High Temperature Thermoelectric Properties of Skutterudite-Bi₂Te₃ Nanocomposites

Jiangying Peng^{a,*}, Jin Zheng^a, Fanhao Shen^b, Kuo Zhang^b, Jian He^c, Jinsong Zeng^a,
Wanli Xiao^a, Bing An^b

^aSchool of Mechanical Science & Engineering, Huazhong University of Science & Technology, Wuhan, 430074, P. R. China

^bState Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science & Technology, Wuhan, 430074, P. R. China

^cDepartment of Physics and Astronomy, Clemson University, Clemson, South Carolina, 29634-0978, USA

Corresponding author:

Dr. Jiangying Peng

School of Mechanical Science & Engineering

Huazhong University of Science & Technology

Wuhan, 430074, P. R. China

E-mail: jiangyingpeng@mail.hust.edu.cn

Abstract: Nanocomposite engineering has been proved effective in diverse regimes of material research to attain a performance beyond each constituent phase. In this work, Yb-filled CoSb₃ (bulk matrix/host)-Bi_{0.4}Sb_{1.6}Te₃ (secondary inclusion) thermoelectric nanocomposites have been synthesized via an *ex situ* process.

$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ inclusions are mainly distributed at the grain boundaries of $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ matrix in the composites. In particular, Te diffuses *in situ* from $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ through $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ matrix during the hot pressing process. This, combined with the grain boundary effect, results in favourable changes in the carrier concentration, carrier mobility, electrical resistivity, Seebeck coefficient, and thermal conductivity. Such synergistic changes are notably absent in the stand-alone Te-doped Yb-filled CoSb_3 , suggesting the key role of diffusion and grain boundaries. As a result, a maximum ZT value of 0.96 has been attained for $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ -2wt% $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ at 650 K. The present work opens a new avenue towards high performance thermoelectric composites via controlled inter-constituent diffusion and grain boundary effect.

Keywords: A. functional alloys; B. thermoelectric properties, diffusion; D. grain boundary.

1 Introduction

Thermoelectric (TE) materials have recently drawn much attention due to the capability of directly converting heat into electricity and *vice versa*. The conversion efficiency of a TE material is determined by its dimensionless figure of merit $ZT = \alpha^2 T / \rho \kappa$, where α , ρ , κ , T are the Seebeck coefficient, electrical resistivity, thermal conductivity and absolute temperature, respectively. The electrical property term α^2 / ρ is called power factor. The total thermal conductivity κ is composed of the electronic component κ_e and the lattice component κ_L . Easing the otherwise adversely inter-dependent Seebeck coefficient, electrical conductivity, and thermal conductivity for higher ZT is at the core of TE study [1]. To this end, the

nanocompositing approach is proven effective to attain a performance beyond the constituent phases [2-6]. In nanocomposites, a number of mechanisms can be implemented concertedly to enhance TE performance. Energy filtering effect at the interface enhances the Seebeck coefficient and the power factor [7,8]. In addition, modulation doping instead of uniform doping can be implemented to increase the carrier concentration without degrading the mobility much [9,10]. In the mean time, all scale hierarchical architectures can be utilized to lower the lattice thermal conductivity [11]. Importantly, the compositing approach can be employed in tandem with the conventional doping approach, e.g., introducing resonant levels [12].

In this work, we composite Yb-filled CoSb₃ (the bulk matrix) and heavily doped Bi₂Te₃ (the secondary inclusion) in the hope of attaining high TE performance. CoSb₃-based skutterudites are well known promising TE material in medium temperature power generation applications. Skutterudites are structurally unique in that their crystal structure contains naturally formed voids (cages). Filling these voids with rare-earth, alkaline-earth, In, or Tl atoms leads to a remarkable decrease of the κ_L [13-17], thereby increasing the ZT . However, the κ_L of skutterudites, especially of *n*-type filled-skutterudites, is still somewhat high compared to other state-of-the-art TE materials such as Bi₂Te₃. To further reduce the κ_L , effective phonon scatters such as grain boundaries and point defects are needed, however, the same will degrade the charge carrier mobility. In light of the numerous grain boundaries in a composite, retaining or even increasing the charge carrier mobility becomes the key issue.

Recently a number of investigations have reported increased carrier mobility in nanocomposites but the underlying mechanisms are not fully clear [18-22]. The study of La-filled CoSb_3 / nano- Al_2O_3 [23] and CoSb_3 / nano- ZrO_2 composites [24] revealed that the ceramic nano particles distributed at the matrix/host grain boundaries degraded the electrical conductivity. On the other hand, introducing metallic Ag [18], semiconducting AgSbTe_2 [19,20] and InSb [21], as well as graphene [22] nanoinclusions effectively enhanced the charge carrier mobility of the composites. These results demonstrated the significance of proper selection of the secondary inclusions and the appropriate connection between constituent phases in composite engineering. Generally, a second phase with high electrical conductivity is preferable to retain the carrier mobility in a composite, furthermore, it is desired if the secondary inclusion itself is a high performance TE material. This motivates us to employ heavily doped Bi_2Te_3 as the secondary inclusion in the present work.

