Thermoelectric properties of Na-doped Zintl compound: $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$

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Abstract: $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ has been prepared successfully by mechanical alloying plus hot pressing to investigate the effects of Na doping on the thermoelectric properties. Thermoelectric properties were characterized by Seebeck coefficient, electrical resistivity, thermal conductivity, and thermoelectric figure of merit (ZT) from 298 to 773 K. Transport measurements reveal that an optimum doping of 1.25 at% Na on Mg achieved ZT of 0.6 at 773 K. The enhancement in ZT is attributed to increased carrier concentration and power factor. The low cost, abundance, and nontoxicity makes this material a potentially promising thermoelectric material for power generation at heat source below 773 K.

Keywords: Mg_3Sb_2 alloy; Nanostructure; Thermoelectric properties; Engineering figure-of-merit.

1. Introduction

Increasing the efficiency of the existing energy systems and discovering new clean energy sources are two of the major issues in today's society [1]. The majority of energy loss is in the form of waste heat. In this case, thermoelectric effects play a significant role by allowing the direct conversion of heat into electricity [2-5]. The efficiency of a thermoelectric material in a power generator depends on the dimensionless thermoelectric figure of merit (ZT), defined as $ZT = (S^2\sigma/\kappa)T$, where S , σ , κ , and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively [6,7]. The numerator $S^2\sigma$ is called power factor PF . Even though PF could be enhanced by engineering the electronic structure, and κ could be reduced by increasing the phonon scattering, it is very difficult to independently optimize them simultaneously since they are interrelated. The concept of "phonon-glass electron-crystal, PGEC" has been considered to be an effective way to decouple these interrelated quantities, but the experimental success is limited in only a few materials so far [8-10].

For many decades, a tremendous amount of efforts has been made to find high performance thermoelectric materials without too much success. The best materials are still Bi_2Te_3 [11,12], PbTe -based materials [13-16], skutterudites [17-19], half-Heusler alloys [20-25] and SiGe alloys [26]. However, many other materials are now emerging as potentially promising bulk thermoelectric materials. Zintl phase compounds, formed between the alkali or alkaline-earth metals and the post-transition elements from group 13-15, have been shown to be promising candidates for thermoelectric materials [27, 28] due to their complex crystal structures, resulting in low lattice thermal conductivities. A variety of Zintl phases, such as $\text{Yb}_{14}\text{MnSb}_{11}$ [29], YbZn_2Sb_2 [30], YbCd_2Sb_2 [31], $\text{Eu}_5\text{In}_2\text{Sb}_6$ [32], $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ [33], and CsBi_4Te_6 [34] have been widely investigated for their thermoelectric properties. However, most of Zintl phase materials are made of expensive rare earth elements and/or toxic elements, resulting in limitation for their application in power generation and refrigeration. The Zintl phase Mg_3Sb_2 , which involve non-toxic, cheap and abundant elements, has also been investigated in hopes of achieving a high ZT for intermediate or high temperature applications [35,36]. Mg_3Sb_2 phase, crystallizing in the same $P-3m1$ space group as the inverse $\alpha\text{-La}_2\text{O}_3$ structure type,

exhibits a characteristic feature of PGEC for potentially high figure of merit [37]. However, due to the difficulties in synthesizing single phase by conventional synthesis routes and more importantly inconsistencies in the transport properties by different research groups, the highest reported ZT is ~ 0.2 between 773 and 873 K, impeding by the high resistivity of Mg_3Sb_2 [36]. Recently, some progress was reported by Bhardwaj et al. [38,39]. They doped Bi in Sb site in the $\text{Mg}_3\text{Sb}_{2-x}\text{Bi}_x$ to enhance the ZT close to 0.6 at ~ 773 K and 10 at% Pb on Sb to improve ZT to 0.84 at ~ 773 K. However, the average ZT of the best composition $\text{Mg}_3\text{Sb}_{1.8}\text{Bi}_{0.2}$ is relatively low and Pb doping does not seem to be attractive due to the toxicity of Pb. In addition to doping in the Sb-site, Zn, Mn, Cd, etc. have been used to dope into the Mg site focusing on low temperature properties [40-42]. Herein, we report our effort on enhancing the electric transport properties by doping Na atoms into the Mg site in Mg_3Sb_2 hoping to increase the carrier concentration for better electric property since Na has been considered as an ideal hole dopant with little effect on the other physical properties in many materials [43,44].

