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# The manipulation of substitutional defects for realizing high thermoelectric performance in Mg<sub>3</sub>Sb<sub>2</sub>-based Zintl compounds<sup>†</sup>

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The introduction of point defects by extrinsic doping is an effective way to optimize the carrier concentration. Here, we show theoretically and experimentally that Pr is a more effective dopant than Te in Mg<sub>3</sub>Sb<sub>2</sub>. Using first-principles defect calculations, the predicted highest carrier concentration with Pr doping at 725 K can be up to ~9.3 × 10<sup>19</sup> cm<sup>-3</sup>, consistent with our experimental measurements. In addition, the point defects introduced by Pr substitution on the Mg sites lead the lattice thermal conductivity to be reduced to as low as 0.429 W m<sup>-1</sup> K<sup>-1</sup>. By optimizing the Pr doping concentration, Mg<sub>3.2</sub>Pr<sub>0.02</sub>Sb<sub>1.5</sub>Bi<sub>0.5</sub> exhibits a peak *zT* value of 1.70 at 725 K.

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## 1. Introduction

Thermoelectric devices, which can enable the direct conversion of heat energy into electrical energy, exhibit excellent development potential for applications in waste heat recovery and power generation.<sup>1-3</sup> The widespread use of these promising devices requires high-performance thermoelectric materials. The performance of a thermoelectric material is determined by the dimensionless figure of merit  $zT = S^2 \sigma T/\kappa$ , in which S,  $\sigma$ , Tand  $\kappa$  are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively.<sup>4-6</sup> The total thermal conductivity  $\kappa$  comprises two main parts: electronic thermal conductivity  $\kappa_{ele}$  and lattice thermal conductivity  $\kappa_{lat}$ .<sup>7,8</sup> Accordingly, the enhancement of the thermoelectric conversion efficiency can be realized by a combination of an excellent power factor ( $S^2 \sigma$ ) and a poor thermal conductivity.

Mg<sub>3</sub>Sb<sub>2</sub>-based Zintl compounds are a class of earthabundant, non-toxic and low-cost thermoelectric materials for mid-temperature applications, and have attracted considerable attention as promising candidates for improving the thermoelectric conversion efficiency.<sup>9-11</sup> In the past few decades, Mg<sub>3</sub>Sb<sub>2</sub>-based thermoelectric materials have been almost exclusively synthesized as a p-type semiconductor with a poor electrical transport property, which limits the overall

<sup>b</sup>Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, People's Republic of China † Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ta06889a thermoelectric efficiency despite the relatively low thermal conductivity.<sup>12-15</sup> Recently, an n-type Mg<sub>3</sub>Sb<sub>2</sub>-based compound with a peak *zT* of 1.51 at 716 K was synthesized by Tamaki *et al.*<sup>16</sup> by introducing extra Mg and Te doping, this was followed by reports of similar results from multiple groups.<sup>17-21</sup> Under Mg-rich growth conditions, p-type Mg<sub>3</sub>Sb<sub>2</sub> can be converted into the n-type with a relatively low intrinsic carrier concentration (~10<sup>18</sup> cm<sup>-3</sup>), and extrinsic doping with Te can lift the Fermi level up to the conduction band, resulting in a significant enhancement of the electron concentration (~10<sup>19</sup> cm<sup>-3</sup>).<sup>22</sup>

As the thermoelectric parameters (S,  $\sigma$  and  $\kappa$ ) are heavily interdependent on the carrier concentration, the maximum thermoelectric performance can be obtained by the optimization of the carrier concentration.<sup>23</sup> The predicted optimal carrier concentration is ~10<sup>20</sup> cm<sup>-3</sup> for the Mg<sub>3</sub>Sb<sub>2</sub>-based Zintl compounds.<sup>24-26</sup> Given that the electron (hole) flow, phonon flow and their intercoupling are closely related to the defects in a material, doping can be used to improve the carrier concentration in thermoelectrics. Therefore, a detailed assessment of the doping behavior of extrinsic dopants is necessary for the screening of effective dopants to increase the carrier concentration and enhance the thermoelectric performance.