In this work, an *ex situ* process was utilized to incorporate $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ inclusion into $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ matrix. High temperature thermoelectric property measurements reveal that a simultaneous optimization in all α , ρ , and κ has been achieved. More interestingly, the simultaneous optimization was absent in the stand alone Te-doped Yb-filled CoSb_3 [25]. Such a stark contrast has been ascribed to the special role of diffusion and grain boundary between the bulk matrix and the secondary inclusions.

2 Experimental procedures

$\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ and $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ were separately synthesized as follows. Stoichiometric amounts of Co powder (99.5%), Sb shot (99.99%), and Yb ingot (99.9%) were mixed

and sealed in evacuated quartz tubes, which then were slowly heated to 1323 K and held for 24h, then cooled to 923 K and held for another 4 days, before furnace cooled to room temperature. $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ was prepared via mechanical alloying method. Stoichiometric amounts of Bi powder (99.99%), Sb powder (99.99%) and Te powder (99.99%) were loaded into a ball mill jar (planetary ball mill: QM-QX2, Nanjing University, China), then mechanically alloyed for 20 h at 400 rpm in vacuum using stainless steel balls and jar. To obtain $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}/x$ wt% $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ composites (x denotes the weight percentage of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$, $x = 0, 2, 4, 6$). Hereafter $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}/x$ wt% $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ composite will be designated as matrix- x , and $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ as BST), the bulk matrix $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ was hand ground and mixed with BST powders in the planetary mill at 400 rpm for 1 h in vacuum. Finally the mixed powders were densified by hot pressing at 873 K and 100 MPa for 2 h in argon atmosphere. For the purpose of measuring the TE properties of the second phase component itself, a BST bulk sample was hot pressed at 773 K and 100 MPa for 2 h in argon atmosphere.

Phase characterization was performed by X-ray powder diffraction (PANalytical Empyrean diffractometer with Cu $K\alpha$ radiation). The lattice parameter of the skutterudite structure was analyzed via Rietveld refinement (2θ : 30-140°, step size: 0.013°). Scanning electron microscopy (SEM, FEI: Quanta 200), and field emission transmission electron microscopy (FE-TEM, FEI: Tecnai G2 F30) equipped with energy dispersive X-ray spectroscopy (EDS) were used to inspect the microstructure. The hot pressed samples were cut by diamond saw into $8\times 8\times 2$ mm³ squares for

thermal diffusivity measurements and $15 \times 3 \times 4 \text{ mm}^3$ bars for electrical resistivity/Seebeck coefficient measurements. All the TE property measurements were carried out from 300 to 773 K. The Seebeck coefficient / electrical resistivity measurements were performed simultaneously on an Ulvac-Riko ZEM-2 system. The uncertainty of the electrical resistivity values is within 5%, and that of the Seebeck coefficients within 2%. The thermal conductivity (κ) was obtained by a combination of thermal diffusivity (D) measurement on the Netzsch Microflash 457 using the transient method, special heat capacity (C_p) measurement on the Netzsch Pegasus DSC and density (d) measurement via Archimedes method, through the relation $\kappa = DC_p d$. Room temperature Hall coefficient measurement was performed on a Hall effect measurement system (Ecopia HMS 5500) using a Van der Pauw method under an applied magnetic field of 0.55 T. The carrier concentration n and Hall mobility μ_H were estimated from the measured Hall coefficient R_H and the electrical resistivity ρ via the relations, $n = 1/eR_H$ and $\mu_H = R_H/\rho$, where e is the electron charge.

3 Results and discussion

3.1 Structural analysis

The phase components of all samples were checked by X-ray powder diffraction. Figure 1 displays the patterns of $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ ingot, mechanical alloyed BST, hot pressed matrix-2 and matrix-6 composites. The pattern of $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ is indexed to Skutterudite structure (JCPDS: 03-065-3144) with good crystallinity and no second phase detected. The pattern of BST shows peaks consistent with a rhombohedral

$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ structure (JCPDS: 01-072-1836). The pattern of matrix-2 composite shows only skutterudite structure without BST peaks due to the low volume content of BST. With increasing amount of BST, weak BST peaks emerge in the patterns of matrix-4 and matrix-6. The lattice parameter L of the skutterudite structure was calculated via the Rietveld refinement, the results are listed in Table 1. As shown the L are increased monotonously with increasing BST content, which is ascribed to the Te diffusion from BST to the matrix (cf. section 3.2). We note that Te is a commonly used n -type dopant in CoSb_3 that substitutes Sb and enlarges the lattice constant [26-28]. Thus the lattice expansion of the skutterudite structure is due to Te from BST entering into and doping the matrix.