2. Experimental section

Magnesium (Mg, Sigma Aldrich, 99.9%, pieces), sodium (Na, Sigma Aldrich, 99.9%, cubes), and antimony (Sb, Sigma Aldrich, 99.9%, chunks) were weighed according to the stoichiometry of $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ with $x = 0, 0.006, 0.0125, \text{ and } 0.025$, and then loaded in a stainless steel jar with stainless steel balls for mechanical alloying by a high energy ball mill (SPEX 8000D) for 20 h. The final nanopowder was then loaded into a graphite die with an inner diameter of 12.7 mm, and consolidated by direct current (DC) hot pressing at ~ 1023 K for 2 min.

X-ray diffraction spectra were collected on a PANalytical multipurpose diffractometer with an X'celerator detector (PANalytical X'Pert Pro). Thermogravimetric analysis (TA instruments Q50) was used to evaluate the thermal stability in nitrogen atmosphere. The microstructures, examined on a freshly broken surface, were investigated by a scanning electron microscope (SEM, JEOL 6330F). Transmission electron microscope (TEM, JEOL 2100F) was used to explore the details of grain size

and microstructures. The electrical resistivity (ρ) and Seebeck coefficient (S) were simultaneously measured on a commercial system (ZEM-3, ULVAC) using the four-point direct-current switching method and the static temperature difference method. The thermal conductivity was measured by measuring the thermal diffusivity (D) on a laser flash apparatus (LFA 457, NETZSCH), specific heat (C_p) on a DSC (404 C, NETZSCH), and volumetric density (ρ_v) by Archimedes method. The carrier concentration was obtained by Hall effect measurement (Van der Pauw method) at room temperature using a modified sample puck in Physical Properties Measurement System (PPMS D060, Quantum Design).

3. Results and discussion

Fig. 1 shows the XRD patterns of $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ ($x = 0, 0.006, 0.0125, \text{ and } 0.025$). Na doped $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ show the same XRD patterns as the pure phase without noticeable peak position shift. All diffraction peaks are indexed with the reported structure of inverse $\alpha\text{-La}_2\text{O}_3$ structure-type [37]. The change in lattice parameters is negligible with Na doping, which should attribute to the very small amount of dopant compared with other groups' prior work [38]. And according to the definition of Zintl compounds, Na and Mg, belonging to alkali and alkaline earth metals, respectively, show similar behaviors by donating electrons to the more electronegative anions Sb to form covalent bonds. Increasing Na content effectively increases carrier concentrations (discussed later). So it clearly demonstrates that Na atoms are successfully doped into Mg site.

The SEM image of the optimized $\text{Mg}_{2.875}\text{Na}_{0.0125}\text{Sb}_2$ sample is displayed in Fig. 2a, from which we can see that the sample is dense, consistent with the density measurement (discussed later). In order to confirm the grain size distribution and phase purity at microscopic scale, TEM investigation was carried out. Fig. 2b is a low-magnification TEM image, which shows the clear grain boundaries and grain sizes are about 1 μm . A selected area electron diffraction (SAED) pattern is recorded from one of these grains, shown in Fig. 2c. All of the spots in Fig. 2c can be successfully indexed according to $P\text{-}3m1$ hexagonal structure along the $[130]$ zone axis with lattice parameters

$a = 4.56 \text{ \AA}$ and $c = 7.23 \text{ \AA}$ which are consistent with the XRD data. Fig. 3d shows a high-resolution TEM image and elucidates three grains adjacent to each other sharing a triple junction with the presence of planes $01\bar{1}0$ (0.39 nm) and $10\bar{1}3$ (0.21 nm) of $\text{Mg}_{2.875}\text{Na}_{0.0125}\text{Sb}_2$. The micrograph, Fig. 3d, clearly reveals that each grain is truly single crystalline with stacking of different planes and with random orientation with respect to each other.

