# Thermoelectric Properties of Mn-doped Mg-Sb Single Crystals

<table>
<thead>
<tr>
<th>Journal:</th>
<th>Journal of Materials Chemistry A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID:</td>
<td>TA-ART-05-2014-002386.R1</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Paper</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>03-Jun-2014</td>
</tr>
</tbody>
</table>
| Complete List of Authors: | Kim, Soo Hyun; Sogang University, Physics 
Kim, Chung Man; Sogang University, Physics 
Hong, Yang-Ki; The university of alabama, electrical and computer engineering 
Onimaru, T; Hiroshima University, ADSM, Department of Quantum Matter 
Suekuni, Koichiro; Hiroshima University, ADSM, Department of Quantum Matter 
Toshiro, Takabatake; Hiroshima University, ADSM, Department of Quantum Matter 
Jung, Myung-Hwa; Sogang University, Physics |
Thermoelectric Properties of Mn-doped Mg-Sb Single Crystals

Soo hyun Kim, Chungman Kim, Yang-Ki Hong, Takahiro Onimaru, Koichiro Suekuni, Toshiro Takabatake, and Myung-Haw Jung

Department of Physics, Sogang University, Seoul 121-742, South Korea
Department of Electrical and Computer Engineering, University of Alabama, Tuscaloosa, Alabama 35487, USA
Department of Quantum Matter, ADSM, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8530, Japan

Abstract

We have grown Mg$_{3-x}$Mn$_x$Sb$_2$ (x = 0, 0.3, and 0.4) single crystals by the vertical Bridgman method to investigate the effects of Mn substitution on thermoelectric properties of Mg$_3$Sb$_2$. The grown crystals were single phased and c-axis oriented with the trigonal crystal structure of inverse α-La$_2$O$_3$ type. The Seebeck coefficient (S), electrical resistivity (ρ), and thermal conductivity (κ) were measured at various temperatures ranging from 4 to 500 K. The electrical resistivity at 500 K decreased to 0.20 Ωcm for x = 0.3 and to 0.16 Ωcm for x = 0.4 from 2.30 Ωcm of Mg$_3$Sb$_2$ (x = 0), but the thermal conductivity was 1.04 W/mK for both x = 0 and 0.4. The Seebeck coefficient became negative when Mn was substituted for Mg, but the absolute value remained almost the same as that for x = 0 in the temperature range between 5 and 600 K. The power factor for x = 0.4 has a large maximum of 370 µW/mK$^2$ at 130 K. As a result, the thermoelectric figure of merit for Mn-substituted Mg$_3$Sb$_2$ is more than one order of magnitude higher than that for pure Mg$_3$Sb$_2$ (x = 0).

Key words: Thermoelectrics, Zintl phase, Mg$_3$Sb$_2$

* Corresponding author: Tel. +82 2 705 8828, mhjung@sogang.ac.kr
1. Introduction

Thermoelectric efficiency of a given material is determined by the figure of merit, $ZT = S^2T/\rho\kappa$, where $S$ is the Seebeck coefficient, $\rho$ is the electrical resistivity, $\kappa$ is the thermal conductivity, and $T$ is the temperature [1,2]. The Seebeck coefficient is large for semiconductors with low carrier concentration, and the electrical resistivity is low for metals with high carrier concentration. Therefore, the thermoelectric power factor ($= S^2/\rho$) can be maximized between metallic and semiconducting properties. It has been known that a narrow-gap band structure of semiconductors favors thermoelectric effects rather than the gapless band structure of metals [3,4]. Further, the $ZT$ can be optimized by adjusting two modes of thermal conductivity: Phonons are responsible for lattice thermal conductivity and electrons for electronic thermal conductivity [5,6]. Then the thermal conductivity of thermoelectric material has two different components; electron- and phonon-based conductivities ($\kappa_{el}$ and $\kappa_{ph}$, respectively). The $\kappa_{el}$ is lower than $\kappa_{ph}$ for semiconductors, and the higher electrical conductivity ($\sigma$) gives the higher $\kappa_{el}$ thereby possibly decoupling $\kappa_{ph}$ from $\sigma$ ($= 1/\rho$). Therefore, the $\kappa_{ph}$ needs to be minimized to achieve high $ZT$. This suggests that the $ZT$ can be controllable by engineering $\kappa_{ph}$.

