Microstructure and thermoelectric properties of CoSb$_{2.75}$Ge$_{0.25-x}$Te$_x$ prepared by rapid solidification

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Abstract

Since the vibration modes of the pnicogen rings in CoSb$_3$-based skutterudites fall within the range of frequencies of heat-carrying phonons, disruption of the rings by doping should have a strong influence on heat transport in this material. To test the premise, single-phase double-doped CoSb$_{2.75}$Ge$_{0.25-x}$Te$_x$ ($x = 0.125–0.20$) compounds were synthesized by combining melt spinning with a spark plasma sintering method. Following the melt-spinning process, the side of the ribbons contacting the copper drum is featureless and reflects its amorphous nature while the free surface of the ribbons is composed of 30–80 nm grains. After spark plasma processing the average grain size of the bulk samples is about 200 nm. High-resolution transmission electron microscopy images show an in situ nanostructure consisting of circular, 15 nm diameter dots of Te- and Ge-enriched skutterudite phase embedded in the skutterudite matrix. Transport properties were measured from 2 to 800 K as a function of Te and Ge content on the pnicogen (Sb) rings and the results were correlated with the structural data. Double-doping on pnicogen rings with Ge and Te, and using melt-spinning processing, results in binary skutterudite compounds that possess an impressive figure of merit of $ZT \approx 1.1$ at 750 K.

Keywords: Melt spinning; Electrical resistivity/conductivity; Nanocomposite; Thermal conductivity

1. Introduction

Unlike mechanical heat engines, thermoelectricity uses a material’s inherent charge carriers (electrons and holes) and their entropy to convert heat directly into electricity [1]. The efficiency of a thermoelectric material is determined by the dimensionless figure of merit $ZT = \frac{2}{\kappa}a^2\sigma T / k$, where $a$, $\sigma$, $\kappa$ and $T$ are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. Although there is no theoretical limit to the practically attainable $ZT$, maximizing one transport parameter adversely affects the other two and it is difficult to achieve values of $ZT$ greater than unity [2].

Recently, CoSb$_3$-based skutterudites have received considerable attention as prospective novel thermoelectric materials due to their medium band gap of 0.22 eV, high carrier mobility and open crystal structure [3,4]. Unfortunately, the thermal conductivity of binary skutterudites is too high and this has been an impediment to their application as thermoelectric materials. Structural voids in the skutterudite lattice can, however, be filled with foreign species, which results in the so-called filled skutterudites [5]. Due to the strong “rattling” motion of fillers, the thermal conductivity is much suppressed [6,7] and filled skutterudites have become a prime focus of research on novel thermoelectric materials. Another interesting structural feature of skutterudites are the near-square planar pnicogen rings. Because vibrational frequencies of pnicogen rings fall within the range of frequencies of heat-carrying phonons, disruption of the rings by doping should have a strong influence on heat transport in this material. To test the premise, single-phase double-doped CoSb$_{2.75}$Ge$_{0.25-x}$Te$_x$ ($x = 0.125–0.20$) compounds were synthesized by combining melt spinning with a spark plasma sintering method. Following the melt-spinning process, the side of the ribbons contacting the copper drum is featureless and reflects its amorphous nature while the free surface of the ribbons is composed of 30–80 nm grains. After spark plasma processing the average grain size of the bulk samples is about 200 nm. High-resolution transmission electron microscopy images show an in situ nanostructure consisting of circular, 15 nm diameter dots of Te- and Ge-enriched skutterudite phase embedded in the skutterudite matrix. Transport properties were measured from 2 to 800 K as a function of Te and Ge content on the pnicogen (Sb) rings and the results were correlated with the structural data. Double-doping on pnicogen rings with Ge and Te, and using melt-spinning processing, results in binary skutterudite compounds that possess an impressive figure of merit of $ZT \approx 1.1$ at 750 K.

