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Simultaneous improvement of power factor and thermal conductivity via Ag doping in p-type Mg_3Sb_2 thermoelectric materials

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Mg_3Sb_2 -based Zintl compounds are potential thermoelectric materials for power generation due to the earth-abundant component elements. Pure Mg_3Sb_2 , however, exhibits an intrinsically low p-type carrier concentration at room temperature. Density functional theory calculations of p-type Mg_3Sb_2 suggest that the carrier density can be tuned by doping at the Mg sites without significant modification of the valence bands and the optimal doping concentration is predicted to be $4.0 \times 10^{19} \text{ cm}^{-3}$. Herein we have successfully synthesized Ag-doped Mg_3Sb_2 samples by a one-step spark plasma sintering method. All Ag-doped samples display increased carrier concentration and enhanced Hall mobility relative to the undoped sample, leading to a significant decrease in the electrical resistivity. As a result of simultaneous improvements in power factor and thermal conductivity, the zT values of Ag-doped samples are strongly enhanced; an optimum value of 0.51 at 725 K in $\text{Mg}_{2.985}\text{Ag}_{0.015}\text{Sb}_2$ is achieved, which is a factor of 2.4 larger than the undoped sample. The average zT is estimated to be 0.21 in $\text{Mg}_{2.985}\text{Ag}_{0.015}\text{Sb}_2$, which is superior to the previous report on Na-doped Mg_3Sb_2 . Thus, Ag-doped Mg_3Sb_2 is a promising candidate for intermediate-temperature power generation.

1. Introduction

The development of thermoelectric (TE) technology, which can realize the direct and reversible conversion between heat and electricity using no moving parts, is being driven by the global demand for sustainable energy.¹ The conversion efficiency of TE devices is critically limited by the performance of TE materials, which is determined by the dimensionless figure of merit, $zT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity, and T the absolute temperature. Hence, a combination of high power factor PF ($S^2\sigma$) and low thermal conductivity is desired for good TE materials. However, it is challenging to realize the simultaneous optimization of electrical and thermal transport properties since usually they are strongly coupled with each other. The “phonon glass, electron crystal” concept proposed by Slack² suggests a general and effective strategy to rationalize TE performance. One effective approach to optimize TE performance is to boost the power factor through band structure engineering, e.g. convergence of electronic bands,^{3–6} or modification of the electronic density of states via introducing impurity levels.⁷ Other strategies focus on reducing lattice thermal conductivity through increasing phonon scattering using nano-structuring⁸ and the inclusion of

loosely bound rattlers.⁹

Zintl compounds have been widely studied as a promising class of thermoelectric materials. Typically, Zintl phases consist of electropositive cations (alkali, alkaline-earth, post transition or rare earth elements) that donate electrons to electronegative anions, which in turn form covalent bonds to satisfy valence.¹⁰ Many explored Zintl compounds such as skutterudites¹¹, clathrates¹², and zinc antimonides¹³ exhibit good thermoelectric efficiency. Among them, Mg_3Sb_2 -based Zintl phases have recently received considerable research interest, owing to the nontoxic, earth-abundant, and low-cost nature of the constituent elements, which is also the case for Mg_2Si . N-type Mg_2Si - Mg_2Sn is known for good performance in the medium temperature range; however, p-type counterparts still show poor performance. In addition, Mg_2Si has been studied for a long time, and it shows obstacles for application, e.g. due to phase decomposition at high temperatures. As a relatively new material, the low-cost Mg_3Sb_2 probably could be competing with Mg_2Si as a promising TE material if the performance is fully optimized.¹⁴ Mg_3Sb_2 was first studied with the hope of good TE performance for high temperature applications.¹⁵ However, the TE efficiency of Mg_3Sb_2 is found to be very low because of poor electrical transport properties despite its rationally low thermal conductivity.

