Promising cubic MnGeTe₂ thermoelectrics

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ABSTRACT Semiconducting cubic group IV monotellurides, including PbTe and SnTe, have historically led most of the advancements in thermoelectrics. Recently, noncubic ones such as GeTe and MnTe have also shown to be promising, which motivates the current work focusing on the thermoelectric properties of MnGeTe₂, a derivative compound of noncubic GeTe and MnTe but crystallizing in a cubic structure. This compound intrinsically comes with a carrier concentration as high as $\sim 3.6 \times 10^{21} \text{ cm}^{-3}$, indicating the existence of high-concentration cation vacancies due to Ge-precipitation. This intrinsic carrier concentration is much higher than that needed for thermoelectric applications but can be successfully decreased to $\sim 9 \times 10^{20} \text{ cm}^{-3}$ for MnGe_{0.9}Bi_{0.1}Te₂ at room temperature. Such a broad carrier concentration not only offers a full assessment of its electronic transport properties according to a single parabolic band model with acoustic scattering, but also enables an optimization for thermoelectric power factor. The low lattice thermal conductivity of $\sim 1.2 \text{ W m}^{-1} \text{ K}^{-1}$ or lower in the entire temperature range, can be understood by the highly disordered cations and cation vacancies. A peak zT approaching 1.0 at 850 K was achieved in materials at an optimal carrier concentration of $\sim 9 \times 10^{20} \text{ cm}^{-3}$, an isotropic cubic structure as well as a Vickers hardness of $>200 H_V$, strongly indicating MnGeTe₂ as a promising thermoelectric material.

Keywords: thermoelectric, MnGeTe₂, zT , SPB model

INTRODUCTION

Without involving any moving parts and emissions, thermoelectrics, enabling direct conversion between heat and electricity, have been considered as a sustainable green energy source for energy crisis [1]. The conversion efficiency largely depends on the dimensionless figure of merit of thermoelectric materials, $zT = S^2 T / \rho(\kappa_E + \kappa_L)$, where T is the absolute temperature, S is the Seebeck coefficient, ρ is the electrical resistivity, κ_E and κ_L are the electronic and lattice components of the thermal conductivity, re-

spectively [2].

The strong coupling effect among S , ρ , and κ_E causes the reduction in the independent parameter κ_L [3] to play the most popular strategy to enhance zT for a long time. This can be realized through approaches including lattice anharmonicity [4,5], low sound velocity [6–8], dislocations [9–11], nanostructuring [12–14] and point defects [15–17]. Alternatively, newly developed strategies of band engineering have been found to successfully decouple the correlation among these electronic parameters, resulting in a significantly enhanced power factor (S^2/ρ) and zT through band convergence [18,19], resonant states [20–23] and nestification [24]. This has been demonstrated in various materials, such as PbTe [25,26], SnTe [27–33], GeTe [34–38], Mg₂Si [18,39], half-Heusler [40] and Te [24].

Group IV monotellurides with a cubic structure, particularly PbTe and SnTe, have historically led most of the advancements in thermoelectrics. The utilization of the strategies mentioned above has successfully realized many breakthroughs in thermoelectric performance in these materials. Recently, noncubic compounds including GeTe [35,37] and MnTe [41,42], crystallizing in rhombohedral (Fig. 1a) and hexagonal (Fig. 1b) structures at room temperature, respectively, have attracted increasing attentions as well due to their promising thermoelectric performance. The peak zT s higher than 2.0 [35,37] and 1.0 [41,42] have been realized in GeTe and MnTe, respectively. The superior thermoelectric performances in both materials inspire interests in their derivative materials for potential thermoelectric applications.

