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Enhanced Thermoelectric Performance of Te-doped $FeSb_2$ Nanocomposite

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Abstract Nanostructured samples of $FeSb_{1.84}Te_{0.16}$ were prepared using a hot-press method and thermoelectric properties were studied. Nanostructured samples exhibited significantly reduced values for the thermal conductivity. Te-doping, in addition to enhancing point-defect scattering, also induced a semiconductor-to-metal transition which increased the power factor value at low temperatures. Both the power factor and the thermal conductivity were shown to decrease with a decrease in hot-pressing temperature. The combined effect resulted in a figure-of-merit *ZT* of 0.022 at 100 K for the optimized sample, a 62 % increase over the single crystal counterpart. Within nanostructured samples, *ZT* increases by as much as 11 times.

Keywords Iron diantimonide · Thermal conductivity · Point-defect scattering

1 Introduction

In the past few decades, the narrow-gap semiconductor $FeSb_2$ has been extensively studied due to its unusual magnetic and electronic transport properties [1–3]. In more recent years, $FeSb_2$ has attracted considerable attention as a thermoelectric material. Efficiency (for thermoelectric power generation) or coefficient of performance (for Peltier cooling) of a thermoelectric material is directly related to a dimensionless

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figure-of-merit (*ZT*) defined by, $ZT = \frac{S^2T}{\rho\kappa}$ where S is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity, and T is the absolute temperature. A *ZT* value of at least 1 is required for a thermoelectric material to be practically useful. Since $ZT \sim S^2$, a high Seebeck coefficient is necessary for a good thermoelectric material. Narrow-gap semiconductors are considered to be one of the best classes of thermoelectric material and for most of these materials the value of the Seebeck coefficient is on the order of 100 μVK^{-1}. For FeSb$_2$, an unusually large Seebeck coefficient of ~45,000 μVK^{-1} has been reported at ~10 K [4] with a moderate value for the electrical conductivity at that temperature. As a result, a record high value for the power factor ($S^2\rho^{-1}$) of 0.23 W m^{-1} K^{-2} at 10 K was observed [4]. Despite the large power factor value, the *ZT* values for single crystal FeSb$_2$ are rather low due to the high thermal conductivity. For undoped FeSb$_2$ single crystals, the reported *ZT* values are around 0.005 at ~10 K [4].

Recently there has been a large amount of interest in reducing the thermal conductivity of FeSb$_2$ while maintaining a high Seebeck coefficient. Specifically, efforts have been made to improve the thermoelectric performance of FeSb$_2$ using the techniques of doping[5–8], nanoinclusions [9,10], nanostructuring [11,12] and stoichiometric adjustment [13]. In our earlier work [11], we were able to reduce the thermal conductivity of FeSb$_2$ by three orders of magnitude using the technique of nanostructuring. Unfortunately, the values of the Seebeck coefficient were drastically reduced in these nanostructured samples possibly indicating a significant phonon-drag contribution[14]. As a result, *ZT* was increased by only one order of magnitude. Data from our earlier work clearly showed that a significant increase in *ZT* of FeSb$_2$ through nanostructuring alone cannot be expected. On the other hand, studies have shown tellurium to be an effective dopant for improving *ZT* of single crystal FeSb$_2$ by reducing the thermal conductivity via point defect scattering. Sun et al. [6] reported a *ZT* value of ~0.013 at around 100 K in FeSb$_{2-x}$Te$_x$ single crystal samples for their optimized doping concentration of x = 0.16. In this report, we present the combined effect of nanostructuring and Te-doping on the thermoelectric properties of FeSb$_2$. To conduct our research, we used the previously reported optimized Te-doped stoichiometric composition (FeSb$_{1.84}$Te$_{0.16}$) and tuned the thermoelectric properties by changing the hot-pressing (HP) temperature. Our results showed a significant drop in thermal conductivity and an enhanced power factor value which lead to improved *ZT* values.

2 Experimental

Stoichiometric amounts of Fe, Sb and Te were mixed and melted at 1,000 °C inside an evacuated and sealed quartz tube. The tube was quenched in cooling water for rapid cooling and solidification. The resulting polycrystalline ingot was ball milled for 15 hours and obtained nanopowder was DC hot pressed under a pressure of 80 MPa for 2 min at several different temperatures (200, 300, 400, 500 and 600 °C). The sample disks were sputtered with gold to optimize electrical and thermal contacts and then cut into rectangular shapes of typical dimension 2 × 2 × 8 mm^3. The Seebeck Coefficient (S), electrical resistivity (ρ), and thermal conductivity (κ) were measured using thermal transport option (TTO) of the Physical Property Measurement System (PPMS).