Figure 1. The powder X-ray diffraction patterns of $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$, $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$, matrix-2 and matrix-6 composites.

Figure 2. (a) A back scattered electron image of polished matrix-2 sample. (b) An enlarged back scattered electron image on the same sample. The red ellipses show the BST phase distributed at the grain boundaries.

Table 1. Some physical and transport properties of the studied materials at room temperature.

Composition	L (Å)	ρ (μohm-m)	n (10^{19} cm^{-3})	μ_H ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	α (μVK^{-1})	m^* (m_0)	κ ($\text{Wm}^{-1}\text{K}^{-1}$)	L_0 ($10^{-8}\text{V}^2\text{K}^{-2}$)	E_g (eV)	ZT
$\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$	9.0446	48	-8.9	15	-176	2.2	2.8	1.66	0.28	0.07
Matrix-2	9.0461	11	-12.3	45	-179	2.8	2.5	1.66	0.31	0.34
Matrix-4	9.0465	13	-13.2	36	-167	2.6	2.3	1.68	0.32	0.27
Matrix-6	9.0467	14	-13.5	33	-160	2.5	2.2	1.70	0.32	0.25
BST	-	21	1.4	221	213	-	0.8	-	-	0.80

SEM analysis has been conducted to investigate the distribution of BST in all samples.

Figure 2(a) shows a back scattered electron image of polished matrix-2 sample.

Figure 2(b) presents an enlarged back scattered electron image on the same sample.

BST phase shows different contrast from the matrix, as confirmed by EDS analysis.

The estimated average grain size of the host matrix is about 3 μm , and it varies little with the BST content.

Figure 3. (a) A TEM bright field image of matrix-4, (b) the EDS result corresponding to the red point in (a).

Figure 4. (a) A high resolution lattice image around matrix/BST boundary in matrix-4 sample, (b) a FFT image calculated from the white color rectangular area in (a), and (c) a FFT image calculated from the red color rectangular area in (a), (d) a SAED pattern obtained in the matrix area.

Figure 3(a) shows a TEM bright field image of matrix-4 sample. Figure 3(b) displays the EDS result corresponding to the point in figure 3(a), which clearly indicates Bi-Sb-Te composition. EDS analysis on the surrounding grains confirmed the bulk matrix/host composition. To further analysis the microstructures, high resolution

lattice image and selected area electron diffraction (SAED) pattern have been obtained. Figure 4(a) shows a high resolution lattice image around a matrix/BST boundary in matrix-4 sample. Figure 4(b) is a Fast Fourier Transformation (FFT) image calculated from the white color rectangular area in Figure 4(a), indexed to skutterudite structure along $[-1\ 1\ 0]$ zone axis; while figure 4(c) is a FFT image calculated from the red color rectangular area in figure 4(a), indexed to $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ structure along $[11\ 1\ -2]$ zone axis. The inset of figure 4(d) is a SAED pattern obtained on the bulk matrix area, which is indexed to skutterudite structure along $[-1\ 1\ 0]$ zone axis. Based on the results of XRD, SEM, EDS, and TEM analysis, it is concluded that the composites are composed of the $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ bulk matrix/ host and BST inclusion, and the BST inclusion is mainly distributed at the grain boundaries of the matrix phase.

3.2 Thermoelectric properties

Figure 5. The electrical resistivity of the studied materials as a function of temperature. The inset shows the temperature dependence of the electrical resistivity of BST. The resistivity of $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{11.4}\text{Te}_{0.6}$ from [25] is also given.

Figure 6. The Seebeck efficient of the studied materials as a function of temperature. The inset shows the temperature dependence of the Seebeck coefficient of BST. The Seebeck coefficient of $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{11.4}\text{Te}_{0.6}$ from [25] is also given.

Figure 5 and 6 show the temperature dependent electrical resistivity and Seebeck

coefficient, respectively. In general, the electrical resistivity is decreased significantly in the entire temperature range compared with the pristine sample. To examine the electrical transport behavior the Hall effect measurement was carried out at room temperature. The physical and transport properties of the studied materials at room temperature are summarized in Table 1. It is interesting to note that both the carrier concentration and the mobility are increased substantially upon BST addition, while these two physical properties are often inversely correlated in single phased material. We herein attribute this interesting observation to the Te diffusion from BST to skutterudite host and the ground boundary effects.

Figure 7. The lattice parameter L of the skutterudite host and carrier concentration n of the composites at room temperature vs. the BST content. Inset shows an empirical correlation between n and L for literature reported Te-doped CoSb_3 [26,30,31] and the samples of this work at room temperature. The estimated increase rate of $\Delta n / \Delta L$ of Te-doped CoSb_3 above the turning point is 2297, and the rate of the samples in this work is 2325.