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phonons, judicious distortions of the rings by substituting for Sb should also be a very effective means of reducing the thermal conductivity. Most recently, incorporation of nanometer-scale inclusions in the bulk skutterudite matrix has proved yet another successful approach to disrupting the flow of heat in the structure [8,9]. Making use of the Callaway model, one can describe the lattice thermal conductivity in terms of the relaxation time as [10,11]:

\[ \tau_{\text{ph}}^{-1} = A\omega^4 + B\omega^2 + C\omega^2/((\omega_0^2 - \omega^2)^2 + D). \]  

(1)

Here \( A, B, C \) and \( D \) are the coefficients of point-defect scattering, phonon Umklapp scattering, resonant scattering and scattering by nanoinclusions, respectively. \( \omega \) is the phonon frequency and \( \omega_0 \) is some resonance frequency. Phonon scattering on nanoinclusions is characterized by the coefficient \( D = 3\pi v_s/2R \), where \( x, R \) and \( v_s \) are the nano-inclusion content, nano-inclusion size and the speed of sound in the matrix [12], respectively.

Point defects and Umklapp processes scatter primarily high-frequency phonons. The task assigned to nano-inclusions is to impede the flow of mid-frequency phonons that otherwise do not scatter readily and carry a significant fraction of heat. In general, the size \( R \), the shape and how nano-inclusions are dispersed are important considerations for effective scattering of phonons. Therefore, how to fabricate bulk nanocomposite materials is an important issue. Of course, for nano-inclusions to enhance thermoelectricity, one implicitly assumes that the nanostructure leaves transport of charge carriers substantially intact. It is here where intuition, experience and knowledge of the phase diagrams come into play. It makes no sense to create a nanocomposite in which charge carriers scatter strongly on nano-inclusions since one could never recover high mobility and any gain in the form of a reduced thermal conductivity would be trumped by the deterioration in the electronic properties. From the perspective of thermoelectricity, effective nanostructures must be coherent with the matrix and should have minimal ionic character. Such nanostructures are termed endotaxial [13].

Recently, we and others have reported on double-doping on the pnicogen rings of CoSb\(_3\) with a combination of dopants that have the average charge of Sb [14,15]. We have also noted that such double-doped skutterudites (in our case pairing Te with Ge) possess a finely dispersed endotaxial nanostructure typified by disk-shape nanodots about 30 nm in diameter of Te- and Ge-enriched skutterudite in the matrix of CoSb\(_3\). We have demonstrated that such double-doped (and unfilled) CoSb\(_3\) structures rival the performance of the best single-filled skutterudites. Since these compounds were prepared by the traditional synthesis method (designated as TM) involving long-term annealing to achieve the skutterudite phase, the grain size of the matrix was large, on the order of micrometers. Clearly, reducing the grain size of the matrix should result in lower thermal conductivities and an even better thermoelectric performance. This is the motivation behind the present work in which we synthesize comparable compositions but use a rapid solidification process called melt spinning that yields structures with the dramatically reduced grain size of the matrix. We designate such melt-spun samples subsequently compacted by spark plasma sintering as MS-SPS. We investigate the evolution of the skutterudite phase, the influence of the fine nanostructure on the transport properties, and we compare the data with those obtained by the traditional method of synthesis.

2. Experiment

Skutterudite compounds were synthesized using high-purity Sb(6N), Co(4N), Te(6N) and Ge(4N) starting materials. Stoichiometric amounts of constituents were weighed in a glovebox under high-purity Ar to prepare CoSb\(_{2.75}\)Ge\(_{0.25}\), Te\(_x\) with \( x \) in the range from 0.125 to 0.20. The charge was sealed in a carbon-coated silica tube under a pressure of \( 10^{-3} \) Pa. The charge was melted and kept at 1373 K for 20 h. Subsequently, the obtained ingots were placed into quartz tubes with a 0.35 mm diameter nozzle and placed under a protective argon atmosphere. Ingots were induction-melted and ejected under a pressure of 0.02 MPa onto a copper roller rotating at a linear speed of 30 m s\(^{-1}\). The obtained ribbons were ground in a glovebox into a fine powder and sintered by SPS at 823 K for 5 min under a pressure of 40 MPa.