With regard to the electrical conductivity $\sigma = ne^2\tau/m$ of metal, where $n$ is the charge carrier density, $e$ is the charge per carrier, $\tau$ is the carrier mean free time between scattering events, and $m$ is the carrier mass, the electrical conductivity is utterly controlled by the carrier mean free time ($\tau$). The electrical conductivity of metals decreases with increasing temperature. This is because the $\tau$ decreases as the temperature increases. On the other hand, the electrical conductivity generally increases with temperature for semiconductors due to an increase in $n$ with temperature. Most Zintl phase compounds are valence balanced and poor conductors or semiconductors, which have been intensively studied as potentially high $ZT$ thermoelectric materials [7,8]. Both ionic and covalent bonds need to coexist in the Zintl phase. Mg$_3$Sb$_2$ has the Zintl phase structure, and is composed of (Mg$_2$Sb$_2$)$^{2-}$ framework and intercalated Mg$^{2+}$ cation layer. The Mg occupies either the tetrahedral site of (Mg$_2$Sb$_2$)$^{2-}$ or octahedral site of Mg$^{2+}$. The covalent bonding of polyanion enhances the mobility of the charge carriers. However, Mg$_3$Sb$_2$ has low mobility because of strong polar covalent bonding in the (Mg$_2$Sb$_2$)$^{2-}$ framework [7]. Very few studies on polycrystalline and nanocrystalline Mg$_3$Sb$_2$ were reported [9-12], but to the best of our knowledge, no study on Mn-substituted Mg-Sb single-crystalline is reported. Kajikawa et al., [9] reported $ZT = 0.55$ at 660 K and Condron et al., [10] reported $ZT = 0.21$ at 875 K for polycrystalline Mg$_3$Sb$_2$. However, extremely low $ZT$ of $5.56 \times 10^{-4}$ at 300 K was reported for Zn-substituted Mg$_3$Sb$_2$[11] and $0.34 \times 10^{-4}$ for nanocrystalline Mg$_3$Sb$_2$ [12]. These different measured $ZT$ values can be explained by microstructure evolution and grain boundary structure [10-12]. The thermal conductivity is low for the nanocrystalline Mg$_3$Sb$_2$, but the electrical resistivity is high. Therefore, a low $ZT$ value is expected for the nanocrystalline Mg$_3$Sb$_2$. This is because more grain boundary scatterings occur in polycrystalline Mg$_3$Sb$_2$. The thermoelectric
properties can be improved in the single crystal form due to the less grain boundary scattering. And also, we try to enhance the electronic transport properties by introducing Mn atoms into Mg$_2$Sb$_2$ because the Mn atoms substituted for Mg in the polyanion (Mg$_2$Sb$_2$)$^{2-}$ layer can weaken the polar covalent bonding and thereby increase the carrier mobility. In this paper, we report the thermoelectric properties of single crystalline Mg$_3$Sb$_2$ and Mn-substituted Mg$_3$Sb$_2$, (i.e., Mg$_{3-x}$Mn$_x$Sb$_2$ with $x = 0, 0.3$, and $0.4$). The figure of merit is compared to that of their polycrystalline counterparts, and interpreted in terms of grain boundary contribution.