Good thermoelectric materials are usually heavily-doped semiconductors¹⁶ with carrier concentrations ranging from 10^{19} to 10^{21} cm^{-3} . Mg_3Sb_2 was reported to be intrinsically p-type¹⁷ with a low carrier concentration on the order of $\sim 10^{17} \text{ cm}^{-3}$. Such a low carrier concentration is much inferior to an optimal value. It is therefore important to tune the carrier

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concentration via doping. Various dopants (Bi¹⁸ and Pb¹⁹ in the Sb sites; Na²⁰, Zn²¹, and Mn¹⁷ in the Mg sites) have been reported to increase the carrier density and the doped samples show enhanced thermoelectric properties at low and high temperatures. To date, there is no systematic study on Ag-doped Mg₃Sb₂. Here we present the considerably enhanced thermoelectric performance in Ag-doped Mg₃Sb₂, achieved by the simultaneous improvement of both power factor and thermal conductivity. Theoretical calculations show a narrow band gap of 0.61 eV for Mg₃Sb₂ and indicate that doping at Mg sites is an effective way to tune the carrier concentration without significant perturbation of the valence band. Ag-doped samples have been successfully synthesized and exhibit enhanced carrier concentration and mobility. A peak zT value of 0.51 at 725 K is realized in Mg_{2.985}Ag_{0.015}Sb₂, suggesting Ag-doped Mg₃Sb₂ as a potential TE candidate.

2. Experimental

2.1 Sample preparation

Ag-doped Mg₃Sb₂ samples were prepared by fast and economic one-step SPS sintering.^{22,23} Stoichiometric amounts of high-purity elements Mg (powder, 99.8%, Alfa Aesar), antimony (powder, 99.5%, SIGMA-ALDRICH CHEMIE GmbH), and silver (powder, 99.99%, SIGMA-ALDRICH CHEMIE GmbH) were used for the synthesis of Mg₃Ag_{3- x} Sb₂ ($0 \leq x \leq 0.4$) samples, and the elements were weighted and mixed in a ball mill mixer (SpectroMill, CHEMPLEX INDUSTRIES, INC) for 15 min. The mixed powders were then loaded into a 12.7 mm diameter graphite die protected by graphite papers, and consolidated by SPS under a pressure of 75 MPa using a SPS-515S instrument (SPS SYNTEX INC, Japan). SPS sintering is conducted in vacuum by heating to 823 K in 11 min followed by 4 min dwell and then heating to 1123 K in 7 min with a 2 min dwell.

2.2 Sample characterization

The SPS-pressed pellets were analyzed by X-ray diffraction (XRD) on a Rigaku Smartlab diffractometer operating at 40 kV and 180 mA with a Cu K α_1 radiation source. The microstructure and composition analysis were studied by scanning electron microscopy (FEI Nova NanoSEM 600) equipped with energy dispersive spectroscopy (EDS). The actual compositions of all the samples measured by SEM-EDS are shown in Table S1. This table shows that the actual Mg contents are slightly lower than the nominal values, indicating that the Mg evaporation during SPS pressing results in the Mg deficiency. But the Mg deficiency might be conducive to the enhancement of p-type performance. In addition, due to the very low Ag doping levels, the actual Ag contents of Ag-doped samples by SEM-EDS show relatively large uncertainties and are nonlinear with respect to the nominal contents. However, the quantification results confirm that Ag does exist in the doped samples. High resolution transmission electron microscopy (HRTEM) images were obtained on a FEI TALOS F200A.

Temperature-dependent electrical resistivity and Hall coefficient were measured on an in-house system using the *Van der Pauw* method under a magnetic field of 1.25 T.²⁴ The SPS-pressed pellets were annealed by running the resistivity measurements during both heating and cooling for 4 cycles. After the first cycle the resistivity measurements of all pellets are consistent for the repeated heating and cooling measurements (one example shown in Fig. S1[†]). The Seebeck coefficients were then measured from room temperature to 725 K on an in-house system which is similar to the one reported by Iwanaga et al.²⁵ Resistivity and Seebeck coefficient of all samples show hysteresis during heating and cooling (Fig. S2[†]). The hysteresis of transport property is consistent upon several repeated heating and cooling measurements (Fig. S1[†]). The good repeatability indicates that the hysteresis in the sample is more likely caused by reversible processes. For convenience the heating curve of the final cycle of electrical transport property is used in the main text. There will be a follow-up study on the structures, which might explain the reason of hysteresis.