MnGeTe₂ can be approximated as a derivative compound of noncubic GeTe and MnTe with highly disordered cation occupancy [43] between 50% Ge and 50% Mn. This highly disordered cations are expected to result in a strong phonon scattering, indicating the potentially low lattice thermal conductivity. Importantly, this com-

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Figure 1 Room temperature crystal structures for rhombohedral GeTe, hexagonal MnTe and cubic MnGeTe₂.

pound is found to crystalize in a cubic structure (Fig. 1c) without any phase transitions. This is quite different from the cases of GeTe and MnTe, both of which show a phase transition at elevated temperatures. The crystal structure stabilization would be considered as an advantage for reliable thermoelectric applications, because a structural phase transition usually leads to a sudden change in volume resulting in a possible failure of thermoelectric devices. Additionally, the cubic structure might offer highly degenerated band valleys for a superior electronic performance. Furthermore, the mechanical property is also important for thermoelectric applications. Interestingly, formation of solid solution between PbTe and MnTe enables a hardness being much higher than that of any individual starting material [41,44] (either PbTe or MnTe). It is therefore reasonable to expect a high mechanical property in MnGeTe₂. Although this compound has been investigated as the diluted magnetic semiconductors involving interesting photo-induced ferromagnetism and carrier-induced ferromagnetism effects [45,46], the thermoelectric properties have so far been rarely investigated.

Motivated by the above mentioned advantages in structural stability, strength and electronic/thermal functionalities, this work focuses on the thermoelectric and mechanical properties of MnGeTe₂. The pristine MnGeTe₂ shows an intrinsically high carrier concentration of $\sim 3.6 \times 10^{21} \text{ cm}^{-3}$ due to native cation vacancies. Such a high carrier concentration can be successfully decreased to $\sim 9 \times 10^{20} \text{ cm}^{-3}$ for MnGe_{0.9}Bi_{0.1}Te₂ at room temperature. This reduction in carrier concentration not only enables a full optimization on electronic performance but also a broad range for understanding the electronic transport properties by a single parabolic band transporting under a charge carrier scattering by acoustic phonons. Resulting from the native cation vacancies and Ge precipitates as well as the highly disordered cations, all of which contribute to a strong phonon scattering, the

lattice thermal conductivity is found to be as low as $0.6 \text{ W m}^{-1} \text{ K}^{-1}$ at 850 K in this compound. This largely leads to a peak zT up to unity in optimally doped materials. Moreover, its Vickers hardness ($200 H_V$) is found to be high among thermoelectric chalcogenides. This work demonstrates MnGeTe₂ as a promising material for thermoelectric applications.

EXPERIMENTAL SECTION

Polycrystalline MnGe_{1-x}Bi_xTe₂ ($x \leq 0.12$) samples were synthesized by sealing the stoichiometric amounts of high purity elements, Mn(99.7%), Ge(99.9%), Bi(99.9%), Te (99.9%) in vacuum quartz ampules, melting at 1,373 K for 10 h, quenching in cold water and then annealing at 950 K for 72 h. The obtained ingots were hand ground into fine powders for hot pressing. The dense pellets (>98% of theoretical density) with $\sim 12 \text{ mm}$ in diameter and $\sim 1.2 \text{ mm}$ in thickness were prepared by an induction-heating hot press system at 900 K for 1 h under a uniaxial pressure of $\sim 50 \text{ MPa}$.

The Seebeck coefficient (S), resistivity (ρ) and Hall coefficient (R_H) were simultaneously measured in the temperature range of 300–850 K under helium. The resistivity and R_H were measured through the van der Pauw technique under a reversible magnetic field of 1.5 T. And the S was obtained from the slope of the thermopower *versus* temperature difference within 0–5 K [47]. The results for all the measurements are collected with a temperature step of 25 K. The thermal conductivity was determined according to $\kappa = dC_p D$, where d is the density estimated by the mass/volume method, D is thermal diffusivity measured using a laser flash technique (Netzsch LFA457 system) with a temperature step of 50 K and C_p is the heat capacity of the Dulong-Petit limit and is assumed to be temperature independent. The uncertainty for the measurement of S , ρ and κ is about 5%.