Herein, we demonstrate theoretically and experimentally that praseodymium acts as a stronger electron donor in Mg<sub>3</sub>Sb<sub>2</sub>-based materials. Using first-principles defect calculations, the maximal achievable free carrier concentration of Pr doping from 300 to 725 K under Mg-rich conditions is located in the range of  $10^{19}$  to  $10^{20}$  cm<sup>-3</sup>, which coincides with the order of magnitude in our experimental measurements. By optimizing the Pr doping concentration, a peak *zT* value of 1.70 at 725 K can be obtained in Mg<sub>3.2</sub>Pr<sub>0.02</sub>Sb<sub>1.5</sub>Bi<sub>0.5</sub>, suggesting Pr-doped Mg<sub>3.2</sub>Sb<sub>1.5</sub>Bi<sub>0.5</sub> as a potential thermoelectric candidate.

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### 2. Methods

#### 2.1 Sample synthesis

High-purity powders of magnesium (Mg, 99.5%, Aladdin Co., Ltd.), antimony (Sb, 99.5%, Aladdin Co., Ltd.), bismuth (Bi, 99.9%, Aladdin Co., Ltd.), praseodymium (Pr, 99.9%, Aladdin Co., Ltd.) and tellurium (Te, 99.99%, Aladdin Co., Ltd.) were weighed according to the compositions of  $Mg_{3,2}Pr_xSb_{1,5}Bi_{0,5}$  (x = 0.01, 0.02, 0.03 and 0.04) and Mg<sub>3.2</sub>Sb<sub>1.48</sub>Bi<sub>0.48</sub>Te<sub>0.04</sub>. All of the weighed powders were loaded into a zirconia ball milling jar and then sealed inside a glove box with an oxygen level below 0.5 ppm. The starting materials were ball milled in a planetary ball mill BM40 (Beijing Grinder Instrument Co., Ltd.) with a rotational speed of 360 rpm for 4.5 hours by repeating a sequence of 15 min milling followed by a 5 min pause. The direction of rotation changed after each pause. The ball milled powders were loaded into a graphite die in a glove box and then sintered using spark plasma sintering (SPS, SPS-211LX, Fuji Electronic Industrial Co., Ltd.). The sintering was conducted in a vacuum at 650 °C for 5 min under a pressure of 50 MPa.

#### 2.2 Structural characterization

The phase purity of all SPS-pressed pellets was examined using X-ray diffraction (XRD) with Cu K $\alpha$  ( $\lambda = 1.5406$  Å) radiation on a Bruker D8 diffractometer at room temperature and the lattice parameters were obtained using Jade software. The microstructural and composition analyses of the high-performance sample with x = 0.02 were characterized using a scanning electron microscope (SEM, FEI Quanta 200F) equipped with an energy dispersive spectroscope.

#### 2.3 Thermoelectric transport property measurements

The 4-point probe van der Pauw technique with a magnetic field of 1.5 T was used for measurement of both the resistivity ( $\rho$ ) and the Hall coefficient  $(R_{\rm H})$ . The Hall carrier concentration  $(n_{\rm H})$  was calculated using  $1/eR_{\rm H}$  and the Hall carrier mobility ( $\mu_{\rm H}$ ) was estimated using  $R_{\rm H}/\rho$ . For comparison, the electrical transport properties, including the electrical resistivity and the Seebeck coefficient, were also measured for high thermoelectric performance samples using a ZEM-3 (Ulvac Riko, Inc.) under a helium atmosphere from 300 to 725 K. Thermal conductivity was calculated using  $\kappa = dDC_p$ , in which d, D, and  $C_p$  are the density of the sample, thermal diffusivity and heat capacity, respectively. The thermal diffusivity (D) was measured using a laser flash method with a Netzsch LFA-457 instrument under a nitrogen atmosphere. The heat capacity  $(C_p)$  from 300 to 725 K was obtained from a study previously published by Agne et al. (see the Table S1<sup>†</sup> for  $C_p$  data).<sup>27</sup> The sample density (d) was measured using the Archimedes method.