The structure was characterized by X-ray diffraction (XRD; PANalytical X’Pert Pro X-ray diffraction CuK\(_\alpha\)). The morphology and element content was determined by back-scattered electron imaging (FESEM, S-4800) and energy dispersive X-ray (EDX) analysis (EDS; Horiba 250). The microstructure was investigated using transmission electron microscopy (TEM; JEM2100F) with EDS. Hall effect measurements were performed from 5 to 300 K in a cryostat equipped with a 5.5 T superconducting magnet. The high-temperature Hall measurements were carried out in a home-built apparatus. Procedures for low-temperature property measurements were the same as described elsewhere [16]. For measurements at high temperatures we relied on a ZEM-1 apparatus (electrical conductivity \( \sigma \) and the Seebeck coefficient \( z \)) and the thermal conductivity \( \kappa \) was calculated from the measured thermal diffusivity \( D \), specific heat \( C_p \) and density \( d \) according to the relationship \( \kappa = D \times C_p / d \). The thermal diffusivity and the specific heat were determined using a laser flash method (NETZSCH, LFA 457) and a power-compensated differential scanning calorimeter (TA, DSCQ20), respectively. Uncertainties in the electrical conductivity, thermopower and thermal conductivity are \( \pm 3\% \), \( \pm 2\% \) and \( \pm 5\% \), respectively, leading to \( \sim 10\% \) uncertainty in \( ZT \).
3. Result and discussion

3.1. Microstructure and phase composition of ribbons

In this study the Ge and Te content has a minor influence on the microstructure and phase composition of the melt-spun ribbons and bulk materials after SPS. Thus, for convenience, we take the compound CoSb$_{2.75}$Ge$_{0.05}$Te$_{0.20}$ as a representative example. Fig. 1 shows the phase composition of a ribbon prepared by ejecting the melt onto a copper roller rotating at $30 \text{ m s}^{-1}$. The ribbon shows a complex phase composition and the diffraction peaks are broad due to the high cooling rate of the melt. The XRD pattern shows that the main phase in the ribbon is CoSb$_2$, Sb and a small amount of CoSb$_3$. We define the side of the ribbon that contacts the copper roller as the contact surface and other side as the free surface. The FESEM image of the free surface of the ribbon is shown in Fig. 2a and depicts evenly distributed nanograins with an average grain size of 30–80 nm. Fig. 2b shows the microstructure of the contact surface of the ribbon. No crystallization phenomena are observed on the contact surface. This is the consequence of the ultrahigh cooling rate when the melt contacts the copper roller rotating at high speed.

We have carried out a thermal analysis of the ribbon using a differential scanning calorimeter and the data are shown in Fig. 3. On the heating cycle, there is a large peak in the range $350$–$500 \text{ °C}$. This peak corresponds to the reaction of CoSb$_2$ with Sb to form the skutterudite CoSb$_3$ phase. Interestingly, the transition temperature is much lower than the $874 \text{ °C}$ predicted by the phase diagram [17]. During the cooling cycle, no peak is observed. This implies that the phase transformation from CoSb$_2$ to the skutterudite phase is completed in less than 4 min. The much lower formation temperature and the rapid transition are due to a much finer (nanometer scale) and homogeneous elemental distribution in the ribbons than in bulk samples prepared by the traditional method (micrometer scale). As a consequence, there is no need for any annealing following the SPS processing of the ribbons.