Figure 7 presents the room temperature lattice parameter of the skutterudite host as well as the composite carrier concentration as a function of the BST content. The lattice parameter L of the skutterudite host systematically increases with increasing BST content. In our previous work on hot

pressed segmented $\text{La}_{0.1}\text{Co}_{3.8}\text{Fe}_{0.2}\text{Sb}_{12} / \text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ TE materials, an opposite diffusion of (Te, Sb) cross the heterogeneous interface had been observed (Figure 4 in [29]). Though here it is very difficult to directly detect the Te content within the

matrix grains after compositing due to the low volume content of BST, the scenario of Te doping is also supported by the variation of the carrier concentration n . The inset of Figure 7 shows an empirical correlation between the n and L for literature reported Te-doped CoSb_3 [26,30,31] and the samples of this work. In Te-doped CoSb_3 , both of the L and n linearly increase with the Te content due to Te substitution of Sb and acting as electron donor [26,30,31], leading to an empirical linear correlation between the n and L . Notably, there is a turning point near the composition of $x=0.02$ of $\text{Co}(\text{Sb}_{1-x}\text{Te}_x)_3$. The same turning point of $x=0.02$ had been reported in the plot of lattice parameter vs. doping content in $\text{Co}(\text{Sb}_{1-x}\text{Te}_x)_3$ [26]. Y. Nagamoto et al. had pointed out there exist two conduction bands in the heavily Te-doped CoSb_3 based on the temperature dependence of the Seebeck coefficient [30]. The lattice parameter of the $x=0$ sample (Yb-filled CoSb_3) is higher than the reported value of the Te-doped CoSb_3 under the same carrier concentration, implying that Yb-filling has more significant effect on the lattice expansion than Te-doping. Importantly, the samples in this work follow a same trend of Δn (the change of carrier concentration) vs. ΔL (the change of lattice parameter) as that of heavily Te-doped CoSb_3 above the turning point, confirming the carrier concentration increment of the composites is ascribed to Te from BST entering into and doping the matrix. In the previous work on hot pressed segmented $\text{La}_{0.1}\text{Co}_{3.8}\text{Fe}_{0.2}\text{Sb}_{12}/\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ composite, hot pressing at 823 K for 2 h and then at 723 K for another 3 h led to an average diffusion distance of $\sim 20 \mu\text{m}$ for Te into $\text{La}_{0.1}\text{Co}_{3.8}\text{Fe}_{0.2}\text{Sb}_{12}$ (Figure 4 in [29]). Here the average diffusion distance of Te into the matrix phase under the synthesis condition was estimated via the diffusion

relation $L_{D1}/\sqrt{D_c t_1} = L_{D2}/\sqrt{D_c t_2}$ [32], where L_D represents average diffusion distance,

D_c is the diffusion coefficient of Te in CoSb₃ at the hot pressing temperature, and t is

the holding time. Using $L_{D1}=20\text{ }\mu\text{m}$, $t_1=5\text{ h}$, $t_2=2\text{ h}$, the average diffusion distance

$L_{D2}=12.6\text{ }\mu\text{m}$ was obtained, which is larger than the average grain size of $3\text{ }\mu\text{m}$.

Therefore Te diffusion is through the inner grains.

Despite the increased carrier concentration, the carrier mobility is enhanced

drastically compared with the BST-free matrix (the pristine sample). This is opposite

to the observation in single phased Te-doped CoSb₃ [30,31,33] and Te-doped Sr-filled

Sr_yCo₄Sb_{12-x}Te_x [34], in which Te substitution decreases the charge carrier mobility

owing to increased ionized impurity scattering. The carrier mobility μ equals $e\tau/m^*$,

where τ is the relaxation time and m^* the effective mass. The room temperature m^*

was thus estimated from the measured Seebeck coefficient and carrier concentration

in the context of a single parabolic band model with acoustic phonon scattering as

predominant carrier scattering mechanism. In this model, α and n can be expressed as

[35]:

$$\alpha = \pm \frac{\kappa_B}{e} \left(\frac{2F_1(\eta)}{F_0(\eta)} - \eta \right) \quad (1)$$

$$n = \frac{4}{\sqrt{\pi}} \left(\frac{2\pi m^* \kappa_B T}{h^2} \right)^{3/2} F_{1/2}(\eta) \quad (2)$$

$$F_i(\eta) = \int_0^\infty \frac{x^i dx}{1 + e^{(x-\eta)}} \quad (3)$$

where F_i are Fermi integrals, $\eta=E_F/\kappa_B T$, E_F is the electron Fermi level measured from

the band edge, κ_B Boltzmann's constant, and h Planck's constant. The calculated

effective masses, as listed in Table 1, are in agreement with the literature data of