2. Experimental

Single crystalline Mg$_{3-x}$Mn$_x$Sb$_2$ with $x = 0, 0.3$, and 0.4 were grown by the vertical Bridgman method from mixtures of Mg (99.99%), Mn (99.999%), and Sb (99.999%). A pre-baked and cleaned Mo crucible containing the nominal Mg-Mn-Sb mixture with 0.5 mole Mg excess was sealed by arc melting under Ar atmosphere, and then was heated up to 800 °C at 100 °C/h rate and kept for 24 h. After homogenizing the mixture at 800 °C, the crucible was cooled to room temperature slowly over a total of ~130 h while rotating the crucible at 5 revolutions per minute (rpm). The crystal structure was analyzed by x-ray diffraction using a Rigaku DMAX 2500 diffractometer equipped with CuKα radiation ($\lambda = 1.5406$ Å). The physical properties were determined by scanning electron microscopy (SEM, JSM-6700F) and x-ray photoelectron spectroscopy (XPS, SIGMA PROBE). The chemical composition of the grown crystals was measured by electron probe microanalyzer (EPMA, JXA-8900R). We measured the electrical resistivity ($\rho$), the Seebeck coefficient ($S$), and thermal conductivity ($\kappa$) at various temperatures ranging from 4 to 500 K. Since the grown single crystals were well-cleaved in parallel to the $ab$ plane, we performed all the measurements in the plane. A four-point probe with a GM refrigerator was used to measure $\rho$. To measure the $S$, we used two different techniques; a slowly varying $T$-gradient technique from 5 to 300 K and commercial MMR Technologies system from 300 to 600 K. The $\kappa$ was measured using a steady-state method with a cryostat at temperatures between 5 and 300 K. By the laser flash method, the thermal diffusivity $D$ was measured for the temperature range from 300 to 600 K in vacuum, then the $\kappa$ could be obtained by $\kappa = DC_pM$, where $C_p$ is the specific heat and $M$ is the mass density. Also, we carried out the Hall measurements using the dc technique at a constant magnetic field of 12 kOe to obtain carrier concentration.

3. Results and discussion

Fig. 1 (a) and (b) show the powder and single crystal x-ray diffraction (XRD) patterns for Mg$_{3-x}$Mn$_x$Sb$_2$ ($x = 0, 0.3$, and $0.4$), respectively. Single crystals were ground for powder XRD measurement. All diffraction peaks are well indexed with the reported structure of inverse $\alpha$-La$_2$O$_3$ structure-type.
The obtained lattice parameters are $a = 4.55(6) \ \text{Å}$ and $c = 7.22(4) \ \text{Å}$. Mn-substituted Mg$_3$Sb$_2$ crystals show the same XRD patterns as the pure Mg$_3$Sb$_2$, and the shift of the peak positions is unnoticeable. Therefore, the change in lattice parameters is negligible with Mn substitution. As shown in Fig. 1 (c), the crystals are well-cleaved in parallel to the $ab$ plane, and are shiny and flat. Single crystal XRD patterns were taken from the shiny and flat surface, which is the $ab$ plane. Thus, the single-crystal diffraction peaks are well labeled with $(00l)$ indices as shown in Fig. 1 (b). It is noted that since the melting point of Mn is higher than the boiling point of Mg, the solubility of Mn in Mg$_3$Sb is limited. This limits stoichiometric composition range for Mg$_{1-x}$Mn$_x$Sb$_2$. By using the electron probe microanalyzer (EPMA), we obtained the actual composition of Mn, that is 0.2 and 0.3 even though the nominal Mn composition was $x = 0.3$ and 0.4. The scanning electron microscopy (SEM) image in Fig. 1 (d) shows that Mg$_{1-x}$Mn$_x$Sb$_2$ crystals are homogeneous in phase. Furthermore, in order to identify the valence state of substituted Mn cation, we have taken the x-ray photoelectron spectroscopy (XPS) spectra as shown in Fig. 2. It is known that the binding energy of $640.8 \pm 0.3 \ \text{eV}$ comes from Mn$^{2+}(2p_{3/2})$ and $641.8 \pm 0.1 \ \text{eV}$ from Mn$^{3+}(2p_{3/2})$ [15,16]. Even though the difference in their binding energies is small, we can fit the XPS spectra with two Gaussian functions from Mn$^{2+}(2p_{3/2})$ and Mn$^{3+}(2p_{3/2})$ contributions. As shown in Fig. 2, for $x = 0.3$ the Mn$^{2+}$ peak (red line) is relatively stronger than the Mn$^{3+}$ peak (blue line), and for $x = 0.4$ the Mn$^{3+}$ peak is stronger than the Mn$^{2+}$ peak. The sum of two Gaussian functions (green line) well fits the experimental data. This means that the more Mn substitution gives more stable Mn$^{3+}$ states instead of Mn$^{2+}$. Then, we can expect an increase of n-type carriers with the substitution of Mn.