#### 2.4 Density functional theory calculations

All first-principles calculations based on the density functional theory (DFT) were carried out using the projector augmented wave (PAW) method as implemented in the Vienna *ab initio* simulation package (VASP).<sup>28,29</sup> Using the optimized crystal structure

parameters from our previous work,<sup>25</sup> the electronic structure of Mg<sub>3</sub>Sb<sub>2</sub> was calculated using the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional.<sup>30</sup> To correctly predict the energy of the point defect, the defect calculations were conducted in a  $2 \times 2 \times 2$  supercell with 40 atoms using the HSE06 functional. A  $2 \times 2 \times 1$   $\Gamma$ -centered k mesh was used for the total energy calculation. A plane-wave cutoff energy of 400 eV along with an energy convergence criterion of  $10^{-4}$  eV was employed. For the optimization of the defect structure, the lattice parameters were fixed at the optimized values of the perfect supercell, while the atomic positions were fully relaxed into their equilibrium positions.

The formation energy of a point defect D in a charge state q can be calculated as follows:<sup>31</sup>

$$E_{\rm f}(D^q) = E_{\rm tot}(D^q) - E_{\rm tot}({\rm Mg}_3{\rm Sb}_2) - \sum_i n_i \mu_i + q(E_{\rm V} + E_{\rm F}) + E_{\rm cor}$$
(1)

in which  $E_{tot}(D^q)$  and  $E_{tot}(Mg_3Sb_2)$  are the total energy derived from a supercell calculation with a defect D in a charged state qand the total energy of the perfect  $Mg_3Sb_2$  supercell, respectively.  $n_i$  indicates the number of atoms of a species i that have been added to  $(n_i > 0)$  or removed from  $(n_i < 0)$  the perfect supercell to form the defect, and  $\mu_i$  represents the corresponding chemical potential of the constituent i.  $E_V$ ,  $E_F$  and  $E_{cor}$  are the valence band maximum (VBM) values of the perfect  $Mg_3Sb_2$  supercell, the Fermi level measured from the energy of the VBM and a correction term to align the reference potential of the defect supercell with that of the perfect supercell, respectively.

The elemental chemical potential  $\mu_i$  depends on the reference elemental phase and can be expressed as  $\mu_i = \mu_i^0 + \Delta \mu_i$ , in which  $\mu_i^0$  is the reference chemical potential of the constituent *i* in the standard elemental condition and  $\Delta \mu_i$  is the deviation from the reference chemical potential.  $\Delta \mu_i = 0$  represents the *i*-rich condition. Under equilibrium growth conditions, the chemical potential must maintain a stable Mg<sub>3</sub>Sb<sub>2</sub> compound:

$$3\Delta\mu_{\rm Mg} + 2\Delta\mu_{\rm Sb} = \Delta H_{\rm f}({\rm Mg}_3{\rm Sb}_2) \tag{2}$$

with  $\Delta \mu_{Mg} \leq 0$  and  $\Delta \mu_{Sb} \leq 0$  to avoid precipitation of the elements, in which  $\Delta H_f(Mg_3Sb_2)$  is the formation energy of  $Mg_3Sb_2$ . To avoid the precipitation of secondary phases between the dopant A (A = Pr and Te) and the host elements B (B = Mg and Sb), the chemical potentials are further limited by:

$$m\Delta\mu_{\rm A} + n\Delta\mu_{\rm B} \le \Delta H_{\rm f}({\rm A}_m{\rm B}_n) \tag{3}$$

with  $\Delta \mu_A \leq 0$  to avoid precipitation of the dopant, and in which  $\Delta H_f(A_m B_n)$  is the formation energy of  $A_m B_n$ .

The concentration of a defect D in the charge state q can be calculated as follows:<sup>32</sup>

$$c(D^q) = N_{\text{site}} \exp\left(-\frac{E_{\text{f}}(D^q)}{k_{\text{B}}T}\right)$$
(4)

in which  $N_{\text{site}}$ ,  $k_{\text{B}}$  and T are the concentration of the possible defect sites, the Boltzmann constant and the absolute temperature, respectively. The free carrier concentrations of the electrons (n) and holes (p) are obtained from the Fermi–Dirac distribution as:<sup>32</sup>

$$n = \int_{E_{\rm C}}^{+\infty} g(E) f(E; E_{\rm F}, T) \mathrm{d}E$$
(5)

$$p = \int_{-\infty}^{E_{\rm V}} g(E) [1 - f(E; E_{\rm F}, T)] \mathrm{d}E$$
 (6)

in which  $E_V$  is the valence band maximum,  $E_C$  is the conduction band minimum, g(E) is the density of states of the ideal host cell and  $f(E;E_F,T)$  is the Fermi–Dirac distribution given by:

$$f(E; E_{\rm F}, T) = \frac{1}{\exp\left(\frac{E - E_{\rm F}}{k_{\rm B}T}\right) + 1}$$
(7)