n-type skutterudites [33], and they slightly increase with BST inclusion. Therefore considering the increased ionized impurity scattering due to Te doping, the increased carrier mobility can't be explained in the context of bulk matrix/host. Though the exact physical mechanisms are not fully clear, it should be noted that generally grain boundaries are high resistive compared with the inner grains, since there are high density of interface states and disorders, and possible segregation of doping atoms. If the inter-grain conductivity is increased remarkably, the electrical conductivity of the composite would be increased considerably. In this work, as known, Yb is ready to oxidize during synthesis process, resulting in the low conductivity in $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$. Note that the BST has good carrier mobility (the room temperature μ_H equals $221 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), hence it is plausible to infer that the apparent increase of the carrier mobility is due to the grain boundaries and the good connection underlain by BST. The Seebeck coefficient and Hall coefficient measurements confirmed *n*-type conduction characteristic. The magnitude of the Seebeck coefficient is decreased with the increasing BST content, due to the increased carrier concentration. However, comparing the Seebeck coefficient of matrix-2 sample with the pristine sample, it is unusual that the absolute Seebeck coefficient value of matrix-2 is increased despite of the increased carrier concentration. The enlarged Seebeck coefficient may be partially ascribed to the energy filtering effect at the matrix/BST heterogeneous interfaces [19], as band bending at the heterogeneous interface produces a potential barrier which preferentially scatters the charge carriers with lower energy [7,8]. In addition, utilizing the Goldsmid method [36], the thermal band gap E_g has been estimated from

the measured Seebeck coefficient via $E_g = 2eS_{max}T_{max}$, where S_{max} and T_{max} are the maximum Seebeck coefficient and the temperature at which S_{max} occurs. The results listed in Table 1 show that the E_g of the composites are slightly increased compared with the pristine sample, which also can be explained via the enlarged Seebeck coefficients in the composites. It is noteworthy that, since there is an opposite diffusion of (Te,Sb) cross the heterogeneous interface of matrix/BST, the BST composition may be different from the nominal composition. However, as indicated by the HR-TEM analysis, rhombohedral $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ structure is still the main phase. High temperature electrical properties measurements have been performed repeatedly and good repeatability was achieved, confirming the stability behavior. As a result, the power factor is enhanced considerably in the composites due to the large decrease of the electrical resistivity and the increase of the Seebeck coefficient (Figure 8).

Figure 8. The power factor of the studied materials as a function of temperature. The power factor of $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{11.4}\text{Te}_{0.6}$ from [25] is also given.

Figure 9. The thermal conductivity of the studied materials as a function of temperature. The inset is the thermal conductivity of BST as a function of temperature. The thermal conductivity of $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{11.4}\text{Te}_{0.6}$ from [25] is also given.

The thermal conductivity κ is plotted in Figure 9 as a function of temperature. The κ is gradually decreased with BST addition. The κ_L was obtained by subtracting κ_e from κ .

Figure 10. The lattice thermal conductivity of the studied materials as a function of temperature.

κ_e is estimated by the

Wiedemann-Franz relation $\kappa_e = L_0 T / \rho$,

where L_0 is the Lorentz constant. L_0 is

calculated by the formula as follows

[35]:

$$L_0 = \frac{\kappa_B^2}{e^2} \frac{3F_0(\eta)F_2(\eta) - 4F_1^2(\eta)}{F_0^2(\eta)} \quad (4)$$

where the reduced Fermi energy η is obtained from the Seebeck coefficient value according to Equation 1. The calculated L_0 values are summarized in Table 1. The estimated κ_L is plotted in Figure 10 as a function of temperature. The considerably suppressed κ_L with BST addition is attributed to three factors. Firstly Te doping effect leads to enhanced point defect scattering in the matrix/host [26-28], secondly the dispersed BST inclusion generates additional interface scattering at the matrix/BST heterogeneous interfaces, besides that BST inclusion with low thermal conductivity is also beneficial to decrease the κ_L . Thus the combined effect leads to the considerable decrease of the κ_L .

The dimensionless figures of merit ZT of all samples have been calculated from the measured α , ρ , and κ . To highlight the difference made by diffusion and the grain boundary effects, it is instructive to apply a two component effective medium model that takes neither diffusion nor grain boundary effects into account. To this end, Gelbstein proposed analytical expressions of $\{\sigma_{eff}, \alpha_{eff}, \kappa_{eff}\}$ for two extreme conditions [37]: one being conductors connected *in parallel* to both thermal and

Figure 11. The observed as well as the modeled ZT values vs. temperature. The modeled ZT values are out of the parallel and the series configurations, respectively.

Figure 12. The dimensionless figure of merit ZT of the studied materials as a function of temperature. The temperature dependent ZT values of $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{11.4}\text{Te}_{0.6}$ from [25] are also given for comparison.

electrical applied gradients and the other conductors connected *in serial*, based on the early work by Bergman [38] and Levy [39] and general effective medium model [40].