The phase composition and microstructure were characterized using X-ray diffraction (XRD) and scanning

Figure 2 Powder XRD patterns (a) and composition dependent lattice parameter (b) for $\text{MnGe}_{1-x}\text{Bi}_x\text{Te}_2$ ($x \leq 0.12$), indicating a solubility of $\sim 10\%$ for Bi-doping in MnGeTe_2 .

electron microscope (SEM, Phenom Pro) equipped with an energy dispersive spectrometer (EDS), respectively. The longitudinal (v_l) and transverse (v_t) sound velocities were measured using an ultrasonic pulse-receiver (Olympus-NDT) equipped with an oscilloscope (Keysight) at room temperature. The Vickers micro-hardness was measured using a diamond indenter and the Vickers hardness is determined by $H_v = 1.854F/(2d)^2$, where F is the indentation force, and $2d$ is the diagonal length of the indentation [41]. The uncertainty in microhardness measurement is about 5%.

RESULTS AND DISCUSSION

Powder XRD diffraction patterns for $\text{MnGe}_{1-x}\text{Bi}_x\text{Te}_2$ ($x \leq 0.12$) are shown in Fig. 2a. All the diffraction peaks for the samples with $x \leq 0.1$ can be well indexed to the cubic structure of MnGeTe_2 . Bi-rich impurity is detected for the sample with 12% Bi-doping of Ge, which suggests a solubility of $\sim 10\%$ for Bi in MnGeTe_2 . As shown in Fig. 2b, the lattice parameter increases linearly with increasing Bi concentration up to $\sim 10\%$ and then saturates, further supporting that the Bi-doping solubility is $\sim 10\%$. The lattice expansion can be understood by the larger size of Bi as compared to that of Ge.

To further confirm the phase composition and to characterize the microstructure, SEM observations and EDS analysis are carried out. Ge precipitates sized in a few microns are found in the material (Fig. 3), which is similar to the case of GeTe [36]. Moreover, the pores (red circle) are also observed in the SEM image. With Bi-doping, the concentration of Ge precipitates in $\text{MnGe}_{1-x}\text{Bi}_x\text{Te}_2$ decreases and eventually disappears at $x \geq 0.06$ (Fig. 4), which suggests a promoted dissolving of

Figure 3 SEM image and corresponding EDS mappings on composition for MnGeTe_2 . Ge-precipitates and pores (red circle) are observed in SEM image.

Ge-precipitates due to Bi-doping in MnGeTe_2 . This can be presumably understood by the increased formation energy of the Ge-vacancy. Such an effect has also been observed in GeTe alloying with PbSe and demonstrated by density functional theory (DFT) calculations [36]. However, the DFT calculation is challenging to be carried out on a material with disordered occupancy of the cations, which limits the calculation of the formation energy for Ge-vacancies in pristine and Bi-doped MnGeTe_2 . No Bi-rich impurity phases can be observed at $x \leq 0.10$ while it can be found at $x = 0.12$ (Figs 4f and 5), consistently indicating a solubility of 10% for Bi/Ge substitution.

As shown in Fig. 6a, pristine MnGeTe_2 comes with an extremely high hole concentration (n_h) of $3.6 \times 10^{21} \text{ cm}^{-3}$ at room temperature. This strongly implies the existence

Figure 4 SEM images for $\text{MnGe}_{1-x}\text{Bi}_x\text{Te}_2$ ($x \leq 0.12$) showing a removal of Ge precipitates due to Bi-doping at $x \sim 0.06$.

Figure 5 SEM image and corresponding EDS mappings for $\text{MnGe}_{0.88}\text{Bi}_{0.12}\text{Te}_2$.

of native cation vacancies, which is confirmed by the observation of Ge precipitates (Fig. 3). The formation of high concentration Ge-vacancies has been observed in GeTe as well [36,48–50]. Trivalent Bi-doping is utilized to reduce the carrier concentration. Assuming each Bi substituted on Ge site introduces one electron, the expected carrier concentration (n) is calculated according to the equation of $n = n_0 - 2N_A x / a^3$, where n_0 is the Hall carrier

