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Daniel R. Thompson,1 Chang Liu,1 Nicole D. Ellison,1 James R. Salvador,2 Martin S. Meyer,2 Daad B. Haddad,2 Hsin Wang,3 and W. Cai3

1Optimal CAE, Plymouth, Michigan 48170, USA
2General Motors Research and Development, Warren, Michigan 48090, USA
3Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

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Thermoelectric (TE) technology for use in automotive waste heat recovery is being advanced by General Motors with support from the US Department of Energy. Skutterudites are a very promising material for this application of TE technology due to their superior mechanical properties and good TE performance. Double-filled Yb3Ba2Co3Sb12 with ZT values around 1.1 at 750 K are the best performing n-type skutterudites produced on a large scale using an economically viable approach of melt spinning (MS) in conjunction with spark plasma sintering (SPS). Another economical production method on the tons scale, the melt quench annealing (MQA) technique, has been recently claimed by Treibacher Industrie AG, further information is available [G. Rogl et al., Acta Mater. 76, 434–448 (2014)]. A possible hurdle to commercial implementation of these materials is the use of rare earths as the fillers to reduce thermal conductivity and improve the electrical transport properties. It will be shown herein that skutterudites double-filled with Ca and Ce, both of which are lower-cost fillers, display markedly different TE properties depending on whether they are produced by MQA or MS + SPS synthesis techniques. Ca and Ce double-filled skutterudites prepared by MS + SPS have TE properties that are superior to the same compositions prepared by MQA and that are comparable to the best performing Yb and Ba filled materials. Furthermore, the results of this study suggest that the unusually poor transport properties of MQA Ca-filled skutterudites can be ascribed to deleterious secondary phases, which is contrary to reports in the literature attempting to explain these irregularities via band structure features. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4904187]

INTRODUCTION

The potential use of thermoelectric (TE) waste heat recovery technology in automobiles for fuel economy improvement has been realized since 1963 when the first exhaust TE generator was constructed.2 The efficiency of a TE material to convert heat to electricity is quantified using the TE dimensionless figure of merit, ZT, which is defined as

\[ ZT = (\alpha^2 T)/\rho \kappa, \]

where \( \alpha \) is the Seebeck coefficient, \( \rho \) is the electrical resistivity, \( \kappa \) is the thermal conductivity consisting of both an electrical \( (\kappa_e) \) and lattice \( (\kappa_L) \) portion, \( T \) is the absolute temperature, and \( \alpha^2/\rho \) is the power factor.3,4

In 2005, it was noted that significant improvements in TE materials occurring during the 1990s reinvigorated interest in TE technology for potential automotive power generation applications.5 Also highlighted in Ref. 5 were the other materials attributes (aside from ZT values) required of TE’s for automotive applications, such as their ability to survive the thermal-mechanical stresses likely to be encountered in the automotive exhaust system and their suitability for incorporating into modules. Of these new TE materials, skutterudites have come to be one of the more promising material systems because they possess the appropriate combination of properties to meet these requirements. Compared to PbTe, skutterudites are more mechanically robust, lend themselves more easily toward power systems integration due to their fairly weak temperature dependence of \( \rho \), and can be made into modules.6

Skutterudites are based on the mineral CoPn3 (Pn = P, As, or Sb). They possess large cages intrinsic to their crystal structure as the result of corner sharing CoPn6 octahedra. A large variety of cations, including lanthanides, alkaline earths, and alkali metals can be introduced, or filled, into these cages to create Einstein-like vibrational modes that can act to scatter phonons and donate electrons to the CoSb3 matrix, respectively, reducing \( \kappa \) and \( \rho \). Skutterudites have been of interest to the TE community since 1994 when Slack first proposed that placing atoms in their crystallographic voids (2d Wyckoff site in the cubic Im3 space group) would substantially reduce their thermal conductivity by introducing phonon-scattering centers.8 Several reviews and book chapters have been published on skutterudites and their potential for mid- to high-temperature TE applications.9–11