3.2. Microstructure and phase composition of the bulk ingots

Bulk ingots are obtained by sintering the ribbons using the SPS technique. Fig. 4 shows the XRD pattern of the CoSb$_{2.75}$Ge$_{0.05}$Te$_{0.20}$ bulk sample. The XRD peaks are sharper than those in Fig. 1 and the patterns demonstrate that all bulk samples are single-phase skutterudite structures without any impurity phase such as GeTe and CoTe$_2$ according to JSPDS78-0976. Therefore, co-doping with Ge and Te in the above range of compositions does not change the crystal structure. The lattice constant increases in proportion to the relative amount of Te doped into the structure (see the inset in Fig. 4) and is similar to the lattice parameter of bulk CoSb$_{2.75}$Ge$_{0.025}$Te$_{0.175}$ skutterudites synthesized by the traditional method. This is understood based on the ionic radius of Te (97 pm), which is larger than that of Sb (76 pm) and consistent with the previous studies of Te-doped CoSb$_3$ [15,18,19]. The linear increase in the lattice constant with $x$ indicates that Te and Ge are being substituted on the Sb sites of the CoSb$_3$ crystal structure. For samples of CoSb$_{2.75}$Ge$_{0.05}$Te$_{0.20}$ and CoSb$_{2.75}$Ge$_{0.075}$Te$_{0.175}$, the solid solubility of Te on the Sb site exceeds the solubility of single-doped Te (no more than 5%) [18,19] because of the partial charge compensation by Ge. The respective valence electron counts of Ge, Sb and Te are 4, 5 and 6. A Ge atom substituting for Sb on the square four-member Sb ring compensates for the charge of Te substituted for Sb on the same ring and effectively increases the solid solubility of Te in CoSb$_3$. This is similar to the case of co-doped Te and Sn in CoSb$_3$ [15].

The microstructure of bulk ingots prepared by the combined MS + SPS processing is shown in Fig. 5. It is clear that the grain size is on the scale of 200 nm, i.e. an order of magnitude finer than in the case of the traditional method of synthesis [14]. The grains are well crystallized and highly compacted. In Fig. 6a we show numerous nanodots embedded in the matrix. Fig. 6b depicts nanodots with an average diameter of 15–20 nm spaced about 80–100 nm apart. The high-resolution TEM image in Fig. 6c shows a nanodot of about 15 nm diameter coherently embedded in the matrix. EDS results give the normalized chemical composition of the nanodot (Fig. 6d) and the matrix (Fig. 6e) as CoSb$_{2.05}$Ge$_{0.13}$Te$_{0.235}$ and CoSb$_{2.87}$Ge$_{0.03}$Te$_{0.145}$, respectively. This indicates that the nanostructured phase is rich in Ge and Te, while the matrix is a region poor in Ge and Te. The presence of Ge thus not only tends to increase the solid solubility of Te but it also leads to the in situ formation of a nanostructure. It is energetically more favorable for a Ge and a Te atom to substitute for two Sb atoms on the same ring (i.e. being nearby each other) rather than having the Ge atom on one ring and the Te atom on some other ring. The formation mechanism of the nanostructure here is very similar to the case of a nanostructure in LAST materials where Ag$^+$ and Sb$^{3+}$.
substituting for Pb\(^{2+}\) tend to congregate near each other to minimize the electrostatic energy \([13,20]\). Thus, the essentially Coulombic forces drive the compositional modulation of regions of high Ge and Te content and low Ge and Te content.

3.3. Electrical transport properties of CoSb\(_{2.75}\)Ge\(_{0.25}\)/Co\(_{x}\)Te\(_{x}\) (x = 0.125–0.20)

The electrical conductivity of CoSb\(_{2.75}\)Ge\(_{0.25}\)–Te\(_{x}\) (x = 0.125–0.20) compounds as a function of temperature is shown in Fig. 7. The electrical conductivity, described as \(\sigma = ne\mu\), where \(n\) is the carrier density, \(e\) the electron charge and \(\mu\) the carrier mobility, increases with the increasing content of Te over the whole temperature range. Carrier concentrations of the compounds are listed in Table 1. Compared with the CoSb\(_{2.75}\)Ge\(_{0.05}\)Te\(_{0.20}\) sample synthesized by the traditional method, the electrical conductivity of the melt-spun skutterudite is lower due to stronger grain boundary scattering. On the other hand, compared with the CoSb\(_{2.75}\)Sn\(_{0.05}\)Te\(_{0.20}\) sample synthesized by ball milling \([15]\) followed by SPS, the conductivity of the melt-spun sample is higher. The ball-milled sample has an average grain size of 140 nm, somewhat smaller than the melt-spun sample. Measurements of the Hall effect in conjunction with...
the electrical conductivity allow the carrier density and mobility of samples synthesized by different methods to be compared. The temperature dependence of the Hall mobility for CoSb$_{2.75}$Ge$_{0.05}$Te$_{0.20}$ synthesized by different methods is shown in Fig. 8. Unfortunately, Ref. [15] did not provide mobility data and thus we can compare only samples prepared by TM and MS-SPS. The mobility decreases substantially in the melt-spun sample due to enhanced grain boundary scattering. At high temperatures (above 200 K), acoustic phonon scattering should start to dominate the scattering mechanism and the temperature dependence should approach the $T^{-\frac{3}{2}}$ power law.