A Netzsch LFA 457 was used to measure the thermal diffusivity up to 725 K (Fig. S3[†]). The thermal conductivity was calculated using $\kappa = DdC_p$, where d is the density of sample, D is the thermal diffusivity, and C_p is the heat capacity. The density of the as-synthesized pellets was measured by the Archimedes method (Table S2). C_p was estimated according to Dulong-Petit relation with $C_p = 3NR$, where N is the atom number per formula unit and R is the gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The estimated uncertainties in the electrical resistivity, Seebeck coefficient and thermal diffusivity are 5%, 5% and 7%, respectively, and the combined uncertainty for zT is ~20%. After all measurements, Mg₃Ag_{3- x} Sb₂ ($x = 0.015$) pellet was then cut through the center of the cylinder along the SPS-pressed direction. Scanning Seebeck coefficient map of the cross section of this sample was measured by a potential Seebeck microprobe (PSM) from PANCO²⁶ (Fig. S4[†]).

2.3 Theoretical calculations

Density Functional Theory (DFT) calculations were carried out using the projector-augmented wave (PAW) method²⁷ as implemented in the Vienna *ab initio* simulation package (VASP).²⁸ The crystal structure parameters including lattice constants and the internal coordinates of Mg₃Sb₂ were relaxed using HSE06 functional.²⁹ The plane-wave energy cutoff was set at 400 eV, and a 6 $\times$ 6 $\times$ 4 Monkhorst-Pack k mesh was used for crystal structure optimization. A 12 $\times$ 12 $\times$ 8 Monkhorst-Pack k mesh was used for electronic structure calculations. An energy convergence criterion of 10^{-4} eV and a Hellmann-Feynman force convergence criterion of 0.01 eV $\text{\AA}^{-1}$ were adopted. Electronic structure calculations including spin orbit coupling were implemented using the TB-mBJ potential^{30,31} to obtain accurate band gaps. Transport property calculations include spin orbit coupling were carried out using a full-potential linear augmented plane-wave plus local orbitals method as implemented in the Wien2k³² code. TB-mBJ potential³⁰ was used. The plane wave cut-off parameter $R_{\text{MT}}K_{\text{max}}$ was set to 9 and the corresponding Brillouin zone was

sampled by a very dense $36 \times 36 \times 24$ k mesh to ensure well-converged transport properties. Electrical transport properties were then calculated by combining the *ab initio* band structure calculations and the Boltzmann transport theory under the constant carrier relaxation time approximation as implemented in the BoltzTraP code.³³

3. Results and Discussion

3.1. Crystal structure and electronic structure

Fig. 1 Crystal structure of layered Mg_3Sb_2 Zintl compound. Mg1 and Mg2 represent the Mg atoms in the Mg^{2+} monolayer and the $[\text{Mg}_2\text{Sb}_2]^{2-}$ layer, respectively.

The Zintl compound Mg_3Sb_2 crystallizes in the layered La_2O_3 -type structure, and can be described as trigonal monolayers of Mg^{2+} cations in the *a-b* plane separating $[\text{Mg}_2\text{Sb}_2]^{2-}$ covalently bound slabs (see Fig. 1).¹⁰ According to the Zintl concept, the Mg^{2+} cations in the monolayers donate electrons to the covalently bonded $[\text{Mg}_2\text{Sb}_2]^{2-}$ anion framework. In Zintl compounds, both ionic and covalent bonds are typically required, where the latter is favorable to maintain reasonable carrier mobility. However, Mg_3Sb_2 shows low mobility due to the strongly polar covalent bonding of $[\text{Mg}_2\text{Sb}_2]^{2-}$ framework.³⁴

Straightforward applications of density functional theory (DFT) using the conventional LDA³⁵ or GGA³⁶ functional usually result in underestimation of the band gaps. Hence, the TB-mBJ potential^{30,31} is used here for more accurate band gap calculations. This method has been successfully applied in many small band gap semiconductors.^{4,37,38} The calculated band structure of Mg_3Sb_2 is shown in Fig. 2a. Mg_3Sb_2 exhibits a small indirect band gap of 0.61 eV, which agrees well with the previous reports.^{4,37} The valence band maximum is located at the Γ point, while the conduction band minimum is at the K point. The electronic transport of p-type Mg_3Sb_2 is closely related to the electronic bands at the valence band maximum. The Γ valence band at the band edge is a relatively light band originating from the p_z orbitals of Sb; whereas there is a secondary Γ band located 0.29 eV below the top valence band and this relatively heavy secondary band is mainly contributed by the $p_{x,y}$ orbitals of Sb.⁴ Previous work has shown how p-type transport performance of Mg_3Sb_2 can be rationalized through manipulating the relative energies of the $p_{x,y}$ and p_z orbitals to realize high orbital degeneracy.⁴ Here we focus on tuning the carrier density to optimize p-type transport properties without significantly changing the valence bands.

