Structure and Transport Properties of Double-Doped CoSb$_{2.75}$Ge$_{0.25-x}$Te$_x$ ($x = 0.125–0.20$) with in Situ Nanostructure

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Abstract: Single-phase skutterudite compounds of composition CoSb$_{2.75}$Ge$_{0.25-x}$Te$_x$ ($x = 0.125–0.20$) were synthesized by the traditional melt-quench-anneal technique followed by spark plasma sintering. Rather than filling the skutterudite structure to reduce the thermal conductivity, the aim here is to use disorder on the pnicogen rings created by doping with both Te and Ge. Since heat-carrying phonons in CoSb$_3$ are those associated with the vibrational modes of the Sb-rings, such disorder should be effective in suppressing heat transport. The electrical transport properties can be tuned by adjusting the relative content of Te and Ge. The electrical conductivity and the thermoelectric power factor of the samples increase with the increasing Te content while the absolute value of the Seebeck coefficient decreases. Compared with the undoped CoSb$_3$, the lattice thermal conductivity is significantly suppressed because of an enhanced solubility of Te leading to an increase in the number of pnicogen rings being distorted. High resolution transmission electron microscopy images reveal an in situ nanostructure consisting of circular, 30 nm diameter dots of a skutterudite phase enriched with the dopants that are embedded in the skutterudite matrix poor in Ge and Te. Apart from phonon point-defect scattering, this nanostructure may also contribute to the overall low lattice thermal conductivity. The thermoelectric figure of merit for the CoSb$_{2.75}$Ge$_{0.05}$Te$_{0.20}$ compound reaches values in excess of 1.1 at 800 K. This value is competitive with single-filled n-type skutterudite compounds.

Keywords: thermoelectric properties, in-situ nanostructure, skutterudite, point defect

Introduction

Thermoelectric (TE) materials are able to convert heat to electricity by purely solid state means. Thermoelectricity has attracted considerable attention as a viable process to convert waste industrial heat into usable electricity as well as for utilization of the solar thermal radiation for environmentally friendly power generation.$^{1–3}$ The efficiency of a TE material is closely related to the dimensionless figure of merit $ZT$, defined as $ZT = \alpha^2 \sigma T / \kappa$, where $\alpha$, $\sigma$, $\kappa$, and $T$ are the Seebeck coefficient, electrical conductivity, total thermal conductivity, and absolute temperature, respectively. To achieve high efficiency, a large $ZT$ is required.

Recently CoSb$_3$-based skutterudites have received considerable attention as prospective novel TE materials because of their unique crystal structure and excellent electronic transport properties.$^{2,4}$ Binary skutterudites are cubic compounds with the chemical formula MX$_3$ where M is a transition metal atom (Co, Rh, or Ir) and X is a pnicogen atom (P, As or Sb). They have small band gaps and possess high carrier mobilities, particularly in the case of p-type skutterudites.$^5$ Unfortunately, the thermal conductivity of binary skutterudites is also high, and this has been a serious impediment to their applications as TE materials. There are numerous ways how one can influence and lower the thermal conductivity of a structure. In the case of skutterudites, the most effective approach turned out to be filling of the structural voids by foreign elements$^2,5,6$ and this recipe has been explored and followed for the past dozen or so years with impressive improvements in the figure of merit of n-type filled skutterudites.$^7,8$

Recently, much attention has been paid to the possibility of importing benefits of lower-dimensional TE structures into the bulk matrix.$^9$ Specifically, incorporation of nanometer-scale inclusions in the bulk structure appears highly prospective for a dramatic lowering of the lattice thermal conductivity as the nanometer-scale structural features have a potential to strongly scatter heat-carrying phonons.$^{10–12}$ It is important to recognize that not just any nanostructure will do. The nanostructure of interest must preferably scatter phonons while leaving the carrier transport substantially unimpeded. Moreover, such a nanostructure must be stable at the temperature regime where the TE converter will operate. The limited experience suggests that nanostructures formed via processes such as spinodal decomposition,$^{10}$ matrix encapsulation,$^{13}$ nucleation and growth,$^{14}$ and special heat treatment processes$^{15}$ are inherently more stable than nanostructures brought into the matrix by external means. Moreover, the nanostructures of the first kind tend to be coherent with the matrix, and this assures minimal disturbance to the mean-free path of charge carriers.