Fig. 3 shows the temperature dependence of electrical resistivity for Mg$_{1-x}$Mn$_x$Sb$_2$ ($x = 0$, 0.3, and 0.4). The Mg$_3$Sb$_2$ ($x = 0$) single crystal possesses $2.52 \ \Omega \ \text{cm}$ of resistivity at room temperature, which is lower than the resistivity reported for polycrystalline or nanocrystalline Mg$_3$Sb$_2$ [11,12]. However, the electrical resistivity is still high compared to other promising thermoelectric materials. This is because the strong polar covalent bonding of (Mg$_2$Sb$_2$)$_2^-$ polyanion limits carrier mobility. In Zintl phase compounds, the carrier mobility is governed by polyanionic bonding. However, the substitution of Mn for Mg sites of Mg$_3$Sb$_2$ crystal causes the polyanionic polar covalent bonding to convert to covalent bonding, thereby enhancing carrier mobility. Therefore, the covalent bonding in Zintl phase compounds leads to lower electrical resistivity as compared to polyanionic polar covalent bonding. The measured electrical resistivity of Mg$_{1-x}$Mn$_x$Sb$_2$ ($x = 0.4$) is $0.09 \ \Omega \ \text{cm}$ at room temperature, which is almost 30 times lower than that of Mg$_3$Sb$_2$ ($x = 0$). With increasing temperature, the electrical resistivity decreases for Mg$_3$Sb$_2$ ($x = 0$), but increases for Mg$_{1-x}$Mn$_x$Sb$_2$ ($x = 0.3$ and 0.4). This suggests that the substitution of Mn for Mg changes semiconducting behavior of Mg$_3$Sb$_2$ ($x = 0$) to metallic behavior. There are two possible explanations for this change. One is an increase in carrier concentration with Mn substitution. Therefore, we have performed the Hall measurements at room temperature to determine carrier concentration. The measured carrier concentrations were $2.2 \times 10^{17}$ cm$^{-3}$, $9.0 \times 10^{17}$ cm$^{-3}$, and $13.3 \times 10^{17}$ cm$^{-3}$ for $x = 0$, 0.3, and 0.4, respectively. The carrier concentration remarkably increases with $x$. Further the carrier type changes from p-type in Mg$_3$Sb$_2$ ($x$
to be n-type in Mg$_3$Mn$_x$Sb$_2$ ($x = 0.3$ and 0.4). It is noted that the valence of Mn can be either divalent (Mn$^{2+}$) or trivalent (Mn$^{3+}$), whereas Mg holds a divalent state (Mg$^{2+}$). As aforementioned, it was confirmed by XPS results that Mn$^{2+}$ and Mn$^{3+}$ cations coexist. Accordingly, the substitution of Mn for Mg provides excess electrons in Mg$_{3-x}$Mn$_x$Sb$_2$, thereby increasing carrier concentration. This results in lowering the electrical resistivity. The other explanation can be made by an increase of carrier mobility with Mn substitution. As aforementioned, Mg$_3$Sb$_2$ with the structure of Zintl phase has strong polar covalent bonding, which decreases the carrier mobility [7]. When Mn is substituted for Mg, the polar covalent bonding of Mg$_3$Sb$_2$ ($x = 0$) becomes weak. Therefore, the weakened polar covalent bonding enhances the mobility, consequently lowering electrical resistivity. To confirm this, we have evaluated the carrier mobility at room temperature from the carrier concentration and electric resistivity data. The evaluated carrier mobility was 11.25 cm$^2$/Vs, 49.24 cm$^2$/Vs, and 53.91 cm$^2$/Vs for $x = 0$, 0.3, and 0.4, respectively. The carrier mobility increases about 340% by substituting Mn for Mg.