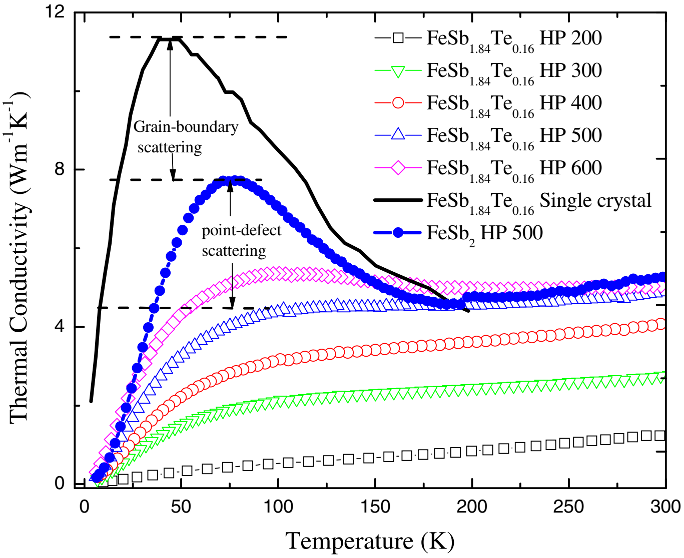

Fig. 1 Thermal conductivity of the samples as a function of temperature (Color figure online)

The Hall coefficient (R_H) was measured using samples with typical dimensions of $1{\times}2{\times}10$ mm^3 employing a five-point configuration on the horizontal rotator option of the PPMS.

3 Results and Discussion

Figure (1) shows the temperature dependence of the thermal conductivity for the samples. The thermal conductivity values of all the nanostructured samples are significantly lower than the values reported for single crystals [4]. For the sample $FeSb_2$ HP 500, κ = 7.08 W m^{-1} K^{-1} at 100 K which is 76 % lower than the value reported for single crystal $FeSb_2$ (∼30 W m^{-1} K^{-1}). By doping with Te, the thermal conductivity was further reduced to 4.38 W m^{-1} K^{-1} in the representative sample $FeSb_{1.84}Te_{0.16}$ HP 500; a reduction by 38 %. In this way an overall reduction in thermal conductivity by 85 % was achieved.

In general, $\kappa = \kappa_{carrier} + \kappa_{lattice}$. Here $\kappa_{carrier}$ and $\kappa_{lattice}$ are the carrier and lattice contributions respectively. Calculations based on the Wiedemann-Franz law ($\kappa_{carrier} = L_0\rho^{-1}T$) show that more than 99 % of the total thermal conductivity of $FeSb_2$ comes from lattice vibrations (phonons). Therefore any reduction in the total thermal conductivity of this system is due to reduction in lattice contribution. The physics of the lattice thermal conductivity is commonly interpreted using the Debye approximation [15,16],

$$\kappa_{lattice} = \frac{k_B}{2\pi^2 v}\left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\frac{\theta_D}{T}} \frac{\tau_c x^4 e^x}{(e^x-1)^2}dx \tag{1}$$

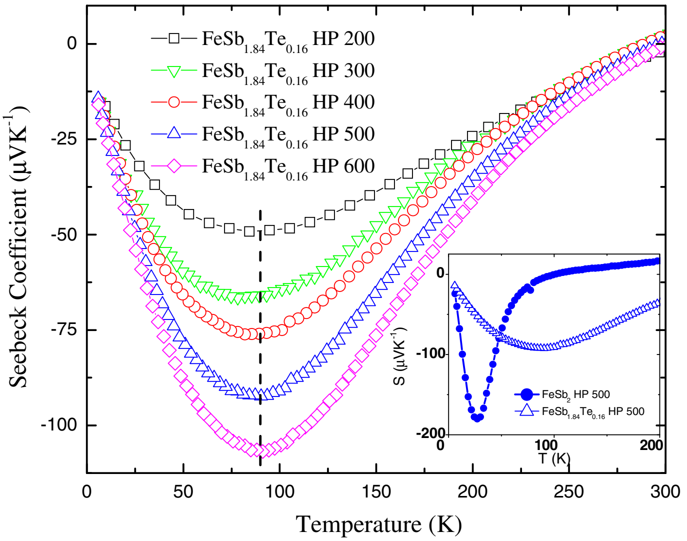

Fig. 2 Seebeck coefficient of the samples as a function of temperature. The *inset* shows the comparison between the temperature dependence of the representative sample $FeSb_{1.84}Te_{0.16}$ HP 500 and an undoped counterpart $FeSb_2$ HP 500 (Color figure online)

where $x = \frac{\hbar w}{k_B T}$, w is the frequency, k_B is the Boltzmann constant, $\hbar$ is the Planck constant, v is the speed of sound, θ_D is the Debye temperature and τ_c is the relaxation time. The overall time constant (τ_c) is given by the Matthiessen's rule,

$$\tau_c^{-1} = \tau_{defect}^{-1} + \tau_{umklapp}^{-1} + \tau_{boundary}^{-1} \tag{2}$$