To determine the effect of Na doping on Mg site on the thermoelectric properties of $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$, electrical resistivity, Seebeck coefficient, and power factor were measured and shown in Fig. 3. Fig. 3a shows the electrical resistivity of all samples up to 773 K. It clearly shows that the electrical resistivity of the doped samples is much smaller than that of the undoped one, which indicates that Na is a very effective hole dopant. To see the difference more clearly, Fig. 3b displays the temperature dependence of electrical resistivity for only the doped samples. The measured electrical resistivity of $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ are 96.9, 46.8, and 29.0 $\mu\Omega \text{ m}$ for $x = 0.006$, 0.0125, and 0.025 at room temperature, respectively, which are almost four orders of magnitude lower than that of Mg_3Sb_2 . With increasing temperature, the electrical resistivity decreases drastically for Mg_3Sb_2 ($x = 0$), corresponding to a strong semiconducting behavior. However, the electrical resistivity of Na doped samples decreases to a minimum around 473 K and then increases, which indicates that Na substitution for Mg changes the semiconducting behavior to metallic behavior. Increasing Na concentration in Mg_3Sb_2 leads to lower electrical resistivity due to the enhanced carrier concentration as listed in Table 1. The carrier concentration remarkably increases with x . The carrier concentration (n) and Hall mobility (μ) listed in Table 1 affect the electrical resistivity (ρ) by the relationship $1/\rho = ne\mu$. With increasing Na content, Hall mobility decreases due to stronger electron scattering by Na, which means the carrier concentration primarily dominates the electronic transport.

Fig. 3c represents the temperature dependent Seebeck coefficient of all the Na doped samples. Doping of Na into Mg site dramatically decreases the Seebeck coefficient and a slight decrease in Seebeck coefficient with increasing Na content is also observed. We can use the relation $E_g = 2eT_{\text{max}}S_{\text{max}}$ for better understanding of the energy gaps

where E_g , $S_{\max}$, and $T_{\max}$ are the band gap, the maximum value of the Seebeck coefficient, and the temperature at the $S_{\max}$, respectively. E_g of all the samples $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ with $x = 0, 0.006, 0.0125, \text{ and } 0.025$ were estimated to be 0.61, 0.35, 0.30, and 0.24 eV, respectively. Thus, E_g of Na doped composition was estimated to be more than 50% lower than that of Mg_3Sb_2 , indicating Na is very effective in modifying the band gap.

Combining the electrical resistivity and Seebeck coefficient, the power factor of all Na doped samples are shown in Fig. 3d. Although the power factor of Na doped samples is much higher than that of the undoped Mg_3Sb_2 , they are still very low as compared to other good materials. The power factor of all the Na doped samples shows no difference when temperature is below 473 K, while with increasing temperature, the power factors for $x = 0.0125$ and 0.025 continue to grow, but saturate at about $7.5 \mu\text{W cm}^{-1} \text{K}^{-2}$.

Fig. 4 shows the temperature-dependent thermal transport behavior of $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ with $x = 0, 0.006, 0.0125, \text{ and } 0.025$. Specific heat (C_p) of $\text{Mg}_{2.975}\text{Na}_{0.025}\text{Sb}_2$, shown in Fig. 4a, is used for all samples since Na has a higher C_p than Mg. The C_p dependence of temperature shows a little bit increase towards 773 K, while at room temperature C_p is 0.4, almost the same as the calculated value based on Dulong-Petit Law. The diffusivity (D) of all samples $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ is shown in Fig. 4b, clearly the higher the Na concentration the higher the diffusivity. C_p and D are used to calculate the total thermal conductivity (κ) of all the doped samples by using $\kappa = D\rho C_p$, where ρ is the measured density of samples. The densities of all the samples $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ with $x = 0, 0.006, 0.0125, \text{ and } 0.025$ measured by Archimedes method are 4.007, 3.996, 3.997, 3.985 g cm^{-3} , respectively, ~98% of the theoretical density 4.088 g cm^{-3} . The temperature dependence of the total thermal conductivity (κ) of Na doped samples is plotted in Fig. 4c. The total thermal conductivity for Na doped Mg_3Sb_2 is higher than that of Mg_3Sb_2 due to the higher electrical conductivity. The thermal conductivity of all samples decreases with temperature.