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Dominant heat-carrying phonons in skutterudites are associated with vibrations of pnicogen rings. Therefore, changes in the phonon vibration spectra created by substitutions on the rings or by deforming the rings should decrease the lattice thermal conductivity. Often, tellurium has been tried as a dopant on the pnicogen rings. However, its solubility is rather low, and the resulting change in the thermal conductivity upon doping is only modest. Recently, Liu et al. prepared double-doped skutterudite compounds based on Sn and Te doping of CoSb$_3$ by mechanical alloying followed by spark plasma sintering. The presence of the group IV Sn compensates for the charge of the group VI Te and, in turn, increases its solubility to $x \sim 0.2$. The authors of ref 17 noted that their double-doped compounds have lower thermal conductivity than the single-doped skutterudites which they explained as a result of the combined influence of the grain boundary scattering and the point defect scattering. They also mentioned that on high resolution TEM images of their samples they detected “black regions” that they tentatively associated with nanodots of the kind seen in the LAST materials and speculated that they might contribute to the overall low thermal conductivity. It is difficult to make a definitive statement regarding the influence of nanodots on the thermal transport in their samples since the authors provided no evidence for the chemical contrast between the matrix and the “black region” of their HRTEM images. Moreover, because their compounds had an average grain size of 140 nm, it is difficult to ascertain whether the reduction in the thermal conductivity is due to a small grain size on account of ball milling or the consequence of any possible nanostructure originating from a segregated nanophase.

To ascertain the presence of nanoinclusions upon double doping on the pnicogen rings and to find out their influence on transport properties, we synthesized a series of skutterudite compounds of composition CoSb$_{2.75}$Ge$_{0.25-x}$Te$_x$ with $x = 0.125 - 0.20$. In contrast to ref 20, our samples were prepared by the traditional method of synthesis based on quenching the melt and subjecting the ingots to a long-term annealing to achieve a pure skutterudite phase. The average grain size of our samples is on the scale of tens of micrometers, the length scale on which phonon scattering cannot be confused with the influence of nanometer-scale inclusions. We indeed detect such nanoinclusions in our HRTEM images, and we provide chemical contrast between them and the matrix.

**EXPERIMENTAL SECTION**

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$_{0.25-x}$Te$_x$, with $x$ in the range from 0.125 to 0.20. The charge was sealed in a carbon-coated silica tube under the pressure of 10$^{-3}$ Pa. The charge was melted and kept at 1373 K for 30 h. Subsequently, ampules with the melt were quenched in a supersaturated salt water bath, and ingots were annealed at 873 K for 7 days. The obtained material was ground in a glovebox into a salt water bath, and ingots were annealed at 873 K for 7 days. The presence of the group IV Sn compensates for the charge of the group VI Te and, in turn, increases its solubility to $x \sim 0.2$. The authors of ref 17 noted that their double-doped compounds have lower thermal conductivity than the single-doped skutterudites which they explained as a result of the combined influence of the grain boundary scattering and the point defect scattering. They also mentioned that on high resolution TEM images of their samples they detected “black regions” that they tentatively associated with nanodots of the kind seen in the LAST materials and speculated that they might contribute to the overall low thermal conductivity. It is difficult to make a definitive statement regarding the influence of nanodots on the thermal transport in their samples since the authors provided no evidence for the chemical contrast between the matrix and the “black region” of their HRTEM images. Moreover, because their compounds had an average grain size of 140 nm, it is difficult to ascertain whether the reduction in the thermal conductivity is due to a small grain size on account of ball milling or the consequence of any possible nanostructure originating from a segregated nanophase.

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**RESULTS AND DISCUSSION**

**Composition and Structure of Specimens.** Figure 1 shows the typical XRD patterns obtained on CoSb$_{2.75}$Ge$_{0.25-x}$Te$_x$ ($x = 0.125 - 0.20$) compounds with different Te doping contents $x$. The XRD patterns demonstrate that all bulk materials are single-phase skutterudite structures without any impurity phases such as GeTe and CoTe$_2$ according to JSPDS 78-0976. Therefore, co-doping with Ge and Te in the above range of $x$ does not change the crystal structure. The lattice constant increases in proportion to the relative amount of Te doped into the structure (see inset of Figure 1). 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 doping in CoSb$_3$. The linear increase of 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 ($x = 0.15$) because of 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 4-member Sb ring compensates for the charge of Te substituted for Sb on the same ring and effectively increases solid solubility of Te in CoSb$_3$. This is similar to the case of co-doped Te and Sn in CoSb$_3$.