Here τ_{defect}, $\tau_{umklapp}$ and $\tau_{boundary}$ are the relaxation times associated with the three scattering mechanisms: phonon-defect scattering, umklapp process and phonon-boundary scattering respectively. The reduced (by 76 %) thermal conductivity in our nanostructured samples is due primarily to scattering of the phonons off the grain boundaries. On the other hand, since addition of a small amount of Te should not change the Umklapp process and grain-boundary scattering that much, the additional reduction (by 38 %) comes mainly from the point-defect scattering. Now the mass difference between Sb (121.75) and Te (127.60) is considerably small; therefore the difference in interatomic coupling force constants probably plays a dominant role in scattering of phonons in doped samples. The contributions of nanostructuring and defect scattering are depicted in Fig (1). A significant reduction of thermal conductivity in Te-doped $FeSb_2$ single crystals has been previously discussed in detail by Sun et al. [6] They attributed the thermal conductivity reduction to the introduced charge carriers rather than chemical disorder whereas Wang et al. [7] attributed the reduction to the enhanced point defect scattering caused by both the different bonding tendency and different thermal conductivities of Sb and Te.

Figure 2 shows the temperature dependence of the Seebeck coefficient. At 300 K, the Seebeck coefficient has a small positive value (p-type) $\sim 2\ \mu V\ K^{-1}$ for all the

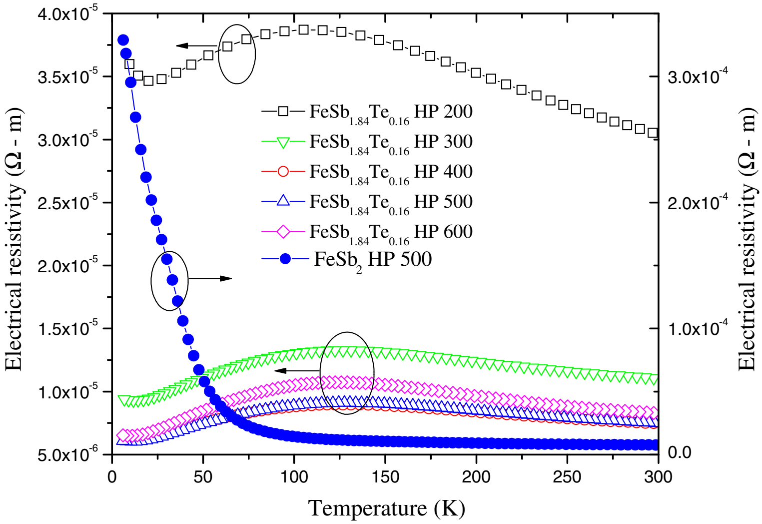

Fig. 3 Electrical resistivity (left *y*-axis) as a function of temperature for the four Te-doped samples. The right *y*-axis corresponds to the electrical resistivity for the undoped sample $FeSb_2$ HP 500 (Color figure online)

Te-doped samples. This value of Seebeck coefficient is significantly less than 31 μV K^{-1} observed for undoped samples. As the temperature decreases, the Seebeck coefficient decreases and changes to a negative (n-type) value at ~290 K. The Seebeck coefficient assumes a peak value at 90 K for all the samples. The largest peak value for the Seebeck coefficient among our samples is ~ -107 μV $K^{-1}$for sample $FeSb_{1.84}Te_{0.16}$ HP 600 which is two orders of magnitude less than the reported value for undoped $FeSb_2$single crystals [4] and is one-fourth of the value (~ - 400 μV K^{-1}) for $FeSb_{1.84}Te_{0.16}$ single crystals [6]. The peak value of the Seebeck coefficient decreases with decreasing HP temperature. This decrease, based on our analysis, comes from two factors: increased carrier density [11] and suppression of the phonon-drag contribution due to increased grain boundary scattering at lower HP temperatures[14]. The inset of Fig. 2 shows the temperature-dependent Seebeck coefficient for the representative sample $FeSb_{1.84}Te_{0.16}$ HP 500 and its undoped counterpart $FeSb_2$ HP 500. Upon Te-doping, the peak value of the Seebeck coefficient decreases and shifts to a higher temperature. A similar shifting of the Seebeck peak with increasing Te-content has been reported also in ref. [6].