To better understand the phonon scattering, we calculated the lattice thermal conductivity by subtracting the electronic contribution from the total thermal conductivity. The electronic thermal conductivity (κ_e) can be calculated using the Wiedemann-Franz relation given by $\kappa_e = L\sigma T$, where L is Lorenz number, σ is the electrical conductivity, and T is the absolute temperature. For most thermoelectric materials, the Lorenz number depends on the reduced Fermi energy $\xi = E_F/k_B T$ and scattering parameter r as shown in the following,

$$L = \left(\frac{k_B}{e}\right)^2 \left(\frac{(r+7/2)F_{r+5/2}(\xi)}{(r+3/2)F_{r+1/2}(\xi)} - \left[\frac{(r+5/2)F_{r+3/2}(\xi)}{(r+3/2)F_{r+1/2}(\xi)} \right]^2 \right) \quad (1)$$

where F_n is the Fermi integral given by

$$F_n(\xi) = \int_0^\infty \frac{\chi^n}{1 + e^{\chi - \xi}} d\chi \quad (2)$$

The reduced Fermi energy can be deduced from the Seebeck coefficient on the basis of single band approximation,

$$S = \pm \frac{k_B}{e} \left(\frac{(r+5/2)F_{r+3/2}(\xi)}{(r+3/2)F_{r+1/2}(\xi)} - \xi \right) \quad (3)$$

In this calculation, we assumed acoustic phonon scattering as the main carrier scattering mechanism using $r = -0.5$. By subtracting the electronic contribution from the total thermal conductivity, the inversely temperature dependence of lattice thermal conductivity (κ_L) is shown in Fig. 4d. It is noted that this method is not accurate enough to estimate κ_L , so only κ_L near low temperature is calculated. The relationship between κ_L and the reciprocal of temperature ($1/T$) is almost linear, which reveals the predominant phonon contribution to the thermal conductivity. Clearly, the lattice thermal conductivity is not reduced by doping but increased, opposite to the normal trend. Typically impurities produce point defect scattering and thereby reduce the lattice thermal conductivity. Thus, some other scattering mechanisms should be dominant instead of point defect scattering. In fact, the phenomenon of increasing lattice thermal conductivity has been observed in some other doped semiconductors, like $\text{Mo}_3\text{Sb}_{7-x}\text{Te}_x$ [45]. Here, we will also assume the lattice thermal conductivity is dominated by the Umklapp scattering and ignore the point defect influence. In addition, the lattice thermal conductivity of Mn doped Mg_3Sb_2 did

not decrease either [42]. One possible reason is that Mn substitutes for Mg in the tetrahedral site rather than in the octahedral site of Mg^{2+} cation layer, and most phonon heat transfer occurs in the Mg^{2+} cation layer. The real reason why lattice thermal conductivity increase deserves further studies.

We have also calculated ZT from the measured electrical resistivity, thermal conductivity, as well as the Seebeck coefficient, and plotted the ZT results in Fig. 5. The maximum ZT for Mg_3Sb_2 was observed to be about 0.3 at 773 K which is higher than most of the reported data by other groups [36-42]. The optimum doping of Na with 1.25 at% in Mg_3Sb_2 drives the system to exhibit an increased ZT of ~ 0.6 at 773 K. For all the Na doped samples, ZT increases almost linearly with temperature and the average ZT is much better than prior work Bi doped Mg_3Sb_2 as shown in the figure [38]. The enhanced ZT is resulted from the increase in power factor. From the peak ZT values shown in Fig. 5, it seems that 1.25 at% Na-doped Mg_3Sb_2 is the best material among the three compositions. However, ZT indicates the ratio of electrical to thermal characteristics only at each instantaneous temperature, so it cannot indicate the practical efficiency of a TE material at a large temperature gradient of its actual operations. Instead of using the peak ZT , Kim et al. proposed the engineering dimensionless figure of merit $(ZT)_{eng}$ as a function of thermal boundaries, *i.e.*, the temperatures of hot side T_h and cold side T_c , which is defined as [46],

$$(ZT)_{eng} = \frac{\left(\int_{T_c}^{T_h} S(T) dT \right)^2}{\int_{T_c}^{T_h} r(T) dT \int_{T_c}^{T_h} k(T) dT} (T_h - T_c) = \frac{(PF)_{eng}}{\int_{T_c}^{T_h} k(T) dT} (T_h - T_c) \quad (4)$$