![Figure 1. XRD patterns of CoSb$_{2.75}$Ge$_{0.25-x}$Te$_x$ ($x = 0.125 - 0.20$) samples.](image-url)

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. For measurements at high temperatures we relied on a ZEM-1 apparatus (electrical conductivity $\sigma$ and the Seebeck coefficient $\alpha$) and thermal conductivity $\kappa$ was calculated from the measured thermal diffusivity $D$, specific heat $C_p$, and density $d$ according to the relationship $\kappa = D \times C_p \times d$. The thermal diffusivity and the specific heat were determined using a laser flash method (NETZSCH: LFA 457) and a power-compensation differential scanning calorimeter (TA: DSCQ20), respectively. Uncertainties in the electrical conductivity, thermopower, and thermal conductivity measurements are $\pm 5\%$, $\pm 5\%$, and $\pm 7\%$, respectively.
microstructure, we used a transmission electron microscope (TEM). The data are shown in Figure 3a. We observe a nanostructure that exhibits a circular shape with the diameter of about 30 nm embedded in the matrix. The grain boundary is clearly visible separating the nanostructure and the matrix. Semiquantitative EDS results give the normalized chemical composition of the matrix (Figure 3c) and of the nanostructured phase (Figure 3b) as CoSb$_{2.90}$Ge$_{0.02}$Te$_{0.135}$ and CoSb$_{2.65}$Ge$_{0.125}$Te$_{0.312}$, respectively, which indicates that the nanostructured phase is rich in Ge and Te while the matrix is a region poor in Ge and Te. A completely homogeneous dispersion of Ge and Te in the skutterudite lattice would require a complete separation of Ge and Te atoms over long distances, which could create charge imbalances in the vicinity of these atoms. To achieve electroneutrality, it is more favorable for Ge to sit on the same pnicogen ring where Te is already located (Figure 3d). The presence of Ge thus not only tends to increase the solid solubility limit of Te, but it also leads to the in situ formation of a nanostructure. The formation mechanism of the nanostructure is akin to the case of the LAST and TAGS systems.$^{10,22,23}$

**Figure 2.** (a) Back scattered electron image. (b) Secondary electron images for CoSb$_{2.75}$Ge$_{0.05}$Te$_{0.20}$ sample.

**Figure 3.** (a) TEM image of CoSb$_{2.75}$Ge$_{0.05}$Te$_{0.20}$. (b) EDS of the nanostructured region. (c) EDS of the matrix. (d) the pnicogen ring co-substituted by Ge and Te, and (e) the pnicogen ring substituted by Te.

**Figure 4.** Electrical conductivity as a function of temperature for CoSb$_{2.75}$Ge$_{0.05}$Te$_{0.20}$ compounds is shown in Figure 4. Except for the compensated sample CoSb$_{2.75}$Ge$_{0.05}$Te$_{0.125}$ all samples behave as highly degenerate semiconductors with their electrical conductivity decreasing as the temperature increases. The compensated sample, in contrast, displays a typical nondegenerate semiconducting behavior. The doping effect of Te is clearly reflected in the enhanced value of the electrical conductivity that reaches 1.60 $\times$ 10$^5$ S/m at 300 K for CoSb$_{2.75}$Ge$_{0.05}$Te$_{0.20}$. Using equation $\sigma = \sigma_0 \exp(-E_g/2k_BT)$,
we attempted to fit the high temperature electrical conductivity of the compensated sample to obtain an estimate of the band gap \( E_g \). The fit returned the value of \( E_g = 0.43 \text{ eV} \), consistent with the literature values.\(^{24,25}\)

In Figure 5, we plot the Hall coefficient \( R_{H} \) as a function of temperature for CoSb\(_{2.75}\)Ge\(_{0.25-x}\)Te\(_x\) compounds. All samples show negative \( R_{H} \) indicating that electrons are the dominant charge carrier. Samples with \( x = 0.15, 0.175, \) and 0.20 show a weak temperature dependence of \( R_{H} \) (in fact, on the scale of Figure 5 they are essentially temperature independent, and we need to expand the scale such as in the inset of Figure 5 to see the effect of temperature). In contrast, the compensated sample CoSb\(_{2.75}\)Ge\(_{0.125}\)Te\(_{0.125}\) displays strong temperature dependence in \( R_{H} \), and its absolute value decreases rapidly with the increasing temperature. At the highest temperatures of the experiment, a positive Hall coefficient is observed. Undoubtedly, this is the consequence of an early onset of intrinsic conduction with a strong participation of mobile holes.