The density of states (DOS) of Mg_3Sb_2 (Fig. 2b) elucidates that the near-edge valence bands are primarily composed of Sb *p* states. Therefore, tuning p-type carrier density by doping

at the Mg sites is likely to have only a minor effect on the valence bands. The rigid band approximation (RBA) can be used to describe the transport properties of Ag-doped Mg_3Sb_2 . Under the RBA, the band structure of the host is assumed to be unchanged with doping, while only the Fermi level varies with carrier concentration and temperature. As a result of the small DOS at the top of valence bands, the Fermi level quickly moves down the top valence band with increasing p-type doping concentration. At room temperature, the secondary Γ valence band can be reached as the hole doping concentration approaches $\sim 4 \times 10^{20} \text{ cm}^{-3}$.

Fig. 2 (a) Calculated band structure of Mg_3Sb_2 . (b) Calculated total and partial DOS of Mg_3Sb_2 . Mg1 and Mg2 represent the Mg atoms in the Mg^{2+} monolayer and the $[\text{Mg}_2\text{Sb}_2]^{2-}$ layer, respectively.

3.2 X-ray diffraction analysis

The X-ray diffraction patterns of the SPS-pressed $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ ($0 \leq x \leq 0.025$) pellet samples are shown in Fig. 3, and can be indexed to the $\alpha\text{-Mg}_3\text{Sb}_2$ with a space group of $P\bar{3}m1$ (PDFICSD #165386).³⁹ The low intensity impurity reflection observed in the $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ ($x=0.015$) sample pattern was assigned to Sb (ICSD #64695), which is likely to arise from the evaporation of Mg during high-temperature SPS sintering. Due to the small amount of Ag dopants, the change in the lattice parameter is negligible with Ag doping (See Fig. S5†).

Fig. 3 PXRD patterns for various $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ ($0 \leq x \leq 0.025$) samples.

3.3 Scanning and transmission electron microscopy investigation

Fig. 4 (a) SEM image of the cross-section and (b) high resolution TEM image of $\text{Mg}_{2.985}\text{Ag}_{0.015}\text{Sb}_2$, and SEM-EDS elemental mapping images of the (c) cross-section and (d) surface for $\text{Mg}_{2.985}\text{Ag}_{0.015}\text{Sb}_2$.

The SEM image of the cross-section of the optimized $\text{Mg}_{2.985}\text{Ag}_{0.015}\text{Sb}_2$ sample (Fig. 4a) confirms that the sample is dense with no remarkable cracks, consistent with the density measurement. Fig. 4b presents a high resolution transmission electron microscopy (HRTEM) image obtained from the $\text{Mg}_{2.985}\text{Ag}_{0.015}\text{Sb}_2$ sample, exhibiting the presence of the crystallographic plane 110 (0.227 nm) of the $\alpha\text{-Mg}_3\text{Sb}_2$ phase and also the Moiré fringes from the overlap of different orientations of the crystallographic planes. The atomic-scale HRTEM image of the undoped sample is shown in Fig S6. Fig.

4c and 4d display the results of SEM-EDS mapping for the cross-section and surface of $\text{Mg}_{2.985}\text{Ag}_{0.015}\text{Sb}_2$, respectively. It is seen that all the elements (Mg, Sb and Ag) are present and distributed uniformly throughout the sample.