The defect and carrier concentrations must satisfy the charge neutrality:<sup>32</sup>

$$\sum_{i} q_i c_i(D^q) + \mathbf{p} - \mathbf{n} = 0 \tag{8}$$

in which the index i corresponds to the charged defect.

The lower limit of the lattice thermal conductivity was calculated from Cahill's expression:<sup>33</sup>

$$\kappa_{\min} = \frac{1}{2} \left[ \left( \frac{\pi}{6} \right)^{1/3} \right] k_{\rm B}(V)^{-2/3} (2\nu_{\rm t} + \nu_{\rm l}) \tag{9}$$

in which *V* is the average volume per atom, and  $v_t v_l$  are the traverse and longitudinal elastic wave velocity, respectively. The input parameters for this calculation are shown in Table S2.† In this calculation, the generalized gradient approximations (GGA) of Perdew, Burke, and Ernzerhof (PBE) were used for the exchange functional.<sup>34</sup>

## 3. Results and discussion

The Zintl compound Mg<sub>3</sub>Sb<sub>2</sub>, crystallized in an inverse  $\alpha$ -La<sub>2</sub>O<sub>3</sub>type (space group:  $P\bar{3}m1$ ) crystal structure, has two Mg Wyckoff sites denoted by Mg1 and Mg2, and one Sb Wyckoff site. A favorable interstitial position is at (0, 0, 0.5) marked by the dotted circles shown in Fig. 1a. The simulated electronic structures of Mg<sub>3</sub>Sb<sub>2</sub> using the HSE06 functional are presented in Fig. 1b and S1,† and the calculated band gap of 0.51654 eV is comparable to the previously reported values calculated using the TB-mBJ potential.<sup>25,26</sup>

Fig. 2a plots the defect formation energies for an n-type doping of Mg<sub>3</sub>Sb<sub>2</sub> with Te and Pr under Mg-rich condition, as a function of the Fermi level. The slope of the curve corresponds to the charge state of each defect. The positive and negative slopes represent the donor and acceptor defects, respectively. Te is an effective n-type dopant in Mg<sub>3</sub>Sb<sub>2</sub>.<sup>16,22</sup> The lower defect formation energies observed for the substitutional donor defect Pr<sub>Mg1</sub> compared to Te<sub>sh</sub> suggest that Pr doping is more stable and easier to form, therefore, Pr is a stronger electron donor in Mg<sub>3</sub>Sb<sub>2</sub>. The important low-energy defects, including Mg vacancies on both Mg sites (V<sub>Mg1</sub> and V<sub>Mg2</sub>), Mg interstitials  $(Mg_I)$  and Pr substitution on the Mg sites  $(Pr_{Mg1})$ , determine the Fermi level of the Pr-doped Mg<sub>3</sub>Sb<sub>2</sub>. As the donor defect Pr<sub>Mg1</sub> possesses a lower defect formation energy compared to the acceptor defects VMg1 and VMg2, the Fermi level is pinned inside the conduction band (see Fig. 2a and S2<sup>†</sup>), which indicates the n-type conduction of Pr-doped Mg<sub>3</sub>Sb<sub>2</sub>. In addition, the higher defect concentration of Pr<sub>Mg1</sub> demonstrates that the n-type carriers of Pr-doped Mg<sub>3</sub>Sb<sub>2</sub> are predominantly contributed by the point defect introduced by Pr substitution on the Mg sites as shown in Fig. 2b.