concentration for pristine MnGeTe_2 , N_A is the Avogadro constant, x is the concentration of Bi doping and a is the lattice parameter for samples with different Bi-doping (Fig. 2b). Bi concentration *versus* expected carrier density at 300 K is shown as solid line in Fig. 6a. It is found that the measured n_H is much lower than expected, which can be understood by the simultaneously promoted dissolving of Ge-precipitates due to Bi-doping (Fig. 4) with $x \leq 0.06$. As $x > 0.06$, all Ge-precipitates tend to be dissolved, the rate of decrease in carrier concentration agrees well with expectation (similar slope on n_H *versus* x), indicating the success of Bi-doping at cation site. Within the solubility of Bi-doping, a minimal n_H of $\sim 9 \times 10^{20} \text{ cm}^{-3}$ for $\text{MnGe}_{0.9}\text{Bi}_{0.1}\text{Te}_2$ at room temperature is obtained. The broad n_H achieved in this work enables a full evaluation on the electronic transport properties.

Temperature dependent Hall mobility (μ_H) for $\text{MnGe}_{1-x}\text{Bi}_x\text{Te}_2$ is shown in Fig. 6b. μ_H decreases with increasing temperature *via* $\mu_H \sim T^{-1.5}$, which indicates the charge carrier scattering dominated by the acoustic phonons. The low μ_H of $\sim 2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature in all the samples results from the large effective mass (Fig. 7a). Temperature dependent Seebeck coefficient and resistivity for $\text{MnGe}_{1-x}\text{Bi}_x\text{Te}_2$ are shown in Fig. 6c and 6d, respectively. Both Seebeck coefficient and resistivity increase with increasing Bi concentration in the entire temperature, stemming from the decrease of Hall carrier concentration. The decrease in Seebeck coefficient and resistivity at $T > 650 \text{ K}$ in low carrier concentration samples suggests an occurrence of bipolar conduction. Positive Seebeck coefficient for all samples indicates a p-type conduction, which is consistent with Hall measurements. Based on the results of the Seebeck coefficient, band gap of MnGeTe_2 is estimated according to the equation of $E_g = 2eS_{\text{max}}T_{\text{max}}$, where e is the elementary charge, S_{max} is the maximum Seebeck coefficient for the sample with bipolar effect, T_{max} is the absolute temperature for the appearance of S_{max} [51]. A band gap of $\sim 0.3 \text{ eV}$ is estimated for MnGeTe_2 .

Assuming a single parabolic band model with acoustic phonon scattering (Fig. 6b), a band degeneracy of 1 is used to understand the electronic transport properties for MnGeTe_2 . Temperature dependent effective deformation potential coefficient (E_{def}), and density of state effective mass (m^*) is shown in Fig. 7a. A E_{def} of $\sim 3.5 \text{ eV}$ and a m^* of $\sim 7.8m_e$ for MnGeTe_2 are obtained at room temperature. The high m^* is found to be comparable to that of Mn-doped GeTe ($\sim 6.15m_e$ [52] and $\sim 5.6m_e$ [38]). It is found that the change of carrier concentration by Bi-doping shows negligible effects on both E_{def} and m^* , in-

Figure 6 Bi-doping dependent expectation on Hall carrier concentration (n_H) at 300 K (a), temperature dependent Hall mobility (μ_H) (b), Seebeck coefficient (c) and electrical resistivity (d) for $\text{MnGe}_{1-x}\text{Bi}_x\text{Te}_2$ ($x \leq 0.1$).

dicating a rigid band behavior for MnGeTe_2 . The increase in m^* with increasing temperature might result from an increase in band gap due to thermal expansion. E_{def} could describe the energy fluctuation of the band edge per unit change of the volume induced by the lattice vibrations. However, the effects of thermal expansion on both the band structure and the modes of the lattice vibrations are too complicate, which makes the understanding of the reasons for temperature-dependent E_{def} to be difficult. Therefore, the temperature dependent E_{def} has been rarely discussed in the literature. Moreover, the increase in m^* and the decrease in E_{def} with increasing temperatures have been observed in a few thermoelectrics including lead chalcogenides [53], CuGaTe_2 [54] and Cu_2SnSe_4 [55].