The temperature dependence of the Seebeck coefficient $a$ of CoSb$_{2.75}$Ge$_{0.25-x}$Te$_{x}$ ($x = 0.125-0.20$) compounds is shown in Fig. 9. The absolute value of the Seebeck coefficient increases with the decreasing content of Te (the number of disordered rings) due to the decreased carrier concentration. We note that at high temperatures the Seebeck coefficient turns over and its magnitude decreases on account of the onset of intrinsic excitations. The effect is most notable on the fully compensated sample with $x = 0.125$, which has, by far, the lowest carrier density. The onset of intrinsic excitations, and therefore the turnover, occurs in this sample at temperatures as low as 475 K. Comparing samples with the same composition $x = 0.20$, the Seebeck coefficient of the melt-spun sample is practically identical with the samples synthesized by the traditional method and by ball-milling. We therefore see no influence of energy filtering; perhaps the grain size is not small enough. Assuming a simple parabolic band and scattering dominated by acoustic phonons, we express the Seebeck coefficient and electrical conductivity as:

$$
\alpha = -\frac{k_B}{e} \times \left[ \left( r + \frac{5}{2} \right) - \zeta \right],
$$

$$
\sigma = \frac{2e}{\pi m_0 k_B T_0} \left( \frac{T}{T_0} \right)^{\frac{3}{2}} \left( \frac{m^*}{m_0} \right)^{\frac{3}{2}} \mu \exp(\zeta),
$$

where $k_B$, $m^*$, $\zeta$, $r$, $T_0$ and $m_0$ are the Boltzmann constant, effective mass, reduced Fermi level, scattering factor and the free electron mass, respectively. We can then write the Seebeck coefficient as a function of the natural logarithm of electrical conductivity in the form:

$$
\alpha = -\frac{k_B}{e} \times \left[ C + \frac{3}{2} \ln \left( \frac{T}{T_0} \right) + \ln U - \ln \sigma \right],
$$

where $C$ is the scattering factor-related parameter equal to $17.71 + r$, and $U$ is the weighted mobility defined as $(\frac{m^*}{m_0})^{\frac{3}{2}} \mu$. According to the above equation, for a given material system, the value of $\frac{\alpha}{\sigma}$ should be equal to $\frac{k_B}{e} \times 86.2 \mu$V K$^{-1}$. Fig. 10 shows the room temperature Seebeck coefficient of samples CoSb$_{2.75}$Ge$_{0.25-x}$Te$_{x}$ ($x = 0.125-0.20$) synthesized by different methods as a function of the natural logarithm of electrical conductivity. For the samples synthesized by the MS-SPS, the slope is $66.00 \mu$V K$^{-1}$. For the samples synthesized by the traditional method, the slope is $71.67 \mu$V K$^{-1}$. For CoSb$_{1-x}$Te$_{x}$ synthesized by ball milling and SPS, the slope is $105 \mu$V K$^{-1}$ [15]. All these values deviate significantly from the classical result of $\frac{k_B}{e} \times 86.2 \mu$V K$^{-1}$. This fact indicates that the carrier effective mass or the carrier mobility $\mu_H$ is considerably affected by doping. Using the room temperature values of the transport parameters, we calculate the effective mass of the carriers.
and the reduced Fermi level. The effective mass increases and, because Te is a donor impurity, the Fermi level moves from the conduction band to the valence band with decreasing Te content. The band gap $E_g$ can be roughly estimated from the equation $E_g = \frac{2}{\alpha^{2} e^{2}} |\alpha_{max}| T_{max}$ [21], where $e$ is the elementary charge, $\alpha_{max}$ is the peak Seebeck coefficient and $T_{max}$ is the corresponding temperature at which the peak occurs. The calculated band gaps are summarized in Table 1 and are almost unchanged with the level of Ge and Te co-doping.