A much weaker temperature dependence of the uncompensated samples \( (x = 0.15, 0.175, \) and 0.20) in the inset of Figure 5 is similar to the temperature dependence of the Hall effect observed in lightly Ni-doped CoSb\(_3\). In particular, the minima on the curves near 100 K (deeper and more pronounced at smaller Te concentrations) are a footprint of the crossover from the predominantly impurity conduction to band conduction.\(^{24,25}\)

Assuming that at 300 K the transport is dominated by single band conduction, the room temperature values of the electron density are listed in Table 1.

Room temperature carrier mobility \( (\mu_H) \) as a function of the carrier concentration \( (n) \) is shown in Figure 6. For comparison, we also display the data for single-doped CoSb\(_3-x\)Te\(_x\). In the single-doped CoSb\(_3\), the carrier mobility rapidly diminishes with the increasing content of Te, that is, with the increasing carrier density. In contrast, in the double-doped CoSb\(_3\) (remember, the total amount of impurity is kept constant at 0.25) the mobility actually increases with the carrier density. This we interpret as a consequence of an apparently much stronger effect of Ge impurity on the mean-free path of electrons. As \( x \) increases, the Te content increases but at the expense of the Ge content, and with less Ge present the mobility seems to increase even though the Te impurity is more abundant. The inset shows this trend more clearly in the form of a plot of the composition ratio of Te to Ge versus the electron mobility.

The temperature dependence of the Hall mobility for CoSb\(_{2.75}\)Ge\(_{0.25-x}\)Te\(_x\) \( (x = 0.125-0.20) \) compounds is shown in Figure 7. Uncompensated samples \( (x = 0.15, 0.175, \) and 0.20) display a very similar trend with the essentially \( T \)-independent mobility at low temperatures \( (T \leq 100 \text{ K}) \) that then rapidly decreases at and above 300 K. In the temperature range 400–700 K, the mobility attains a \( T^{-3/2} \) dependence characteristic of the

Table 1. Nominal Composition and Some Properties of CoSb\(_{2.75}\)Ge\(_{0.25-x}\)Te\(_x\) Compounds at 300 K

<table>
<thead>
<tr>
<th>nominal composition</th>
<th>( \sigma ) (10(^8) S/m)</th>
<th>( R_{H} ) (cm(^3)/C)</th>
<th>( N_p ) (10(^{19})/cm(^3))</th>
<th>( \mu_H ) (cm(^2)/(V s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSb(<em>{2.75})Te(</em>{0.20})</td>
<td>16.0</td>
<td>-0.0121</td>
<td>51.6</td>
<td>19.4</td>
</tr>
<tr>
<td>CoSb(<em>{2.75})Ge(</em>{0.075})Te(_{0.175})</td>
<td>13.0</td>
<td>-0.0143</td>
<td>43.7</td>
<td>18.5</td>
</tr>
<tr>
<td>CoSb(<em>{2.75})Ge(</em>{0.10})Te(_{0.15})</td>
<td>7.3</td>
<td>-0.0219</td>
<td>28.6</td>
<td>16</td>
</tr>
<tr>
<td>CoSb(<em>{2.75})Ge(</em>{0.125})Te(_{0.125})</td>
<td>0.75</td>
<td>-0.205</td>
<td>3.0</td>
<td>15.3</td>
</tr>
</tbody>
</table>

Figure 5. Hall coefficient as a function of temperature for CoSb\(_{2.75}\)Ge\(_{0.25-x}\)Te\(_x\).

Figure 6. Room temperature Carrier mobility as a function of Carrier concentration for CoSb\(_{2.75}\)Ge\(_{0.25-x}\)Te\(_x\). (Inset Figure: Room temperature Carrier mobility as a function of ratio of Te/Ge content for CoSb\(_{2.75}\)Ge\(_{0.25-x}\)Te\(_x\)).

Figure 7. Carrier mobility as a function of temperature for CoSb\(_{2.75}\)Ge\(_{0.25-x}\)Te\(_x\).
dominance of acoustic phonon scattering. At the highest temperatures the mobility decreases even faster, reflecting the contribution of optical phonons in scattering processes. We note a slight increase in the mobility with the increasing $x$, that is, the decreasing content of Ge, substantiating the data in the inset of Figure 6. The mobility of the compensated sample ($x = 0.125$) with its highest Ge content tends distinctly toward the $T^{3/2}$ dependence below 100 K suggesting that impurity scattering is an important limiting mechanism in this sample.