where $S(T)$, $\rho(T)$, and $\kappa(T)$ are temperature dependent thermoelectric properties, and $(PF)_{eng}$ is the engineering power factor with respect to the boundary temperatures. $(ZT)_{eng}$ implies the cumulative effect of TE properties at a given thermal boundary [46]. $(PF)_{eng}$ has unit of $\text{W m}^{-1} \text{K}^{-1}$, different from the conventional unit of $\text{W m}^{-1} \text{K}^{-2}$ due to its cumulative effect associated with the temperature gradient. Fig. 6 shows the calculated $(ZT)_{eng}$ and $(PF)_{eng}$ dependence of the hot side temperature up to 773 K while the cold side temperature is kept at 323 K. It is noted that this study improves the materials' performance by a factor of 40 in terms of $(ZT)_{eng}$ as compared with Mg_3Sb_2 and by a

factor of 4 as compared with Bi doped Mg_3Sb_2 at the same conditions (Fig. 6a). Based on $(ZT)_{eng}$, 0.6 at% Na-doped Mg_3Sb_2 shows similar performance to 1.25 at% Na-doped Mg_3Sb_2 at $T_h = 773$ K even though the peak ZT of the latter at that temperature is 14% higher than the former. In addition, 0.6 at% Na-doped Mg_3Sb_2 shows higher $(ZT)_{eng}$ through whole temperature range below $T_h = 723$ K at $T_c = 323$ K. Thus, 0.6 at% Na-doped Mg_3Sb_2 is slightly better in terms of the efficiency when the temperature difference is limited below 400 K at $T_c = 323$ K while 1.25 at% Na-doped Mg_3Sb_2 should be selected if larger electric power generation is more concerned since power factor is dominant on power output (Fig. 6b).

4. Conclusion

Nanostructured Zintl phase of Mg_3Sb_2 and Na doped $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ were synthesized successfully by ball milling and hot pressing. Na doping into Mg enhances the power factor by increasing carrier concentration but not decreasing the carrier mobility much. A peak ZT of ~ 0.6 at 773 K has been achieved for the optimum doping with $x = 0.0125$. Mg_3Sb_2 based Zintl compounds free of expensive rare earth elements have advantages of low cost, environmentally friendly, and non-toxicity.

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Figure Captions

Figure 1. XRD patterns of $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ ($x = 0, 0.006, 0.0125, \text{ and } 0.025$).

Figure 2. SEM and TEM images of sample $\text{Mg}_{2.9875}\text{Na}_{0.0125}\text{Sb}_2$: (a) SEM image; (b) medium magnification TEM image; (c) selected area electron diffraction (SAED) pattern; and (d) high resolution TEM image.

Figure 3. Temperature dependent thermoelectric properties of $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ ($x = 0, 0.006, 0.0125, \text{ and } 0.025$): (a) electrical resistivity; (b) electrical resistivity of the doped samples; (c) Seebeck coefficient; and (d) power factor.

Figure 4. Temperature dependent thermal transport properties of $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ ($x = 0, 0.006, 0.0125, \text{ and } 0.025$): (a) Specific heat; (b) thermal diffusivity; (c) total thermal conductivity; and (d) lattice thermal conductivity.

Figure 5. Temperature dependent ZT for $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ ($x = 0, 0.006, 0.0125, \text{ and } 0.025$). The temperature dependent ZT for $\text{Mg}_3\text{Sb}_{1.8}\text{Bi}_{0.2}$ is also plotted for comparison [38].

Figure 6. Calculated $(ZT)_{\text{eng}}$ and $(PF)_{\text{eng}}$ dependence of the hot side temperature up to 773 K while the cold side temperature is kept at 323 K for $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ ($x = 0, 0.006, 0.0125, \text{ and } 0.025$). The Calculated $(ZT)_{\text{eng}}$ and $(PF)_{\text{eng}}$ of $\text{Mg}_3\text{Sb}_{1.8}\text{Bi}_{0.2}$ are also plotted for comparison [38].

Figure 1. Jing Shuai *et al.*

Figure 2. Jing Shuai *et al*

Figure 3. Jing Shuai *et al.*

Figure 4. Jing Shuai *et al.*

Figure 5. Jing Shuai *et al.*

Figure 6. Jing Shuai *et al.*

Table 1. Carrier concentration and Hall mobility at room temperature of $\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$ ($x = 0, 0.006, 0.0125$, and 0.025).

$\text{Mg}_{3-x}\text{Na}_x\text{Sb}_2$	$x = 0$	$x = 0.006$	$x = 0.0125$	$x = 0.025$
Carrier concentration (10^{19} cm^{-3})	0.00026	3.87	8.41	17.1
Hall mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	23.2	16.7	15.9	12.6