The predicted n-type carrier concentrations from 300 to 725 K under Mg-rich conditions are in the range of  $10^{19}$  to  $10^{20}$  cm<sup>-3</sup>, which coincides with the order of magnitude in the experimental measurements of Pr-doping (Fig. 3a). The predicted carriers of Pr-doping at 725 K are ~9.3 ×  $10^{19}$  cm<sup>-3</sup>, more than three times higher than the value of ~2.8 ×  $10^{19}$  cm<sup>-3</sup> for Te-doping (see Fig. S3b†). When comparing samples with the same nominal concentration of dopant, the carrier concentrations of Mg<sub>3.2</sub>Pr<sub>0.04</sub>Sb<sub>1.5</sub>Bi<sub>0.5</sub> and Mg<sub>3.2</sub>Sb<sub>1.48</sub>Bi<sub>0.48</sub>Te<sub>0.04</sub> at 691 K are measured to be ~9.39 ×  $10^{19}$  cm<sup>-3</sup> and ~4.2 ×  $10^{19}$  cm<sup>-3</sup> respectively. These results clearly indicate that Pr is a more effective n-type dopant leading to better thermoelectric properties in the Mg<sub>3</sub>Sb<sub>2</sub>-based materials.

Fig. 3b presents the temperature-dependent Hall mobility of the n-type  $Mg_{3.2}Pr_xSb_{1.5}Bi_{0.5}$  samples. As the temperature increases, the mobility shows an increasing trend at lower temperatures and a decreasing trend at higher temperatures, therefore, the mobility can be divided into two different regions, that is, the ionization scattering dominated region (below 450 K) and the acoustic phonon scattering dominated region (above 550 K). Below 450 K,  $\mu \propto T^p$  (1.7  $\leq p \leq 4.3$ ) shows ionized



Fig. 1 (a) Crystal structure and (b) band structure of Mg<sub>3</sub>Sb<sub>2</sub>.





Fig. 2 (a) Calculated defect formation energies of charged point defects as a function of the Fermi level in  $Mg_3Sb_2$  for n-type doping under Mgrich conditions. Doping with Te (dark yellow line) and Pr (orange lines), the native defects contain the Mg1 vacancy (magenta line), the Mg2 vacancy (olive line) and the Mg interstitial (blue line). The green vertical line represents the Fermi level at 300 K with Pr doping. The solid and dashed lines represent the Mg1 substitution and Mg2 substitution, respectively. (b) Temperature dependence of the defect concentration for ntype Pr-doped  $Mg_3Sb_2$  under Mg-rich conditions.



Fig. 3 (a) The Hall carrier concentration and (b) the mobility of n-type  $Mg_{3,2}Pr_xSb_{1.5}Bi_{0.5}$  samples as a function of temperature. The bold black line represents the predictions of the maximal achievable carrier concentration of n-type Pr-doped  $Mg_3Sb_2$  under Mg-rich conditions by DFT calculations. The olive squares, orange circles, blue diamonds and magenta triangles are the experimental values of  $Mg_{3,2}Pr_xSb_{1.5}Bi_{0.5}$  (x = 0.01, 0.02, 0.03 and 0.04) samples from this work.

impurity scattering in the Mg<sub>3.2</sub>Pr<sub>x</sub>Sb<sub>1.5</sub>Bi<sub>0.5</sub> samples. Above 550 K,  $\mu \propto T^{-1.3}$  indicates that the acoustic phonon scattering mechanism is dominant in the electronic transportation.

The XRD patterns of the SPS-pressed  $Mg_{3.2}Pr_xSb_{1.5}Bi_{0.5}$  (x = 0.01-0.04) pellets are displayed in Fig. 4. All diffraction peaks of the samples are well indexed to the  $\alpha$ -Mg\_3Sb\_2 with a space group of  $P\bar{3}m1$  (Standard Identification Card, JCPDS 65-9363). Owing to the very small amount of the Pr dopant, the change in the lattice parameters is negligible with Pr doping (Fig. S4†). All samples show a relative density larger than 95% (Table S3†). The SEM image of the fractured cross section of the Mg\_{3.2}-Pr\_{0.02}Sb\_{1.5}Bi\_{0.5} sample (Fig. 5a) demonstrates that the sample is dense with no obvious cracks or holes, which is in accordance with the density measurements. To further confirm the phase compositions, the EDS elemental mapping images of the fractured cross section of the fractured cross section of the ractured cross section of the ractured cross section of the gase of the fractured cross for holes, which is in accordance with the density measurements. To further confirm the phase compositions, the EDS elemental mapping images of the fractured cross section for the fractured cross for the fractured cross section



Fig. 4 XRD patterns of the  $Mg_{3,2}Pr_xSb_{1,5}Bi_{0,5}$  (x = 0.01, 0.02, 0.03 and 0.04) samples.