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 $L = 2.45 \times 10^{-8} \, \text{V}^2/\text{K}^2$. The lattice thermal conductivity is then obtained by

![Figure 8. Seebeck coefficient as a function of temperature for CoSb$_{2.75}$-Ge$_{0.25-x}$Te$_x$.](image1)

![Figure 9. Thermal conductivity as a function of temperature for CoSb$_{2.75}$-Ge$_{0.25-x}$Te$_x$. Solid line represents data of ref 19.](image2)

![Figure 10. Lattice thermal conductivity as a function of temperature for CoSb$_{2.75}$Ge$_{0.05}$Te$_{0.20}$. Solid line represents data of ref 19.](image3)
subtracting $k_C$ from the total thermal conductivity, see Figure 10. With the increasing temperature, the lattice thermal conductivity decreases, and the trend regarding the dependence on the Te content extends to the highest temperatures. Thus, in comparison to the undoped CoSb3 (see inset of Figure 10) the lattice thermal conductivity of CoSb2.75Ge0.25–xTex ($x = 0.125–0.20$) compounds is reduced quite dramatically.

Substitution of Ge and Te on the ring-sites of Sb results in mass fluctuation scattering because of the mass difference of Te, Ge, and Sb atoms which, in turn, leads to a reduction in the lattice thermal conductivity. The scattering parameter $A$ can be written in the form:

$$A = \frac{\Omega_0}{4\pi^2 v} x(1 - x) \left( \frac{\Delta M}{M} \right)^2$$

(3)

where $\Omega_0$, $v$, $x$, $\Delta M$, and $M$ stand for the volume of the unit cell, the sound velocity, the fraction of guest atoms, the atomic mass difference between the guest and host, and the average mass of the cell, respectively. According to this equation, the value of $k_L$ should increase with the increasing $x$ because the atomic mass difference between Te and Sb, $\Delta M_{\text{Te/Sb}}$, is much smaller than that between Ge and Sb, $\Delta M_{\text{Ge/Sb}}$. The substitution of Ge atoms on Sb sites should thus decrease the thermal conductivity more dramatically than the substitution of Te atoms on Sb sites. In reality, an inverse effect is seen in our experiments. We argue that this is due to a larger number of Sb rings that must accommodate Te as $x$ increases. Since Ge atoms preferentially occupy those Sb rings where Te is already present (a lower energy state because of charge compensation of Ge and Te), the number of distorted rings is determined by the number of available Te atoms. In our series of compounds, Ge atoms never exceed the number of Te atoms. Although the presence of Ge and Te-rich nanodots embedded in the skutterudite matrix is likely further reducing the thermal conductivity, the actual contribution is difficult to quantify in this limited series of samples against the background of strong point-defect scattering. The lowest lattice thermal conductivity is obtained for CoSb2.75Ge0.05Te0.20 yielding the value of 0.87 W m$^{-1}$ K$^{-1}$ at 800 K. This value is comparable to the lattice thermal conductivity of filled skutterudites.7–10

**Phonon Scattering Mechanism.** Low values of the lattice thermal conductivity and the trend in the data indicate that perturbation of the ring structure of Sb is an important issue in heat transport of skutterudites. Consequently, we attempted to collect Raman spectra on our compounds by using a Renishaw Invia Raman system with a 514.5 nm excitation source and a spectra resolution of 1 cm$^{-1}$. The crystal symmetry Im3 implies eight Raman-active phonon modes related to vibrations of the pnictogen rings: 2 $A_g + 2 E_g + 4 F_g$ where the $A_g$ mode is single degenerate, the $E_g$ mode is doubly degenerate, and the $F_g$ mode is triply degenerate. The presence of Te and Ge on the rings of Sb is expected to alter the ring structure bonding, to lead to small changes in the $d_1$ and $d_2$ bond lengths, and to lower the symmetry of the ring.

Room temperature Stokes Raman spectra of CoSb3 and CoSb2.75Ge0.05Te0.20 are shown in Figure 11. Since no distinct peak was observed above 200 cm$^{-1}$, such data are omitted. Comparing Raman spectra for pure CoSb3 with those of CoSb2.75Ge0.25–xTex ($x = 0.125–0.20$) we note appreciable differences. The most notable one is the missing 134 cm$^{-1}$ $E_g$ peak (elongation of all sides of one rectangle, shortening of all sides of another)16,17 in the spectrum of CoSb2.75Ge0.05Te0.20. All other peaks seem to be slightly shifted to higher frequency when Ge and Te substitutes for Sb, see Table 2. This is due to a marginally smaller average mass of a ring that is occupied by Te and Ge in comparison to a ring occupied by Sb atoms only. The theoretical $F_g$ mode (178 cm$^{-1}$) and $A_2$ mode (179 cm$^{-1}$) are too close to each other, and we cannot distinguish them on either sample. The broadening of the two $A_g$ modes in Te and Ge doped skutterudites in comparison to the pure CoSb3 is due to disorder induced by the random distribution of the Te and Ge on the Sb rings.18 The observed changes and shifts in the Raman spectrum indirectly confirm the accommodation of Te and Ge on the Sb rings.