3.4. Thermal conductivity of CoSb$_{2.75}$Ge$_{0.05}$Te$_{0.20}$

Thermal conductivity as a function of temperature for different Te contents is shown in Fig. 11. In comparison to the sample synthesized by the traditional method, the thermal conductivity of MS-SPS samples is dramatically lower over the whole temperature range. The prominent peak observed in the thermal conductivity of the sample prepared by the traditional method at 41 K is essentially washed out in the MS-SPS sample and becomes a very broad feature akin to amorphous-like thermal transport. For samples with $x = 0.125, 0.150$ and $0.175$ the peak in the thermal conductivity diminishes with increasing content of Te and shifts to higher temperatures. This reflects enhanced phonon scattering as the number of disordered rings increases. The peak on the fully compensated sample, $x = 0.125$, is very pronounced as it corresponds to the smallest number of disordered rings (Ge and Te are paired on the same ring). The ball-milled sample [15] seems to have even lower thermal conductivity but the data do not extend to temperatures below 300 K and so a more detailed comparison is not possible.
The total thermal conductivity $\kappa$ can be written as:

$$\kappa = \kappa_L + \kappa_C,$$

where $\kappa_L$ and $\kappa_C$ are the lattice and carrier thermal conductivity contributions, respectively. The carrier component ($\kappa_C$) can be calculated using the Wiedemann–Franz law as:

$$\kappa_C = L \sigma T,$$

where $L$ is the Lorenz number, $\sigma$ is the measured electrical conductivity and $T$ is the absolute temperature. In this study, we use the fully degenerate value of the Lorenz number $L = 2.45 \times 10^{-8}$ V$^2$ K$^{-2}$. The lattice thermal conductivity is then obtained by subtracting $\kappa_C$ from the total thermal conductivity (see Eq. 12). Again, comparing samples produced by melt spinning and by the traditional method, both with $x = 0.20$, we note a significantly lower lattice thermal conductivity of the former. We also note that the lattice thermal conductivity of MS-SPS samples decreases with increasing Te content, reflecting a greater number of distorted Sb rings. To assess the combined influence of the much reduced grain size in melt-spun samples and the presence of nanodots, we calculate the percentage reduction of the lattice thermal conductivity for samples of the same composition but prepared by the traditional synthesis and by melt spinning (shown in the inset of Fig. 12) as:

$$\text{Reduction Percentage} = \frac{\kappa_{TR} - \kappa_{MS-SPS}^{L}}{\kappa_{TR}^{L}} \times 100\%.$$

The nanostructure lowers the thermal conductivity at low temperatures more dramatically than it does at high temperatures.

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>$\sigma$ ($10^3$ S m$^{-1}$)</th>
<th>$x$ (µV K$^{-1}$)</th>
<th>$R_H$ (cm$^3$ C$^{-1}$)</th>
<th>$N_p$ ($10^{19}$ cm$^{-3}$)</th>
<th>$\mu_H$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$m^*/m_0$</th>
<th>$\eta$</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSb$<em>{2.75}$Ge$</em>{0.25}$Te$_{0.20}$</td>
<td>13.6</td>
<td>-136.3</td>
<td>-0.0132</td>
<td>47.3</td>
<td>16.3</td>
<td>4.54</td>
<td>1.34</td>
<td>0.29</td>
</tr>
<tr>
<td>CoSb$<em>{2.75}$Ge$</em>{0.075}$Te$_{0.175}$</td>
<td>8.2</td>
<td>-157.2</td>
<td>-0.0163</td>
<td>38.3</td>
<td>13.4</td>
<td>5.55</td>
<td>0.87</td>
<td>0.32</td>
</tr>
<tr>
<td>CoSb$<em>{2.75}$ Ge$</em>{0.10}$Te$_{0.15}$</td>
<td>5.0</td>
<td>-217.7</td>
<td>-0.0262</td>
<td>23.9</td>
<td>13.1</td>
<td>6.0</td>
<td>-0.21</td>
<td>0.33</td>
</tr>
<tr>
<td>CoSb$<em>{2.75}$Ge$</em>{0.125}$Te$_{0.125}$</td>
<td>1.0</td>
<td>-297.8</td>
<td>-0.125</td>
<td>5.0</td>
<td>13</td>
<td>6.47</td>
<td>-1.33</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Using a simple kinetic formula for the lattice thermal conductivity:

\[
\kappa_L = \frac{1}{3} \frac{C_v}{v} \frac{l}{C_T}
\]  

we calculate the phonon mean-free path (see Fig. 13) and the percentage reduction of the phonon mean-free path in the MS-SPS and the TM samples. The phonon mean-free path in the TM sample is about 9 μm at 2.6 K, while the phonon mean-free path in the MS-SPS sample is only about 1.4 μm at 2.6 K. At room temperature, the two respective values are 2.2 and 1.3 nm. The nanostructure thus scatters phonons at low temperatures more effectively than it does at high temperatures.

### 3.5. Dimensionless thermoelectric figure of merit $ZT$

The dimensionless thermoelectric figure of merit $ZT$ for our MS-SPS processed compounds is shown in Fig. 14. The analysis of both the electrical and thermal transport properties shows that the increased Seebeck coefficient and the reduced lattice thermal conductivity more than compensate for the reduced electrical conductivity, and $ZT$ is enhanced over the entire range of temperatures compared to the values reported previously for the TM-prepared samples. The
highest ZT in the present series of samples is achieved with CoSb\textsubscript{2.75}Ge\textsubscript{0.05}Te\textsubscript{0.20} and reaches a value in excess of 1.1 at 750 K. The comparison is perhaps most meaningful in terms of the average ZT values between 300 and 800 K. For the MS-SPS sample CoSb\textsubscript{2.75}Ge\textsubscript{0.05}Te\textsubscript{0.20} the average values is 0.73, while for the TM sample of the same composition it is 0.64, i.e. \(~14\%\) enhancement. The improvement in ZT translates into an enhancement in the thermoelectric conversion efficiency \(\eta\). According to the formula \([21]\),

\[
\eta_{opt} = \frac{T_h - T_l}{T_h} \times \frac{(1 + ZT_{avg})^{0.5} - 1}{(1 + ZT_{avg})^{0.5} + T_l/T_h},
\]

where \(T_h\), \(T_l\) and \(ZT_{avg}\) represent the temperature of the hot side, the temperature of the cold side and the average ZT value over the whole temperature range, respectively. Calculated \(\eta_{opt}\) values of 11.7\% compared with 10.5\% are expected for the melt-spun sample and the sample prepared by the traditional synthesis, respectively.

4. Conclusions

Nanostructured single-phase CoSb\textsubscript{2.75}Ge\textsubscript{0.05}Te\textsubscript{x} (\(x = 0.125-0.20\)) compounds were synthesized using the MS-SPS method. The skutterudite phase CoSb\textsubscript{3} is completed in about 4 min. The average grain size after SPS is about 200 nm. High-resolution TEM images reveal the presence of nanodots with diameters of \(~15\) nm embedded in the matrix. The endotaxial nature of the nanostructure scatters phonons more effectively than electrons, resulting in an overall beneficial effect on the thermoelectric properties. ZT values in excess of 1.1 have been achieved at 750 K and the average figure of merit of 0.73 for MS-SPS samples exceeds by 14\% the average ZT value measured on TM-fabricated compounds of identical composition. Compensating double-doping on the pnictogen rings, particularly when used in conjunction with the melt-spinning fabrication route, yields binary skutterudite compounds with impressive thermoelectric performance that rival the properties of the best single-filled skutterudites.

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References