Here the $\{\alpha_{eff}, \sigma_{eff}, \kappa_{eff}\}$ are the effective Seebeck coefficient and the electrical and thermal conductivities, respectively, of the two component composite. In this model, the $\{\alpha_{eff}, \sigma_{eff}, \kappa_{eff}\}$ of the parallel configuration can be expressed as [37]:

$$\begin{aligned}\sigma_{eff} &= \sigma_1 x_1 + \sigma_2 (1 - x_1) \\ \alpha_{eff} &= \frac{\alpha_1 \sigma_1 x_1 + \alpha_2 \sigma_2 (1 - x_1)}{\sigma_1 x_1 + \sigma_2 (1 - x_1)} \\ \kappa_{eff} &= \kappa_1 x_1 + \kappa_2 (1 - x_1)\end{aligned}\tag{5}$$

Where α , σ , κ are the Seebeck coefficient, the electrical and thermal conductivity, respectively, of the various components, and x_1 is the volume fraction of the first component. On the other hand, the $\{\alpha_{eff}, \sigma_{eff}, \kappa_{eff}\}$ of the serial configuration are as follows [37]:

$$\begin{aligned}\sigma_{eff} &= \frac{\sigma_1 \sigma_2}{\sigma_1 (1 - x_1) + \sigma_2 x_1} \\ \alpha_{eff} &= \frac{\alpha_1 \kappa_2 x_1 + \alpha_2 \kappa_1 (1 - x_1)}{\kappa_2 x_1 + \kappa_1 (1 - x_1)}\end{aligned}\tag{6}$$

$$\kappa_{eff} = \frac{\kappa_1 \kappa_2}{\kappa_1(1-x_1) + \kappa_2 x_1}$$

For matrix-2, 4, 6 samples, the volume fractions of BST are calculated to be 2.6, 5.1, 7.6 vol%, respectively. Using the measured $\{\alpha, \rho, \kappa\}$ of $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ and BST, the $\{\alpha_{eff}, \sigma_{eff}, \kappa_{eff}\}$ of the composites under the two conditions were estimated via Equation 5 and 6. The calculated ZT values under these two extreme conditions are compared with the observed values. As shown in Figure 11, the observed ZT values are far beyond the modeled ZT values, which indirectly support the key role of diffusion and grain boundary. Figure 12 displays the observed ZT values of all samples. ZT of the composites have been enhanced significantly due to the enhancement of the power factor and the decrease of the thermal conductivity, and a maximum ZT of 0.96 has been obtained in matrix-2 at 650 K. It should be noted that the enhanced ZT is attained via simultaneous optimization of the $\{\alpha, \rho, \kappa\}$, with the n and μ increased, which is unfeasible in single phased TE materials. For comparison, we plot in Figure 12 the ZT of stand alone Te-doped Yb-filled CoSb_3 [25]. Apparently, $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ -BST composites show superior TE performance, owing to better power factor. Further enhancement of the ZT is expected through the optimization of the matrix composition, second phase composition, and structural design for wide scale phonon scattering.

4 Conclusions

$\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ - $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ composites have been synthesized via an *ex situ* process. $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ inclusions are mainly distributed at the grain boundaries of $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ matrix in the composites. Te from $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ enters through and dopes the matrix

phase/host during hot pressing. This, combined with the grain boundary effect, leads to thermoelectrically favorable changes in the carrier concentration, carrier mobility, Seebeck coefficient, electrical resistivity and thermal conductivity. Notably these synergistic changes are absent in stand alone Yb-filled Te-doped CoSb₃, which points to the key role of diffusion and grain boundaries. As a result the ZT is increased remarkably with Bi_{0.4}Sb_{1.6}Te₃ addition, and a maximum ZT of 0.96 is obtained in matrix-2 at 650 K. Further enhancement of the ZT is expected through the optimization of the matrix composition, second phase composition, and structural design.

Acknowledgements:

This work is co-supported by National Natural Science Foundation of China (51271084) and the Natural Science Foundation of Hubei province (2012FFB02215). The work at Clemson University is supported by National Science Foundation of the United States (DMR-1307740). The technical assistance from the Analytical and Testing Center of Huazhong University of Science & Technology is also gratefully acknowledged.

References:

- [1] M. S. Dresselhaus, G. Chen, M.Y. Tang, R.G. Yang, H. Lee, D.Z. Wang, Z.F. Ren, J.P. Fleurial, P. Gogna, New directions for low-dimensional thermoelectric materials, Adv. Mater. 19(8) (2007) 1043-1053.