![Figure 11](image1.png)

**Figure 11.** Raman shift of the samples CoSb3 and CoSb2.75Ge0.05Te0.20. The data of theoretical calculated modes for CoSb3 from ref 23 are also presented.

![Figure 12](image2.png)

**Figure 12.** $ZT$ as a function of temperature for CoSb2.75Ge0.125–xTex.

<table>
<thead>
<tr>
<th>CoSb3 theory a</th>
<th>83 (Fg1)</th>
<th>97Fg2</th>
<th>139 (Fg)</th>
<th>150Ag</th>
<th>157Fg3</th>
<th>178Fg4</th>
<th>179Ag</th>
<th>182 (Fg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSb3</td>
<td>133.94</td>
<td></td>
<td></td>
<td>148.034</td>
<td>176.156</td>
<td>181.419</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoSb2.75Ge0.05Te0.20</td>
<td>149.794</td>
<td></td>
<td></td>
<td>177.911</td>
<td>183.173</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Dimensionless TE Figure of Merit ZT. The dimensionless TE figure of merit ZT for our compounds is calculated from the measured values of the electrical conductivity $\sigma$, the Seebeck coefficient $a$, and the thermal conductivity $\kappa$ and is shown in Figure 12. ZT values of all samples increase with the increasing temperature and with the increasing content of Te. The highest ZT in the present series of samples is achieved with CoSb$_{2.75}$Ge$_{0.05}$Te$_{0.20}$ and reaches the value of 1.1 at 800 K. This represents nearly an order of magnitude increase over the figure of merit of pure CoSb$_3$ and the double-doped skutterudites are competitive with the best of single-filled n-type skutterudites.

The major beneficial factor is a much reduced lattice thermal conductivity that is dominated by point defect scattering which is augmented by the presence of in situ formed nanodots the origin of which is compositional variation between purely Sb occupied rings and rings accommodating Te and Ge impurities. The mechanism of the nanostructure formation seems akin to that of the LAST material where the regions of one composition are endotaxially embedded in a matrix of slightly different composition.

**CONCLUSIONS**

Single-phase CoSb$_{2.75}$Ge$_{0.25-\chi}$Te$_\chi$ ($\chi = 0.125-0.20$) skutterudite compounds were synthesized using a melt-quench-anneal-SPS method. The samples possess nanostructural features consisting of circular domains of 30 nm diameter where the skutterudite phase is enriched with Ge and Te. These nanodots are uniformly dispersed in the skutterudite matrix that is poor in the content of Ge and Te. Energy considerations imply that Ge preferentially seeks pnicogen rings that already accommodate Te as the proximity of tetravalent Ge and hexavalent Te mimics the penta-valent site of Sb and neutralizes the change. The formation mechanism of this in situ nanostructure is similar to the case of nanostructures in the LAST materials. The electrical transport properties can be modulated by adjusting the relative content of Ge and Te. Atoms of Ge and Te that substitute on the pnicogen rings alter the bonding and symmetry of the rings and cause appreciable changes in phonon vibration spectra. As a consequence, the thermal conductivity of these double-doped skutterudites is greatly suppressed in comparison to the thermal conductivity of a pure CoSb$_3$. Undoubtedly, point defect scattering is the dominant scattering mechanism of phonons and is made more effective by the presence of Ge that, moreover, enhances the solubility of Te in CoSb$_3$. Although we were unable to quantify the influence of the nanostructure on the thermal transport, the uniformly distributed nanodots with the caliper of 30 nm are of the right size to interact with long and midfrequency phonons and likely contribute to the overall low lattice thermal conductivity of these double-doped skutterudites. The TE figure of merit of our compounds is strongly enhanced in comparison to that of pure binary CoSb$_3$ and reaches values in excess of 1.1 at 800 K for CoSb$_{2.75}$Ge$_{0.05}$Te$_{0.20}$. Such high values of ZT are very competitive with the best values of single-filled skutterudites. It will be interesting to apply this double-doping approach in the fabrication of filled skutterudites with the hope of achieving n-type TE materials with very high ZT.

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