This result suggests that the polar covalent bonding of polyanion (Mg$_3$Sb$_2$)$^{2-}$ is weakened or destroyed when Mn substitutes for Mg in the tetrahedral site of polyanion framework rather than in the octahedral site of Mg cation layer. Consequently, the electrical resistivity decreases with the substitution of Mn for Mg. The schematic crystallographic structure of Mg$_{3-x}$Mn$_x$Sb$_2$ is shown in the inset of Fig. 3.

Fig. 4 shows the temperature dependence of Seebeck coefficient for Mg$_3$Mn$_x$Sb$_2$ ($x = 0$, 0.3, and 0.4). The Seebeck coefficient is positive and large for $x = 0$, but becomes negative value when Mn substituted for Mg. These results are in good agreement with our Hall measurement results, which show that the carrier type changes from p-type to be n-type with Mn substitution for Mg. The Seebeck coefficient for $x = 0$ is 591 µV/K at 300 K, which is higher than polycrystalline Mg$_3$Sb$_2$ [9-11] but lower than nanocrystalline Mg$_3$Sb$_2$ [12]. However, the measured value for $x = 0.4$ is -496 µV/K at 300 K, the absolute value of which is unexpectedly high as compared to other substituted materials [11]. Therefore, we have tried to understand this through the following analysis. The maximum Seebeck coefficient ($S_{\text{max}}$) is given by the relation $S_{\text{max}} \sim E_g/2eT_{\text{max}}$ [17], where $S_{\text{max}}$ is the maximum value of the Seebeck coefficient, $E_g$ is the band gap, and $T_{\text{max}}$ is the temperature at the $S_{\text{max}}$. The $E_g$ was estimated to be 0.8 eV from the Seebeck coefficient versus temperature plot ($T_{\text{max}} = 580$ and 570 K for $x = 0$ and 0.3), and is close to the band gap of Mg$_3$Sb$_2$ measured by an optical technique [18,19]. This means that the substitution of Mn for Mg of Mg$_3$Sb$_2$ is not sufficiently effective in changing the band gap. Therefore, the Seebeck coefficient of Mg$_3$Mn$_{0.4}$Sb$_2$ ($x = 0.4$) remains high.

In order to assess the ability of Mg-Mn-Sb crystals to produce useful electric power, we have calculated the power factor ($S^2/\rho$) from the measured electrical resistivity ($\rho$) and Seebeck coefficient ($S$). Fig. 5 shows the temperature dependence of the power factor for Mg$_3$Mn$_x$Sb$_2$ ($x = 0$, 0.3, and 0.4). The power factor for $x = 0.3$ and 0.4 increases up to 150 K and then decreases, while the power factor for $x = 0$ monotonically increases with the temperature. The power factor of single crystalline Mg$_3$Sb$_2$ is about 14 µW/mK$^2$ at room temperature, and is close to that of polycrystalline Mg$_3$Sb$_2$ [11], but is much higher than nanocrystalline Mg$_3$Sb$_2$ [12]. It is noted that the power factor becomes the
same at 500 K for both Mg$_{3-x}$Mn$_x$Sb$_2$ ($x = 0.3$ and 0.4) single crystals. It can be concluded that the power factor is increased with the substitution of Mn for Mg of Mg$_3$Sb$_2$ due to remarkable decrease in electrical resistivity as shown in Fig. 3.