3.4 Electrical transport properties

The electrical resistivity values of all samples as a function of temperature are depicted in Fig. 5a. It is clear that the electrical resistivity values of the Ag doped samples are much smaller than that of pure Mg_3Sb_2 . This can be mainly attributed to the increase of carrier concentrations, indicating that Ag is an effective dopant. For clarity, Fig. 5b shows the temperature dependent electrical resistivity values for the doped samples. The electrical resistivity values of the Ag-doped samples show three regions: i) first metallic behavior from 300 to ~ 450 K, ii) then a change to thermally activated semiconducting behavior, iii) and finally an increasing temperature-dependent trend up to 725 K. With increasing Ag content, the transition temperature between the second and the third regions gradually increases while the local minimum of resistivity decreases. The temperature dependence of the resistivity of $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ ($x=0.025$) depicts only the first two regions, which is probably because the third region lies above the maximum temperature measured (725 K). Fig. 5c displays the temperature dependent Seebeck coefficient of all the Ag doped samples. Compared with the pure sample, Ag doping at the Mg sites decreases the value of the Seebeck coefficient. The Seebeck coefficient of Ag-doped Mg_3Sb_2 exhibits a similar temperature-dependent behavior (three regions) as the electrical resistivity (Fig. 5d).

At room temperature, pure Mg_3Sb_2 shows an intrinsically low p-type carrier concentration of $1.75 \times 10^{18} \text{ cm}^{-3}$. The room-temperature Hall carrier concentrations of Ag-doped Mg_3Sb_2

Fig. 5 Temperature dependent thermoelectric properties of $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ ($0 \leq x \leq 0.025$): (a) electrical resistivity; (b) electrical resistivity of the doped samples; and (c) Seebeck coefficient; (d) Seebeck coefficient of the doped samples.

Table 1. Room temperature hole carrier concentration and Hall mobility of $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ ($x=0, 0.005, 0.010, 0.015, 0.020, 0.025$).

Composition	n_{H} (10^{19} cm^{-3})	μ_{H} ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
Mg_3Sb_2	0.175	28.3
$\text{Mg}_{2.995}\text{Ag}_{0.005}\text{Sb}_2$	1.47	50.1
$\text{Mg}_{2.99}\text{Ag}_{0.01}\text{Sb}_2$	1.26	47.6
$\text{Mg}_{2.985}\text{Ag}_{0.015}\text{Sb}_2$	1.51	47.3
$\text{Mg}_{2.98}\text{Ag}_{0.02}\text{Sb}_2$	1.33	48.9
$\text{Mg}_{2.975}\text{Ag}_{0.025}\text{Sb}_2$	1.27	43.7

samples are at least 7 times larger than that of the undoped sample (Table 1), suggesting that Ag doping is effective in tuning carrier density. Surprisingly, the Ag-doped samples show room temperature Hall mobility within the range of 43.7–50.1 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is at least 50% higher than that of the pure sample. The enhancement of Hall mobility is probably caused by the weakening of the polar covalent bonding in the $[\text{Mg}_2\text{Sb}_2]^{2-}$ layer, induced by the substitution of Ag on Mg sites. Accordingly, the combination of enhanced carrier concentration and mobility results in the low resistivity of the Ag-doped samples. There is very little effect on the room-temperature carrier concentration and mobility with varying Ag concentration.

Fig. 6 Temperature dependence of (a) Hall carrier concentration and (b) Hall mobility of $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ ($0 \leq x \leq 0.025$).

Fig. 6a shows the Hall carrier concentrations, n_{H} , of the $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ samples as a function of temperature. n_{H} of Mg_3Sb_2 remains constant up to ~ 650 K, while, for the Ag-doped samples, the Hall carrier concentration values are constant only in a small temperature range of 300–400 K, and then start to increase due to the activation of intrinsic carriers. The slope of the Hall carrier concentration curve increases

with increasing Ag concentration ($0 \leq x \leq 0.02$), which is possibly due to the enhanced intrinsic carriers activation induced by the narrowing band gaps with Ag doping. The high-temperature Hall mobility values of the Ag-doped samples are displayed in Fig. 6b. For all samples, the mobility values follow the relation $\mu \propto T^{-p}$ ($1 \leq p \leq 1.5$), suggesting that the transport is dominated by acoustic phonon scattering.

Fig. 7 (a) The Seebeck coefficient versus Hall carrier concentration (n_{H}) at 300 K. The red solid line represents the prediction of p-type Mg_3Sb_2 from full DFT band structure calculation. Green and blue dashed lines show the expected Seebeck coefficient versus n_{H} behavior for single parabolic bands with effective masses equal to 0.75 m_e and 1.47 m_e , respectively. The black square and red triangular solid points are the p-type undoped and Ag doped Mg_3Sb_2 from this work, respectively. The pink round solid points represent Na-doped Mg_3Sb_2 compounds from ref. 20. (b) Calculated room-temperature power factor as a function of n_{H} in p-type Mg_3Sb_2 .