Fig. 5 (a) SEM image and (b)–(f) SEM–EDS elemental mapping images of a fractured cross section of the  $Mg_{3,2}Pr_{0.02}Sb_{1.5}Bi_{0.5}$  sample.

the elements (Mg, Sb, Bi and Pr) are present and distributed almost uniformly throughout the sample.

The electrical resistivity of all Pr-doped samples as a function of the temperature are shown in Fig. 6a. It is clear that the electrical resistivity decreases with the increasing Pr content. This phenomenon is mainly due to the increase of the carrier concentration as displayed in Fig. 3a. Fig. 6b presents the

temperature-dependent Seebeck coefficient for all samples. As the Seebeck coefficient is negatively correlated with the carrier concentration, an obvious decrease in the absolute values of the Seebeck coefficient with increasing Pr content is observed. The Seebeck coefficient is related not only to the carrier concentration, but also the density of states effective mass. To study whether Pr doping at the Mg sites has an influence on the conduction band, a Pisarenko plot at room temperature is shown in Fig. 6c in which all of the Pr-doped samples agree well with the simulations. This result indicates that at least at room temperature, the conduction band of Mg<sub>3</sub>Sb<sub>2</sub> is not significantly affected by Pr doping. Combining the electrical resistivity and Seebeck coefficient, Fig. 6d shows the power factor of all of the Mg<sub>3.2</sub>Pr<sub>x</sub>Sb<sub>1.5</sub>Bi<sub>0.5</sub> samples. The power factor increases with the increasing Pr concentration and Mg<sub>3.2</sub>Pr<sub>0.04</sub>Sb<sub>1.5</sub>Bi<sub>0.5</sub> with a carrier concentration of  $\sim 9.4 \times 10^{19}$  cm<sup>-3</sup> at 725 K exhibits a high power factor of 18.6  $\mu$ W cm<sup>-1</sup> K<sup>-2</sup>, which can be explained by the fact that an optimal carrier concentration of  $\sim 10^{20}$  cm<sup>-3</sup> was obtained for the electronic transport properties of the Mg<sub>3</sub>Sb<sub>2</sub>-based Zintl compounds.

Fig. 7 presents the thermal transport properties as a function of the temperature for the n-type  $Mg_{3,2}Pr_xSb_{1.5}Bi_{0.5}$  samples. Fig. 7a shows a decrease in the total thermal conductivity with



**Fig. 6** (a) The electrical resistivity and (b) the Seebeck coefficient of n-type  $Mg_{3.2}Pr_xSb_{1.5}Bi_{0.5}$  samples as a function of the temperature. (c) A Pisarenko plot at room temperature. (d) The temperature dependence of the power factor of the n-type  $Mg_{3.2}Pr_xSb_{1.5}Bi_{0.5}$  samples. In (c), the blue line represents the prediction of the n-type  $Mg_3Sb_2$  using the full DFT band structure calculation from our previous work<sup>25</sup> and the pink line represents the result from a three band model (TBM).<sup>26</sup> The olive squares, orange circles, blue diamonds and magenta triangles are the experimental values for the Pr-doped  $Mg_{3.2}Sb_{1.5}Bi_{0.5}$  samples from this work.



Fig. 7 The temperature dependence of the (a) total thermal conductivity, (b) Lorenz number, (c) electronic thermal conductivity and (d) lattice thermal conductivity of the n-type Mg<sub>3.2</sub>Pr<sub>x</sub>Sb<sub>1.5</sub>Bi<sub>0.5</sub> samples.