Hall carrier concentration dependent Seebeck coefficient, Hall mobility and power factor (PF) at different temperatures are shown in Fig. 7b–d, respectively. Based on estimated average m^* and E_{def} at each temperature (in Fig. 7a), the SPB model with the acoustic phonon scattering enables reasonable predictions at different temperatures. It is found that both peak PF and optimal

carrier concentration (n_{opt} required for peaking PF) increase with increasing temperature. The optimal hole concentration agrees well with the relationship of $n_{\text{opt}} \propto (m^* T)^{1.5}$ as predicted by the SPB model (Fig. 7d) [56].

Temperature dependent total thermal conductivity (κ) and lattice thermal conductivity (κ_L) for $\text{MnGe}_{1-x}\text{Bi}_x\text{Te}_2$ are shown in Fig. 8. κ_L is obtained by subtracting the electronic thermal conductivity (κ_E) from the total thermal conductivity via the Wiedemann-Franz Law, $\kappa_E = LT/\rho$, where L is the Lorenz factor determined by the SPB model with the acoustic phonon scattering. κ decreases with increasing Bi concentration, due to the reduced carrier concentration leading to a κ_E -reduction. The κ_L as low as $\sim 0.6 \text{ W m}^{-1} \text{ K}^{-1}$ is obtained at 850 K, which can be understood by the additional phonon scatterings due to the highly disordered cations [43], cation vacancies and Bi/Ge substitutional defects.

Longitudinal (v_L) and transverse (v_T) sound velocities (v_s) are measured to evaluate its effect on κ_L . The results along with other estimated physical parameters based on these measurements, including Debye temperature (Θ_D),

Figure 7 Effective deformation potential coefficient (E_{def}) and density of state effective mass (m^*) (a), Hall carrier concentration dependent Seebeck coefficient (b), Hall mobility (c) and power factor (d) at different temperatures, with a comparison to SPB model predictions (solid curves in b–d).

Figure 8 Temperature dependent total thermal conductivity and lattice thermal conductivity for MnGe_{1-x}Bi_xTe₂ ($x \leq 0.1$).

Poisson ratio (ν), bulk modulus (B) and Grüneisen parameter (γ), are listed in Table 1. The Grüneisen parameter (γ) is estimated according to the equation of $\gamma = (3/2) \times [3(\nu_L)^2 - 4(\nu_T)^2] / [(\nu_L)^2 + 2(\nu_T)^2]$ [57,58]. It is shown

that the change in sound velocities for all the samples does not exceed 5%, which is within the measurement uncertainty. Therefore, the effect due to lattice softening can be excluded to understand the low κ_L observed. In order to estimate the available room for a further reduction on κ_L , the amorphous limit ($\kappa_L^{\min} \sim 0.43$ W m⁻¹ K⁻¹) is estimated according to the Cahill approximation [59], which is much lower than the measurement. Therefore, it still remains a big room for further reduction by other strategies.

Temperature dependent figure of merit (zT) for MnGe_{1-x}Bi_xTe₂ is shown in Fig. 9a. zT of all samples increases with increasing temperature and Bi concentration. A significantly enhanced zT up to unity is obtained in Bi-doped samples due to carrier concentration optimization. The SPB model further enables a prediction in carrier concentration dependent zT at different temperatures using the experimental κ_L . The predicted zT agrees with the measurements as shown in Fig. 9b. Moreover, an even higher peak zT for MnGeTe₂ is expectable through a further reduction in κ_L and/or a band engineering approach for enhancing the electronic performance.

