensile strain along the *a* axis and *c* axis, respectively. For (b) and (d) pCOHP and –ICOHP of Sb-Mg1 and Sb-Mg2, the former is plotted in solid lines and the latter dashed lines. The black line, the orange line, and the blue line are the results of the original cell, the *a*-axis strained cell, and the *c*-axis strained cell, respectively. Fermi level is set at 0 eV. The SOC effect is not considered herein.



FIG. 5. mBJ band structures for (a) Mg_3Sb_2 and (b) Mg_3Bi_2 of (a) 1-3. orbital projected band structure of Mg_3Sb_2 for Mg1, Mg2, and Sb, respectively, and (b) 1-3. orbital projected band structure of Mg_3Bi_2 for Mg1, Mg2, and Bi respectively. Fermi level is set at 0 eV.

Figure 5 shows the mBJ band structures with SOC of Mg_3Sb_2 and Mg_3Bi_2 . Mg_3Sb_2 and Mg_3Bi_2 show similar orbital characteristics, where conduction-band minimum (CBM) and valence-band maximum (VBM) states are mostly derived from Mg (Sb or Bi) atoms, but a slight trace of band inversion driven by SOC can be observed in Mg_3Bi_2 [see Fig. 5(b3)]. Combining COHP and DOS calculation results in Fig. 3, it is reasonable to conclude that no obvious overlap behavior is detected between Mg1-Mg1 and Mg1-Mg2, and the VBM and the CBM of Mg_3X_2 (X = Sb or Bi) formed by the bonding state and the antibonding state of *s* orbit of Mg and *p* orbit of the anion.

By replacing Sb with Bi, an increase in the energy of anion p orbit will give rise to the energy changing of band edges, which means that Bi-6p with higher energy (set the vacuum level as zero, $E_{Bi-6p} = -0.180 \text{ eV}$, $E_{Sb-5p} = -0.186 \text{ eV}$) and less energy difference compared to the Mg-3s ($E_{Mg-3s} =$ -0.175 eV) will lead to a narrower Eg in Mg₃(Sb, Bi)₂-based alloy. Furthermore, without an inverted band structure, the Eg of Mg₃Sb₂ can be easily tuned down by strengthening the SOC effect because of the heavy atom substitution. The energy contribution of SOC (E_{SOC}) of each atom in both strained and nonstrained lattices is given in Table S1. A stronger SOC will intrinsically result in a small Eg [55]. To certify that, an mBJ band calculation of Mg₃Bi₂ without SOC was conducted (Fig. 6), where the overlap between the conduction band and valence band is opened. This result also shows no band-inversion behavior, i.e., the conduction-band minimum located at Γ has no contribution from Bi-6*p* orbits.

Since Eg manipulation can be performed as an effective strategy to promote PF, we executed our experiment

in Mg₃(Sb, Bi)₂, which shows the most significant variation of Eg. Mg₃Sb_{0.3}Bi_{1.7} is chosen as the base sample because its Eg is near zero based on the linear interpolating the first-principles calculation results [Fig. 7(a)]. It is first studied by first-principles calculations. Instead of studying the exact composition, the mBJ band structure with SOC of Mg₃Sb_{0.25}Bi_{1.75} is calculated by building a 2 × 2 × 2 supercell generated by the Special Quasi-random Structures method by using the ATAT code [56] (convergence test with the *k* mesh and supercell size are given in Fig. S3). As shown in Fig. 7(b), a nearly zero Eg is obtained and the conduction-band minimum and valence-band maximum are overlapped slightly, which is reflected in the DOS



FIG. 6. Orbital projected band structure of Mg_3Bi_2 without SOC. The 6s orbit and 6p orbit of Bi are projected on the band structure.



FIG. 7. Electric properties and structural properties simulation and examination of Mg₃(Sb,Bi) and the Mg₃Sb_{0.3}Bi_{1.7} of interest: (a) The composition-dependent band gap *Eg* by first-principles calculation. (b) Effective band structure and DOS for Mg₃Sb_{0.25}Bi_{1.75}; Fermi level is set at 0 eV. (c) The Rietveld refinement results of the Mg₃Sb_{0.3}Bi_{1.7} sample. The lattice constants (a = 4.666Å, c = 7.401Å) of the Mg_{3.2}Sb_{0.3}Bi_{1.7} sample are obtained based on the Rietveld refinement. An expansion of ~1.6% and an expansion of ~1.7% in the *a*- and *c* directions are obtained, respectively. (d) Comparing the lattice constants of Mg₃Sb_{0.3}Bi_{1.7} with former experimental and calculation results [60].