The electronic transport properties are analyzed by the semi-classical Boltzmann transport theory based on full *ab initio* band structures as well as a single parabolic band model. The doping dependence of the Seebeck coefficient at 300 K is shown in Fig. 7a. The experimental data of Ag-doped and Na-doped Mg_3Sb_2 agrees very well with the curve simulated by the integrated *ab initio* full band structure and semi-classical Boltzmann transport theory under a rigid band approximation, confirming the validity of this approach. The effective mass $m_d^* = 0.75m_e$ is estimated by fitting the Seebeck coefficient of a single parabolic band at a low carrier concentration of 10^{17} cm^{-3} to the *ab initio* calculated Seebeck coefficient. It is found that the Seebeck coefficient simulated by a single parabolic band model with effective mass of 0.75 m_e has perfect agreement with that calculated by the semi-classical Boltzmann transport theory in the carrier concentration range from 10^{17} to $\sim 4 \times 10^{19} \text{ cm}^{-3}$.

Fig. 8 Temperature dependence of (a) power factors, (b) total thermal conductivities, (c) lattice thermal conductivities, and (d) zT values of $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ ($0 \leq x \leq 0.025$).

As the carrier concentration increases from $\sim 4 \times 10^{19}$ to 10^{21} cm^{-3} , both the experimental and ab initio calculated Seebeck coefficients increase and approach the curve predicted by a single parabolic band with a higher effective mass of $1.47m_e$. This result indicates that the secondary Γ band starts to play a role for the electronic transport as the Fermi level approaches the secondary valence band with the increasing carrier density. The room-temperature carrier concentration of all the Ag-doped samples shows a small distribution from 1.26×10^{19} to $1.51 \times 10^{19} \text{ cm}^{-3}$, in which the single parabolic band model is still valid. However, for the reported Na-doped Mg_3Sb_2 samples²⁰ with larger than $8 \times 10^{19} \text{ cm}^{-3}$, the single parabolic band model is no longer a good approximation, and a two-band model is required to describe the electronic transport.

The dependence of the calculated power factor of p-type Mg_3Sb_2 on Hall carrier concentration by semi-classical Boltzmann transport theory is depicted in Fig. 7b. The theoretical power factor increases and then decreases, displaying a peak value at an optimal carrier concentration of $4.04 \times 10^{19} \text{ cm}^{-3}$. It should be noted that the present Ag-doped Mg_3Sb_2 samples show carrier concentration close to this optimal value. The experimental power factors of all Ag doped samples are shown in Fig. 8a. In comparison with the undoped Mg_3Sb_2 , the Ag doped samples exhibit much higher power factors, due to the considerable decrease of electrical resistivity values. Among the doped samples, $\text{Mg}_{2.985}\text{Ag}_{0.015}\text{Sb}_2$ shows the highest power factor within the entire measurement temperature range, and has a power factor which is at least 2 times greater than the undoped sample. The power factors of all the doped samples are between 2.7 and $4.6 \mu\text{W cm}^{-1} \text{K}^{-2}$ and show weak temperature dependence.

3.5 Thermal transport properties

The total thermal conductivities as a function of temperature for all $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ samples are plotted in Fig. 8b. With

increasing temperature, the total thermal conductivities of all samples decrease. The room-temperature thermal conductivity of pure Mg_3Sb_2 is $1.4 \text{ W m}^{-1} \text{K}^{-1}$, which is comparable to the previous report.¹⁸ Most of the Ag doped Mg_3Sb_2 samples have lower total thermal conductivity values than that of the undoped Mg_3Sb_2 . The $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ ($x=0.005$ – 0.01 , 0.025) samples show a decreasing trend of total thermal conductivity with the increasing Ag content which might be attributed to the enhanced point defects or electron-phonon scattering. For the $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ ($x=0.015$), i.e. the sample with the highest power factor, the total thermal conductivity ranges from 1.24 to $0.65 \text{ W m}^{-1} \text{K}^{-1}$ at 300–725 K, which is comparable to the lowest thermal conductivity in the other Ag-doped samples. Using the Wiedemann–Franz relation, the electronic contribution to the thermal conductivity is estimated by $\kappa_e = L\sigma T$, where the Lorenz numbers (L) can be calculated through a single parabolic band model under the assumption of acoustic phonon scattering.¹⁶ The calculated Lorenz numbers are between 1.54×10^{-8} and $1.69 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ for all samples (Fig. S7†). By subtracting κ_e from the total thermal conductivities, the lattice thermal conductivities (κ_L) were obtained for all samples (Fig. 8c). The lattice component clearly is the dominant contribution to the total thermal conductivity for each sample. In addition, the κ_L of all Ag-doped samples roughly obey a T^{-1} dependence, indicating the Umklapp processes to be dominant.