Table 1 Measured sound velocities and other estimated physical parameters for $\text{MnGe}_{1-x}\text{Bi}_x\text{Te}_2$ ($x \leq 0.1$) at room temperature

Bi content	v_L (m s ⁻¹)	v_T (m s ⁻¹)	v (m s ⁻¹)	Θ_D (K)	ε	G (GPa)	B (GPa)	γ	C_p (J g ⁻¹ K ⁻¹)	d (g cm ⁻³)
$x=0.00$	3760	2080	2310	233	0.28	51.9	26.7	1.65	0.26	6.08
$x=0.02$	3730	2060	2290	230	0.28	51.4	26.2	1.66	0.26	6.05
$x=0.04$	3750	2070	2300	231	0.28	51.7	26.4	1.66	0.26	6.03
$x=0.06$	3720	2090	2320	232	0.27	49.8	27.1	1.60	0.26	6.11
$x=0.08$	3680	2020	2250	225	0.28	50.3	25.3	1.68	0.25	6.14
$x=0.10$	3670	2040	2270	226	0.27	49.0	25.8	1.63	0.25	6.12

Figure 9 Temperature (a) and Hall carrier concentration (b) dependent figure of merit (zT) for $\text{MnGe}_{1-x}\text{Bi}_x\text{Te}_2$ ($x \leq 0.1$), with a comparison to SPB model predictions (solid curves in b).

Figure 10 Vickers hardness (H_V) for Bi-doped MnGeTe_2 , with a comparison to that of the existing thermoelectric materials [41,44,60–69].

In addition to the promising thermoelectric performance, the mechanical properties are important as well for thermoelectric applications. Vickers hardness for $\text{MnGe}_{1-x}\text{Bi}_x\text{Te}_2$ are measured using a Vickers micro-

indentation method [41,70], as shown in Fig. 10. It is found that the Vickers hardness for $\text{MnGe}_{1-x}\text{Bi}_x\text{Te}_2$ is much higher than those of MnTe [41] and GeTe [64], which is actually higher than many well-known thermoelectrics [44,60–63,65–69]

CONCLUSION

In this work, cubic MnGeTe_2 is demonstrated as a promising thermoelectric material. The Bi-doping at Ge site leads to a broad carrier concentration, which enables a reasonable assessment of electronic transport properties by a single parabolic band model with acoustic phonon scattering. The highly disordered cations and cation vacancies as well as Bi/Ge substitutional defects result in a lattice thermal conductivity as low as $\sim 0.6 \text{ W m}^{-1} \text{ K}^{-1}$ at 850 K. A peak zT up to unity is obtained for $\text{MnGe}_{0.9}\text{Bi}_{0.1}\text{Te}$ at 850 K. Moreover, this material shows a high Vickers hardness $>200 H_V$ among thermoelectric chalcogenides. MnGeTe_2 retains the availabilities for further increased zT by reducing the lattice thermal conductivity, and/or an enhancement in electronic performance such as by band engineering approaches.

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立方相MnGeTe₂: 一种有前景的热电材料

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摘要 具有立方结构的IV族碲化物半导体(PbTe和SnTe)已经引领了热电领域的诸多革新. 近年来, 非立方相化合物GeTe与MnTe也表现出很好的热电前景. 基于此, 本文对GeTe与MnTe的衍生物(MnGeTe₂)的热电性能进行了探究. 在本工作中, 本征态MnGeTe₂因单质锗的析出而存在高浓度的阳离子空位, 载流子浓度高达 $\sim 3.6 \times 10^{21} \text{ cm}^{-3}$, 远高于热电应用所需, 通过Bi的掺杂可使得载流子显著降低(室温下MnGe_{0.9}Bi_{0.1}Te₂载流子约为 $\sim 9 \times 10^{20} \text{ cm}^{-3}$). 在这样大的载流子浓度范围内, 一方面可以基于声学声子散射机制下的单抛物带模型, 实现对载流子输运性质进行全面的评估; 另一方面还可以实现热电功率因子的优化. 此外, 由于材料中存在高度无序的阳离子和阳离子空位, 可在测试温度范围内获得 $1.2 \text{ W m}^{-1} \text{ K}^{-1}$ 甚至更低的晶格热导率. 当载流子浓度达到优化值 $\sim 9 \times 10^{20} \text{ cm}^{-3}$ 时, 在850 K各向同性的立方相下可获得接近1.0的 zT 值以及高于200 H_V 的维氏硬度值, 进一步证实MnGeTe₂是一个很有前景的热电材料.