- [2] W. S. Liu, X. Yan, G. Chen, Z.F. Ren, Recent advances in thermoelectric nanocomposites, *Nano Energy* 1(1) (2012) 42-56.
- [3] H. Alam, S. Ramakrishna, A review on the enhancement of figure of merit from bulk to nano-thermoelectric materials, *Nano Energy* 2(2) (2013) 190-212.
- [4] K.F. Hsu, S. Loo, F. Guo, W. Chen, J.S. Dyck, C. Uher, T. Hogan, E.K. Polychroniadis, M.G. Kanatzidis, Cubic $\text{AgPb}_m\text{SbTe}_{2+m}$: Bulk Thermoelectric Materials with High Figure of Merit, *Science* 303 (2004) 818-821.
- [5] X.B. Zhao, X.H. Ji, Y.H. Zhang, T.J. Zhu, J.P. Tu, and X.B. Zhang, Bismuth telluride nanotubes and the effects on the thermoelectric properties of nanotube-containing nanocomposites, *Appl. Phys. Lett.* 86 (2005) 062111.
- [6] B. Poudel, Q. Hao, Y. Ma, Y.C. Lan, A. Minnich, B. Yu, X. Yan, D.Z. Wang, A. Muto, D. Vashaee, X.Y. Chen, J.M. Liu, M.S. Dresselhaus, G. Chen, Z.F. Ren, High-thermoelectric performance of nanostructured bismuth antimony telluride bulk alloys, *Science* 320 (2008) 634-638.
- [7] J.P. Heremans, C.M. Thrush, and D.T. Morelli, Thermopower enhancement in PbTe with Pb precipitates, *J. Appl. Phys.* 98 (2005) 063703.
- [8] A. Shakouri, M. Zebarjadi, *Thermal Nanosystems and Nanomaterials*, Ed: S. Volz, Springer, Berlin, 2009.
- [9] M. Zebarjadi, G. Joshi, G.H. Zhu, B. Yu, A. Minnich, Y.C. Lan, X.W. Wang, M. Dresselhaus, Z.F. Ren, and G. Chen, Power Factor Enhancement by Modulation Doping in Bulk Nanocomposites, *Nano Lett.* 11 (2011) 2225-2230.

- [10] B. Yu, M. Zebarjadi, H. Wang, K. Lukas, H.Z. Wang, D.Z. Wang, C. Opeil, M. Dresselhaus, G. Chen, and Z.F. Ren, Enhancement of Thermoelectric Properties by Modulation-Doping in Silicon Germanium Alloy Nanocomposites, *Nano Lett.* 12 (2012) 2077-2082.
- [11] K. Biswas, J.Q. He, I.D. Blum, C.-I Wu, T.P. Hogan, D.N. Seidman, V.P. Dravid, M.G. Kanatzidis, High-performance bulk thermoelectrics with all-scale hierarchical architectures, *Nature* 489 (2012) 414-418.
- [12] J.P. Heremans, V. Jovovic, E.S. Toberer, A. Saramat, K. Kurosaki, A. Charoenphakdee, S. Yamanaka, G.F. Snyder, Enhancement of thermoelectric efficiency in PbTe by distortion of the electronic density of states, *Science* 321 (2008) 554-557.
- [13] B.C. Sales, D. Mandrus, R.K. Williams, Filled Skutterudite Antimonides: A New Class of Thermoelectric Materials, *Science*, 272 (1996) 1325-1328.
- [14] T. He, J.Z. Chen, H.D. Rosenfeld and M.A. Subramanian, Thermoelectric Properties of Indium-Filled Skutterudites, *Chem. Mater.* 18 (2006) 759-762.
- [15] J. Yang, W. Zhang, S.Q. Bai, Z. Mei, and L.D. Chen, Dual-frequency resonant phonon scattering in $\text{Ba}_x\text{R}_y\text{Co}_4\text{Sb}_{12}$ ($\text{R} = \text{La}$, Ce , and Sr), *Appl. Phys. Lett.* 90 (2007) 192111.
- [16] X. Shi, J. Yang, J.R. Salvador, M.F. Chi, J.Y. Cho, H. Wang, S.Q. Bai, J.H. Yang, W.Q. Zhang, L.D. Chen, Multiple-filled skutterudites: high thermoelectric figure of merit through separately optimizing electrical and thermal transports, *J. Amer. Chem. Soc.* 133 (2011) 7837-7846.

- [17] J.Y. Peng, W. Xu, Y.G. Yan, J.Y. Yang, L.W. Fu, H. Kang, and J. He, Study on lattice dynamics of filled skutterudites $\text{In}_x\text{Yb}_y\text{Co}_4\text{Sb}_{12}$, J. Appl. Phys. 112 (2012) 024909.
- [18] X.Y. Zhou, G.Y. Wang, L. Zhang, H. Chi, X.L. Su, J. Sakamoto, C. Uher, Enhanced thermoelectric properties of Ba-filled skutterudites by grain size reduction and Ag nanoparticle inclusion, J. Mater. Chem. 22 (2012) 2958-2964.
- [19] J.Y. Peng, L.W. Fu, Q.Z. Liu, M. Liu, J.Y. Yang, D. Hitchcock, M.H. Zhou, J. He, A study of $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ - AgSbTe_2 nanocomposites: simultaneous enhancement of all three thermoelectric properties, J. Mater. Chem. A 2 (2014) 73-79.
- [20] L.W. Fu, J.Y. Yang, Y. Xiao, J.Y. Peng, M. Liu, Y.B. Luo, G. Li, AgSbTe_2 nanoinclusion in $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$ for high performance thermoelectric, Intermetallics 43 (2013) 79-84.
- [21] G.J. Tan, H. Chi, W. Liu, Y. Zheng, X.F. Tang, J. He and C. Uher, Toward high thermoelectric performance p-type $\text{FeSb}_{2.2}\text{Te}_{0.8}$ via *in situ* formation of InSb nanoinclusions, J. Mater. Chem. C 3 (2015) 8372-8380.
- [22] B. Feng, J. Xie, G.S. Cao, T.J. Zhu, X.B. Zhao, Enhanced thermoelectric properties of p-type CoSb_3 /graphene nanocomposite, J. Mater. Chem. A 1 (2013) 13111-13119.
- [23] T. Itoh, M. Matsuhara, Influence of Addition of Alumina Nanoparticles on Thermoelectric Properties of La-Filled Skutterudite CoSb_3 Compounds, Mater. Trans. 53(10) (2012) 1801-1805.