temperature. Increasing the Pr doping concentration is detrimental to the total thermal conductivity. The electronic thermal conductivity can be obtained using the Wiedemann–Franz relationship given by  $\kappa_{\rm e} = LT/\rho$ , in which *L*,  $\rho$  and *T* are the Lorenz number, electrical resistivity and temperature, respectively.<sup>35</sup> Based on a single parabolic band (SPB) model with acoustic phonon scattering, *L* can be given as:<sup>36</sup>

$$L = \left(\frac{k_{\rm B}}{\rm e}\right)^2 \frac{3F_0(\eta)F_2(\eta) - 4F_1^{\ 2}(\eta)}{F_0^{\ 2}(\eta)} \tag{10}$$

in which  $F_n(\eta) = \int_0^\infty \frac{x^n \mathrm{d}x}{1 + \exp(x - \eta)}$  are the Fermi integrals and

 $\eta$  is the reduced chemical potential.  $\eta$  can be derived from the Seebeck coefficient:

$$S = \frac{k_{\rm B}}{\rm e} \left( \frac{2F_1(\eta)}{F_0(\eta)} - \eta \right) \tag{11}$$

The electronic thermal conductivity increases with the amount of doping, which can be ascribed to the enhanced Lorenz number and the reduced electrical resistivity. By subtracting the electronic thermal conductivity from the total thermal conductivity, the temperature dependence of the lattice thermal conductivity data of all Mg<sub>3.2</sub>Pr<sub>x</sub>Sb<sub>1.5</sub>Bi<sub>0.5</sub> samples can be obtained and is shown in Fig. 7d. Clearly, the introduction of the point defect by Pr/Mg substitutions leads to a significant decrease in the lattice thermal conductivity. The slightly higher

lattice thermal conductivity of the sample with Pr content x = 0.04 may be attributed to the existence of an impurity phase which was not found in the XRD results as the nominal amount of Pr is too small to detect. The reduced lattice thermal conductivity of 0.429 W m<sup>-1</sup> K<sup>-1</sup> for the x = 0.03 sample was consistent with Cahill's minimum lattice thermal conductivity. Additionally, the lower minimum lattice thermal conductivity



Fig. 8 The dimensionless figure of merit as a function of temperature for n-type  $Mg_{3,2}Pr_xSb_{1,5}Bi_{0,5}$  samples.

for Pr-doped  $Mg_3Sb_{1.5}Bi_{0.5}$  (0.451 W m<sup>-1</sup> K<sup>-1</sup>) compared to  $Mg_3Sb_{1.5}Bi_{0.5}$  (0.491 W m<sup>-1</sup> K<sup>-1</sup>) further demonstrates that Pr doping is beneficial to the lattice thermal conductivity in  $Mg_3Sb_2$ -based materials (Table S2†).

The dimensionless figure of merit as a function of the temperature for all  $Mg_{3.2}Pr_xSb_{1.5}Bi_{0.5}$  samples is shown in Fig. 8. The introduction of a point defect by Pr substitution on the Mg sites contributes to the high thermoelectric figure of merit ranging from 1.37 to 1.70 at 725 K. Through the optimization of the Pr doping concentration, the  $Mg_{3.2}Pr_{0.02}Sb_{1.5}Bi_{0.5}$  sample exhibits the best thermoelectric performance with a *zT* value of 1.70 at 725 K.

## 4. Conclusions

In this work, we computationally and experimentally investigated the doping behavior of a Pr dopant in Mg<sub>3</sub>Sb<sub>2</sub>-based materials. By using first-principles defect calculations, we found that the Pr element is an effective electron donor to increase the carrier concentration and enhance the thermoelectric performance. The maximal achievable free carrier concentration of Pr doping at 725 K under Mg-rich conditions is close to  $10^{20}$  cm<sup>-3</sup>. Then, we verified this theoretical prediction through experiments. Mg<sub>3.2</sub>Pr<sub>0.04</sub>Sb<sub>1.5</sub>Bi<sub>0.5</sub> with a carrier concentration of ~9.4  $\times 10^{19}$  cm<sup>-3</sup> at 725 K exhibits a high power factor of 18.6  $\mu$ W cm<sup>-1</sup> K<sup>-2</sup>. Furthermore, Mg<sub>3.2</sub>Pr<sub>0.02</sub>Sb<sub>1.5</sub>Bi<sub>0.5</sub> exhibits the best thermoelectric performance, with a *zT* value of 1.70 at 725 K.

## Conflicts of interest

There are no conflicts to declare.

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