Figure 3 shows the temperature dependence of the electrical resistivity for the samples. The electrical resistivity of the sample $FeSb_2$ HP 500 is represented by the right *y*-axis. The undoped sample exhibits semiconducting behavior throughout the temperature range 5–300 K with increasing resistivity as temperature decreases. A sharp increase in resistivity below 70 K indicates an insulating ground state. In contrast to the undoped $FeSb_2$, the Te doped samples exhibit suppressed electrical resistivity with a metallic ground state. The electrical resistivity decreases by one order of magnitude at 100 K. The semiconductor to metal transition temperature for the different samples falls within the range of 100–130 K.

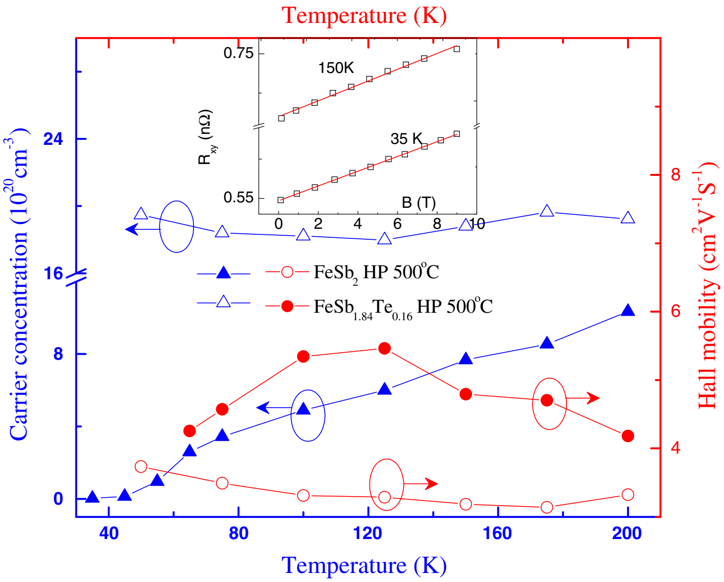

Fig. 4 Carrier concentration (left y-axis) and Hall mobility (right y-axis) as a function of temperature in the temperature range of 60–200 K. *Inset* shows the magnetic field dependence of Hall resistivity for representative sample FeSb$_{1.84}$Te$_{0.16}$ HP 500 at 35 and 150 K (Color figure online)

Figure 4 shows the temperature dependence of the carrier concentration (n) and the Hall mobility (μ) for the undoped and doped nanostructured samples pressed at 500 °C. In the inset of the Fig. 4, we have plotted the magnetic field dependence of the Hall resistivity (R_{xy}) for the samples FeSb$_{1.84}$Te$_{0.16}$ HP 500 both below (35 K) and above (150 K) the semiconductor to metal transition temperature. A linear relationship as expected in single band model is observed.n and μ were estimated from the Hall coefficient (R_H) and electrical resistivity (ρ) measurements using $n = 1/|R_H|e$ and $\mu = |R_H|/\ \rho$, under the single band model. Here $e = 1.6\ \times 10^{-19}$ C is the electronic charge. At 100 K, the carrier concentration of the doped sample is increased by one order of magnitude when compared with that of undoped sample. Also, the carrier concentration is less temperature sensitive for doped samples, a result consistent with the metallic nature seen in the electrical resistivity data at lower temperatures. The Hall mobility is reduced in the doped sample. For example, $\mu = 5.3$ and 3.3 cm^2 V^{-1} S^{-1} for samples FeSb$_2$ HP 500 and FeSb$_{1.84}$Te$_{0.16}$ HP 500, respectively at 100 K.

Figure 5 shows the temperature dependence of the power factor ($S^2\rho^{-1}$). When compared with the undoped nanostructured samples, the power factors in the Te-doped samples increased significantly. For example, $S^2\rho^{-1} = 9.9 \times 10^{-4}$ W m^{-2} K^{-1} at 80 K for the representative sample FeSb$_{1.84}$Te$_{0.16}$ HP 500, which is an increase of 386 % from the corresponding value for the undoped sample FeSb$_2$ HP 500. Among the Te-doped samples, the peak values for the power factor decrease with decreasing the HP temperature.