- [24] Z.M. He, C. Stiewe, D. Platzek, G. Karpinski, E. Muller, S.H. Li, M. Toprak, M. Muhammed, Nano ZrO₂/CoSb₃ composites with improved thermoelectric figure of merit, *Nanotechnology* 18 (2007) 235602.
- [25] J. Khaliq, Q.H. Jiang, J.Y. Yang, K. Simpson, H.X. Yan, and M.J. Reece, Utilizing the phonon glass electron crystal concept to improve the thermoelectric properties of combined Yb-stuffed and Te-substituted CoSb₃, *Scripta Mater.* 72-73 (2014) 63-66.
- [26] K.T. Wojciechowski, J. Tobola, J. Leszczynski, Thermoelectric properties and electronic structure of CoSb₃ doped with Se and Te, *J. Alloys Compd.* 361 (2003) 19-27.
- [27] X.Y. Li, L.D. Chen, J.F. Fan, W.B. Zhang, T. Kawahara, T. Hirai, Thermoelectric properties of Te-doped CoSb₃ by spark plasma sintering, *J. Appl. Phys.* 98 (2005) 083702.
- [28] W.S. Liu, B.P. Zhang, J.F. Li, H.L. Zhang, L.D. Zhao, Enhanced thermoelectric properties in CoSb_{3-x}Te_x alloys prepared by mechanical alloying and spark plasma sintering, *J. Appl. Phys.* 102 (2007) 103717.
- [29] J.Y. Peng, T.J. Zhang, J.Y. Yang, K. Cui, Preparation and interface analysis of the segmented CoSb₃/Bi₂Te₃ thermoelectric materials, *Mater. Sci. Forum* 423-425 (2003) 373-376.
- [30] Y. Nagamoto, K. Tanaka, T. Koyanagi, Transport Properties of Heavily Doped N-Type CoSb₃, in *Proc. of 17th Int. Conf. on Thermoelectrics*, IEEE, 1998, 302-305.

- [31] B. Duan, P.C. Zhai, L.S. Liu, Q.J. Zhang, X.F. Ruan, Synthesis and high temperature transport properties of Te-doped skutterudite compounds, *J. Mater. Sci.: Mater. Electron.* 23 (2012) 1817-1822.
- [32] J.H. Huang, *Diffusion in Metals and Alloys*, Metallurgical Industry Press, Beijing, 1996.
- [33] T. Caillat, A. Borshchevsky, J.P. Fleurial, Properties of single crystalline semiconducting CoSb_3 , *J. Appl. Phys.* 80 (1996) 4442-4449.
- [34] X.Y. Zhao, S.Q. Bai, X.Y. Li, Y.F. Zhou, L.D. Chen, Effect of Te Doping on Thermoelectric Property of $\text{Sr}_y\text{Co}_4\text{Sb}_{12-x}\text{Te}_x$ Compounds, *J. Inorg. Mater.* 24 (2009) 803-807.
- [35] V.I. Fistul, *Heavily Doped Semiconductors*, Plenum, New York, 1969.
- [36] H. Goldsmid, J. Sharp, Estimation of the Thermal Band Gap of a Semiconductor from Seebeck Measurements, *J. Electron. Mater.* 28 (1999) 869-872.
- [37] Y. Gelbstein, Thermoelectric power and structural properties in two-phase Sn/SnTe alloys, *J. Appl. Phys.* 105 (2009) 023713.
- [38] D.J. Bergman and O. Levy, Thermoelectric properties of a composite medium, *J. Appl. Phys.* 70 (1991) 6821-6833.
- [39] O. Levy and D.J. Bergman, Scaling behaviour of the thermopower in a two-component composite near a percolation threshold, *J. Phys. A: Math. Gen.* 25 (1992) 1875-1884.
- [40] D.S. McLachlan, M. Blaszkieicz and R.E. Newnham, Electrical Resistivity of Composites, *J. Am. Ceram. Soc.* 73 (1990) 2187-2203.