Up to now, we have discussed the temperature dependence of electrical resistivity, Seebeck coefficient, and power factor. Here, we will discuss the thermal conductivity $\kappa$ to estimate the $ZT$ and understand the effect of Mn substitution on the $ZT$. Fig. 6 shows the temperature dependence of $\kappa$ for $x = 0$ and 0.4 on a double logarithmic scale. The value of $\kappa$ increases with the temperature up to about 30 K, and then more or less linearly decreases to 600 K. It is striking that $\kappa$ of Mg$_{3-x}$Mn$_x$Sb$_2$ ($x = 0.4$) is lower than Mg$_3$Sb$_2$ ($x = 0$) below 30 K, but remains the same as that of Mg$_3$Sb$_2$ ($x = 0$) above 30 K. The values at 300 K for both crystals are 1.55 W/mK, which is close to the reported one for polycrystalline Mg$_3$Sb$_2$ [11]. As aforementioned, there are two components for $\kappa$, namely electron- and phonon-based conductivities. The electronic thermal conductivity $\kappa_{el}$ can be estimated by the Wiedemann-Franz law, $\kappa_{el} = LT/\rho$, where $L$ is the Lorenz number, and $\rho$ is the electrical resistivity. For non-metallic systems, the lattice thermal conductivity $\kappa_{ph}$ is dominant, which is related to the structural disorder such as grain boundary and impurity. In an ideal single crystal, the grain boundary effect is negligible. Accordingly, an increase of impurity concentration leads to a decrease in $\kappa_{ph}$. In the case of Mg$_3$Sb$_2$ system ($x = 0$), we calculated the $\kappa_{el}$, which is negligible due to the large electrical resistivity (see the inset of Fig. 6). As shown in Fig. 6, the $\kappa_{ph}$ has a dominant role in the temperature dependence of total thermal conductivity. Above 30 K, $\kappa(T)$ is almost identical to each other. This cannot be generally accepted because $\kappa_{ph}$ should be decreased by Mn impurities which act as impurity scattering center. However, as aforementioned, Mn substitutes for Mg in the tetrahedral site of (Mg$_3$Sb$_2$)$_2^3$ polyanion framework rather than in the octahedral site of Mg$^{2+}$ cation layer, and most phonon heat transfer occurs in the Mg$^{2+}$ cation layer. Therefore, $\kappa$ is unchanged by the substitution of Mn. Furthermore, we analyze the linear temperature dependence (blue line) above 30 K with the scattering mechanism of phonons. This dependence of $\kappa_{ph}$ indicates umklapp scattering to be the dominant mechanism in Mg$_{3-x}$Mn$_x$Sb$_2$ [20].

Finally, we have calculated the figure of merit, $ZT (= S^2T/\rho\kappa)$, from the measured electrical resistivity, thermal conductivity, as well as the Seebeck coefficient, and plotted the figure of merit, $ZT (= S^2T/\rho\kappa)$ of Mg$_{3-x}$Mn$_x$Sb$_2$ ($x = 0$, 0.3, and 0.4) single crystals in Fig. 7 as a function of sample temperature. The $ZT$ for all the single crystals increases as the temperature increases, and the Mn-substituted Mg$_3$Sb$_2$ single crystals show much higher $ZT$ than the pure Mg$_3$Sb$_2$ single crystal. For example, the $ZT$ for $x = 0.4$ is almost 20 times higher than that for $x = 0$ at 300 K. The Mn substitution for Mg is more effective in increasing $ZT$ than other substituted Mg$_3$Sb$_2$ [11]. This is because the electrical resistivity is remarkably decreased with the Mn substitution. Furthermore, it is noted that the $ZT$ for the single crystalline Mg$_3$Sb$_2$ is much higher than the $ZT$ reported for polycrystalline and nanocrystalline Mg$_3$Sb$_2$ [11,12]. The $ZT$ of about 0.11 at 500 K for $x = 0.4$ is one order of magnitude higher than that for $x = 0$. This implies that the substitution of Mn for Mg of Mg$_3$Sb$_2$ single crystal
can effectively increase the figure of merit, $ZT$, and improve high-temperature thermoelectric properties.