3.6 Figure of merit

Fig. 8d shows the temperature dependent zT of all the Ag-doped samples. Pure Mg_3Sb_2 exhibits an optimum zT value of 0.21 at 725 K, as a result of the intrinsically low carrier concentration. All Ag-doped samples show considerably enhanced zT throughout the whole temperature range. The

$\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ ($x=0.015$) sample has the highest performance with a peak zT of 0.51 at 725 K, which is a factor 2.4 larger than that of the undoped sample. In comparison to other p-type doped samples such as Na-doped Mg_3Sb_2 ,²⁰ Pb-doped Mg_3Sb_2 ,¹⁹ $\text{Mg}_3\text{Sb}_{1.8}\text{Bi}_{0.2}$,¹⁸ and $\text{Mg}_{2.9}\text{Zn}_{0.1}\text{Sb}_2$,²¹ it is seen that $\text{Mg}_{2.985}\text{Ag}_{0.015}\text{Sb}_2$ displays higher zT values in the low temperature range of 300–550 K as well as comparably good performance at higher temperatures (Fig. 9a). The conversion efficiency of a TE device for waste heat recovery is actually determined by the average zT over a wide temperature range rather than the maximum zT . Hence, the average zT of the $\text{Mg}_{2.985}\text{Ag}_{0.015}\text{Sb}_2$ sample was calculated with the cold side temperature kept at 333 K while hot side temperature up to 725 K. As Fig. 9b depicts, the average zT of $\text{Mg}_{2.985}\text{Ag}_{0.015}\text{Sb}_2$ is 0.21, which is ~24% higher than that of Na-doped Mg_3Sb_2 ²⁰ and Pb-doped Mg_3Sb_2 ,¹⁹ and at least a factor 5 larger than those of $\text{Mg}_3\text{Sb}_{1.8}\text{Bi}_{0.2}$ ¹⁸ and Zn-doped Mg_3Sb_2 .²¹

According to DFT calculations, p-type Mg_3Sb_2 shows a small indirect band gap of 0.61 eV and an optimal doping concentration of $4.04 \times 10^{19} \text{ cm}^{-3}$. The experimental results show the simultaneous improvement of power factor and thermal conductivity in Ag-doped $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ samples with much higher carrier concentration and Hall mobility. A maximum zT value of 0.51 was achieved at 725 K for sample $\text{Mg}_{2.985}\text{Ag}_{0.015}\text{Sb}_2$, revealing a promising thermoelectric material for intermediate-temperature applications.

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Fig. 9 (a) Temperature-dependent figure of merit zT of $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ ($x=0$ and 0.015). (b) The average zT of $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ ($x=0.015$). The data of other p-type Mg_3Sb_2 -based compounds $\text{Mg}_{2.9875}\text{Na}_{0.0125}\text{Sb}_2$,²⁰ $\text{Mg}_3\text{Sb}_{1.8}\text{Pb}_{0.2}$,¹⁹ $\text{Mg}_{2.9}\text{Zn}_{0.1}\text{Sb}_2$,²¹ and $\text{Mg}_3\text{Sb}_{1.8}\text{Bi}_{0.2}$ ¹⁸ are plotted for comparison.

4. Conclusions

In summary, Ag-doped samples of p-type $\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$ ($x = 0, 0.005, 0.010, 0.015, 0.020, 0.025$) were successfully prepared by a fast efficient one-step SPS synthesis process. Since undoped Mg_3Sb_2 exhibits a low carrier concentration, Ag doping at the Mg sites was investigated to increase the carrier concentration towards the optimal carrier concentration.

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