calculation result. The CBM is located on the low-symmetry path, M^*-L^* , and the second conduction-band minimum is located at the Γ point, and the valence band maximum (VBM) is also located at the Γ point. These essential features are identical to Mg_3Sb_2 . Both Eg and the energy difference between and the second conduction-band extrema are narrowed compared to the Sb-rich counterpart, revealing the remarkable band-sharpening effect. These first-principles calculation results show a good correspondence with the linear interpolation result [57]. On the experimental aspect, a series of Mg_{3.2}Sb_{0.3-0.5y}Bi_{1.7-0.5y}Te_y samples was synthesized using our previous methods [58,59], for y = 0, 0.002, 0.005, 0.0075, and 0.01, respectively. The lattice structure, phase structure, and composition of the undoped sample are measured by XRD, backscattered electrons (BSE), and energy-dispersive spectroscopy (EDS), respectively, shown in Fig. 7 and Fig. S4 (for BSE and EDS) and Table S2 (for actual composition obtained by EDS). Besides, there is little deviation between the actual composition and nominal composition, which implies that the influence of these associated point defects on thermoelectric properties can be neglected. The trigonal lattice structure is maintained for our synthesized samples, without any detected second phase. Lattice parameters are given by the Rietveld refinement results, compared with former experimental and theoretical reports [Figs. 7(c) and 7(d)].

Samples with different Te contents feature different *n*-type carrier concentrations but a nearly constant band structure at CBM, as Xia et al. studied before [61], so Te can be seen as an ideal donor that only tunes the carrier constant in this study. TE performance of all these samples is measured, which is shown in Fig. 8. The Seebeck coefficient of $Mg_{3,2}Sb_{0,3}Bi_{1,7}$ is plotted in Fig. 8(b), which shows a positive Seebeck coefficient at room temperature but *n*-type behavior in the high-temperature range, which is contributed by the eminent electric transport properties of the conduction band comparing with the valence band. The significant increase in the Seebeck coefficient at high temperatures can be attributed to the superior mobility of the conduction band compared to the valence band [see Figs. S5(a)-S5(c) for the doubleband simulation [62] results, considering the alloy scattering process [63], including the Seebeck coefficient, the carrier concentration, and the Hall coefficient]. Considering the fact that Mg_{3.2}Sb_{0.3}Bi_{1.7} is lightly doped with excess Mg and has a low carrier concentration, it is notable that a Seebeck coefficient near 0 is still observed at room temperature. This can be attributed to the offset effect between the Seebeck



FIG. 8. Electric properties measurement and simulation of $Mg_3(Sb, Bi)_2$ systems and the composition of interests $Mg_{3,2}(Sb_{0,3-0.5y}Bi_{1,7-0.5y})Te_y$ (y = 0, 0.002, 0.005, 0.0075, and 0.01): (a) electronic conductivity, (b) Seebeck coefficient, (c) power factor, (d) Hall carrier concentration and Hall carrier mobility, (e) The Hall mobility for *n*-type $Mg_{3+\delta}Sb_{2-x}Bi_x$ -based samples [22,67,76,77] (whose carrier concentration ranges from 3 to $5 \times 10^{19} \text{ cm}^{-3}$) depends on *x* in $Mg_{3+}Sb_{2-x}Bi_x$ -based *n*-type TE materials, as simulated by the SKB model. The blue scatters represent experimental results from early works, while the black solid line represents the simulated result by the SKB model. The black dashed line indicates the extrapolated result due to the failure of the SKB model when the Eg approaches zero or becomes negative Additionally, the gray dashed line represents the simulated result where only the alloy scattering effect is considered, and the band sharpening effect is absent. (f) *PF* at room temperature, compared with other $Mg_3(Sb, Bi)_2$ materials, Refs. [22,23,70,76,78–86]. (g) The simulated cooling power ($T_C = 300 \text{ K}$, $\Delta T = 5 \text{ K}$) of the unicouple devices where commercial Bi_2Te_3 is selected as the *p*-type counterpart (see Fig. S10 for the TE performance of the commercial Bi_2Te_3 [24]) of the advanced $Mg_3(Sb, Bi)_2$ materials for cooling application [23,24,58,59]. The blue scatters represent the cooling-power density (Q_C) under the optimized condition (see Table S3 for the optimized current and the optimized An/Ap values for each *n*-type material). (h) Thermal conductivity and (i) *ZT* value of each sample with different Te doping concentrations.

effects contributed by electrons and holes. Again, the zero-gap feature is confirmed when the Sb:Bi ratio is near 0.3:1.7. As the Sb:Bi ratio and the actual Mg content are always close to the theoretical value (see Fig. S6 for the nominal Sb:Bi ratio and the actual Sb:Bi ratio for different compositions [23,27,64–70]; see Fig. S7 for the ratio between the actual Mg content and the nominal Mg content [23,27,64–72]), samples with different Sb/Bi compositions can be seen as ideal solid solutions with continuous physical properties. The Hall

mobility depended on the composition fitted by the SKB model [Fig. 8(e)], where the acoustic phonon scattering mechanism with the deformation potential theory and the alloy scattering mechanism are considered as the main scattering processes [73] The SKB model instead of the SPB model is applied here because of the failure of the SPB model in the simulation of Mg₃Bi₂, which is rooted in the near-linear band nature of Mg₃Bi₂ [74] (see Fig. S8 for the comparison between the SPB model and the SKB model).