4. Conclusion

Thermoelectric $\text{Mg}_3x\text{Mn}_x\text{Sb}_2$ ($x = 0$, 0.3, and 0.4) single crystals, grown by the vertical Bridgman method, are single phased and $c$-axis oriented with the trigonal crystal structure of inverse $\alpha$-$\text{La}_2\text{O}_3$ type. There are three main conclusions. First, the carrier type of $\text{Mg}_3\text{Sb}_2$ is changed from p-type to n-type by introducing Mn. Second, the $ZT$ of single crystalline $\text{Mg}_3\text{Sb}_2$ is higher than their polycrystalline and nanocrystalline counterparts due to fewer grain boundary scatterings. Third, the $ZT$ value is increased by the substitution of Mn and is the largest at $x = 0.4$, which is the limit of solubility of Mn in $\text{Mg}_3x\text{Mn}_x\text{Sb}_2$ phase. Single crystalline $\text{Mg}_3x\text{Mn}_x\text{Sb}_2$ could potentially pave the way for improving high-temperature thermoelectric efficiency.

Acknowledgment

This work was supported by the Basic Science Research Program of NRF, the Ministry of Education, Science and Technology of Republic of Korea (South Korea) under Award number 2012R1A1A2039944, and in part by the Sogang University Research Grant of 201310026.01.
References

Fig. 1 (a) Powder x-ray diffraction and (b) single-crystal x-ray diffraction patterns for Mg$_{3-x}$Mn$_x$Sb$_2$ ($x = 0, 0.3$ and $0.4$). The bars represent the reference data of MgSb$_2$ with the inverse $\alpha$-La$_2$O$_3$ type structure. (c) Photograph and (d) scanning electron microscope image of single crystal Mg$_3$Sb$_2$. 
Fig. 2 X-ray photoelectron spectroscopy spectra corresponding to Mn$^{2+}$ and Mn$^{3+}$ binding energies for Mg$_{3-x}$Mn$_x$Sb$_2$ ($x = 0.3$ and 0.4). Dashed lines represent the binding energy of Mn$^{3+}$(3p$_{3/2}$) and Mn$^{2+}$(3p$_{3/2}$). The blue and red lines are Gaussian functions from Mn$^{2+}$(2p$_{3/2}$) and Mn$^{3+}$(2p$_{3/2}$) contributions, and the green line is the sum of them. The yellow line represents the experimental data.
Fig. 3 Temperature dependence of electrical resistivity, $\rho$ for Mg$_{3-x}$Mn$_x$Sb$_2$ ($x = 0$, 0.3 and 0.4). Note that the $y$ axis is on a logarithmic scale. The inset represents the schematic crystallographic structure of Mg$_{3-x}$Mn$_x$Sb$_2$. 
Fig. 4 Temperature dependence of Seebeck coefficient, $S$ for $\text{Mg}_{33-x}\text{Mn}_x\text{Sb}_2$ ($x = 0, 0.3$ and $0.4$).
Fig. 5 Temperature dependence of power factor, $S^2/\rho$ for Mg$_{3-x}$Mn$_x$Sb$_2$ ($x = 0, 0.3$ and $0.4$).
Fig. 6 Temperature dependence of thermal conductivity, $\kappa$ for Mg$_{3.4}$Mn$_x$Sb$_2$ ($x = 0, 0.4$), plotted in a double logarithmic scale. Open symbols represent the experimental data corresponding to the total thermal conductivity, and narrow lines represent lattice thermal conductivity that subtracts the electronic thermal conductivity from the total thermal conductivity. The solid line represents the $1/T$ fit of $\kappa$. The inset shows the electronic thermal conductivity that is negligible.
Fig. 7 Temperature dependence of dimensionless figure of merit, $ZT$ for $\text{Mg}_{3-x}\text{Mn}_x\text{Sb}_2$ ($x = 0$, 0.3 and 0.4). The inset shows the enlarged plot of $ZT$ vs. $T$ for $x = 0$. 