In Figure 6, we have presented ZT as a function of temperature. For all the doped samples, the curve assumes a peak value (ZT_{max}) at around 100 K. For the optimized

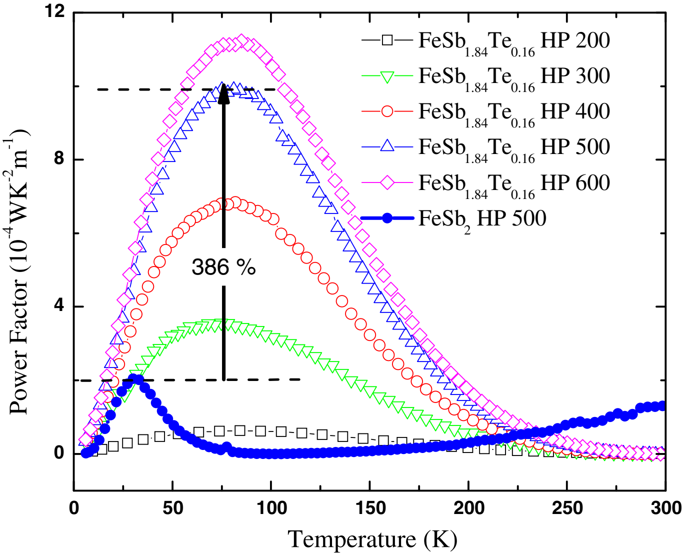

Fig. 5 Power factor as a function of temperature (Color figure online)

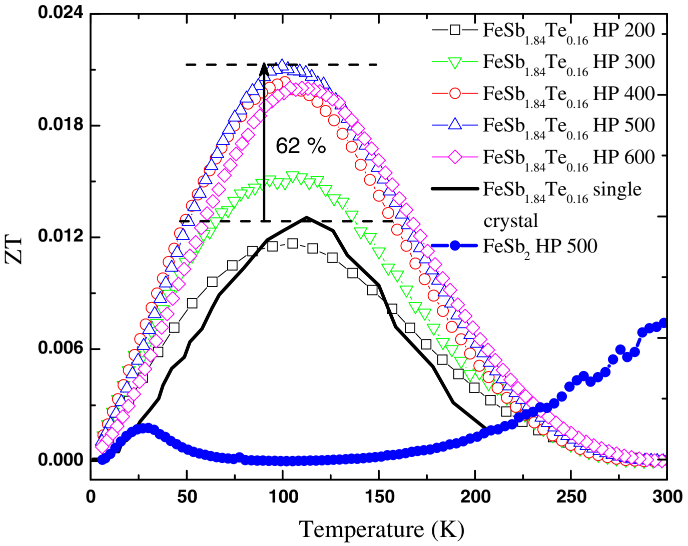

Fig. 6 *ZT* as a function of temperature. Data for FeSb$_{1.84}$Te$_{0.16}$ single crystal (taken from ref. [6]) are also included for comparison (Color figure online)

sample FeSb$_{1.84}$Te$_{0.16}$ HP 500, ZT_{max} = 0.022 at 100 K, this is an increase of 62 % compared with the optimized value for the Te-doped single crystal which was 0.012 in ref. [6]. When compared with the *ZT* of FeSb$_2$ HP 500 (ZT_{max} = 0.0017 at 25 K), the *ZT* values for the optimized sample FeSb$_{1.84}$Te$_{0.16}$ HP 500 is increased by a factor of 11.

4 Conclusion

In conclusion, nanostructured samples of $FeSb_{1.84}Te_{0.16}$ have been prepared using the hot-press method and their thermoelectric properties have been studied in the range of temperatures 5–300 K. Based on our analysis, the grain-boundary scattering and the point-defect scattering are the two dominant phonon scattering mechanisms that contributed to a significantly reduced (by 85 % at 100 K) thermal conductivity in Te-doped nanostructured samples. Te-doping in $FeSb_2$ contributed not only to the thermal conductivity reduction but also to an enhanced power factor by inducing a semiconductor to metal transition. With a decrease in HP temperature, both the thermal conductivity and the power factor decreased. The optimal conditions for *ZT* were observed for the doped sample hot pressed at 500 °C. The *ZT* value of 0.022 at 100 K was observed for the optimized sample $FeSb_{1.84}Te_{0.16}$ HP 500, 62 % higher than the corresponding value for the single crystal. Therefore, it has been successfully demonstrated that combining the technique of doping with nanostructuring significantly enhances the thermoelectric performance of $FeSb_2$ at low temperatures. This approach can easily be extended to improve ZT of other phonon dominated thermoelectric systems at low temperatures.

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