In the formula of the relaxation time for the alloy scattering, the composition-related denominator indicates a parabolic varied trend as the alloying content is increased. As shown in Fig. 8(e) by the gray dashed line, if Eg manipulation presents no effect on Hall mobility, the Hall mobility versus composition curve will present as a "U" shape [44]. In sharp contrast, the mobility-composition curve shows great growth in the Bi-rich range, which is caused by the band-sharpening effect. The drift mobility where the band anisotropic factor is excluded is also calculated and shows a similar tendency (see Fig. S9 for the calculated Hall factor and the drift mobility). Mg₃SbBi alloy whose mobility sacrifices the most from the alloy scattering also shows higher carrier mobility than Mg₃Sb₂, based on the simulation result and previous reports. By fitting the experimental Hall mobility, the alloy scattering potential (E_{all}) of 1.5 eV is obtained, which is in the typical range as reported before [75]. The fact that alloying can perform as a method to increase carrier mobility goes against our common sense, but it reflects the effectiveness of Eg narrowing as well.

Our work obtained a remarkable Hall mobility $\mu_{\rm H} = 264.4 \,{\rm cm}^2 \,{\rm V}^{-1} \,{\rm s}^{-1}$ compared with other high performance Mg₃(Sb, Bi)₂-based TE materials. Thanks to the optimistically high carrier mobility, a decent TE performance is achieved when a preferred carrier concentration is realized for Mg_{3,2}(Sb_{0,3-0,5y}Bi_{1,7-0,5y})Te_y, y = 0.0075 sample [Fig. 8(e)], whose PF value is recorded as high $[PF_{rt} =$ $38.5 \,\mu\text{W}\,\text{cm}^{-1}\,\text{K}^{-2}$, Fig. 8(f)]. It can be seen from Fig. 8, for heavily doped samples (y > 0.005), since the major carrier concentration is high enough, that the side effect of intrinsic excitation in the high-temperature range is not significant. This means no evident deterioration in the high-temperature Seebeck coefficient [see Fig. S5(d) for the temperaturedependent Seebeck coefficient and the Hall factor of the y = 0.0075 sample; see also Figs. S5(e) and S5(f) for the contribution of both the major carrier and the minor carrier on the carrier concentration and the Seebeck coefficient]. For this optimized composition concerning the high PF, a compromise is reached by tuning Eg to nearly zero but avoiding the band overlapping, leading to a promising application on high cooling density under small ΔT for room-temperature precise temperature control [87]. The simulated cooling power of the unicouple devices using different n legs and commercial *p*-Bi₂Te₃ is given in Fig. 8(g). Here, for small ΔT , for example, 5 K, materials with prominent PF can outperform those with higher ZT. An advantage over other highperformed Mg₃(Sb, Bi)₂-based materials in cooling density

is achieved in the simulated performance of the unicouple cooling device constructed by $Mg_{3,2}(Sb_{0,3-0.5y}Bi_{1,7-0.5y})Te_y$ (y = 0.0075) with commercial p-Bi₂Te₃, whose performance is also comparable to the commercial Bi₂Te₃-based unicouple device. Due to the optimized carrier concentration, the contribution of the bipolar thermal conductivity is moderate (see Fig. S11 for the calculated result of the bipolar thermal conductivity). Regarding the final *ZT*, a decent value of 0.63 [Figs. 8(h) and 8(i)] at room temperature can be achieved in zero band-gap materials, which is beyond conventional thinking.

IV. CONCLUSION

To optimize the functional properties of semiconductor devices, it is essential to adjust Eg to an appropriate range. The potential of tuning Eg has been discussed in this work by comparing three typical TE isoelectronic alloys, (Sb, Bi)₂Te₃, Pb(Se,Te), and Mg₃(Sb, Bi)₂. The SOC effect and the lattice constant are found to be two main factors affecting the variation trend of Eg during the alloying process. Utilizing this manipulation can enable a remarkable change of Eg for TE material designing. Taking Mg₃(Sb, Bi)₂-based TE material as a typical example, a high room-temperature *PF* is obtained (\sim 38.5 µW cm⁻¹ K⁻²) in $Mg_{3.2}(Sb_{0.3-0.5y}Bi_{1.7-0.5y})Te_y$, y = 0.0075 sample. The superior performance is attributed to a high carrier mobility ($\mu_{\rm H} =$ $264.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) due to a sharpened conduction-band edge simultaneously without the deterioration of Seebeck coefficients in semimetal Mg3Bi2. Our work provides an understanding of Eg variation in isoelectronic alloys and opens up alternative perspectives for the design of highperformance TE materials.

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