Of the possible fillers, Ca is a more attractive one due to its natural abundance and its ability to form filled skutterudites that have a higher degree of stability as compared to other readily abundant fillers, such as Li, Na, or K. Several thorough reports published on the TE properties of single-filled Ca3Co4Sb12 found them to have mediocre peak ZT values of ~0.45 at 800 K.12–15 It was also reported that small amounts of Ni doping for the Co lead to enhancement in the TE performance of Ca-filled skutterudites.12,16 The observation of poor TE performance in Ca-containing n-type skutterudites is not limited to single-filled samples; others found
similarly poor performance in double-filled Yb-Ca and Ca-Ce skutterudites.\textsuperscript{17,18} Common to all of these reports is the requirement of large nominal compositions of Ca to approach the filling fraction limit (FFL) in the material, and yet the resistivities of these samples are still quite high particularly when compared to those of optimally doped n-type skutterudites with other filler species. These high resistivities in the Ca-filled samples correlate to low Hall mobilities ($\mu_H$), which is contrary to the general observation in n-type skutterudites was first reported by Li and Tang for Yb\textsuperscript{3+} for TE performance for lower cost filler materials.\textsuperscript{20} Conversely, here we demonstrate its wider applicability to enhance their unusual electrical transport properties.\textsuperscript{13} Therefore, the question remains, “What is the source of this higher resistivity and unusually low $\mu_H$ for previously published Ca-filled skutterudites?” Band structure calculations performed on Ca-filled n-type skutterudites suggest that the presence of a large density of states peak from the Ca 4s-band located at the conduction band edge is the reason for their unusual electrical transport properties.\textsuperscript{13} Conversely, we contend that the low $\mu_H$ that has been reported in Ca-containing skutterudites to date is not intrinsic to Ca filling. Instead, it is a result of secondary phases that are deleterious to TE performance. We will show that when a combination of melt spinning (MS) followed by consolidation using spark plasma sintering (SPS) is applied to single or double-filled Ca-containing skutterudites, large improvements in $\mu_H$ and ZT are realized by minimizing oxide formation. MS of skutterudites was first reported by Li and Tang for Yb\textsubscript{0.06}Co\textsubscript{0.8}Sb\textsubscript{1.2}, and here we demonstrate its wider applicability to enhance TE performance for lower cost filler materials.\textsuperscript{20}

**EXPERIMENTAL**

**Sample synthesis**

Sample compositions will be denoted herein by their nominal compositions, and further compositional details are found in Table I. Several MS + SPS Ca\textsubscript{x}Ce\textsubscript{1-x}Co\textsubscript{4}Sb\textsubscript{12} samples were prepared by combining Co (arc melted pellets from Puratronic, 22 mesh powder, 99.995%) and Sb (Strem, bar, 99.999+%) in approximately a 1:3 ratio in a boron nitride crucible. The crucible and charge were sealed turnings, 99.9%), Ce (Alfa Aesar, rod, 99.8%), and Sb in a crucible with subsequent induction melting at 1673 K for 99.999 Pa and purged with Ar before the dynamic vacuum was allowed to reach ~2 Pa. Approximately 6 g of powdered ribbons were loaded in a 12.7 mm internal diameter graphite die coated with boron nitride spray. A pressure of 50 MPa was applied and an on:off pulse ratio of 12:2 (32.4:5.4 ms) was selected. The sample was heated using a programmed temperature profile set to heat linearly from 25°C to 650°C over 10 min followed by holding 650°C for 20 min. At the end of the temperature profile, the pressure was removed, and the sample was allowed to cool under vacuum. The resulting billets were approximately 12.7 mm diameter by 6 mm long cylinders. The densities ($d$) of the as-pressed samples were measured by mass and dimensions of the uncut billets. The relative density of all samples, as shown in Table I, achieved at least 98% of the theoretical density, 7.64 g/cm\textsuperscript{3} for unfilled Co\textsubscript{4}Sb\textsubscript{12}.

A sample with the nominal composition Ca\textsubscript{1-x}Ce\textsubscript{x}Co\textsubscript{4}Sb\textsubscript{12} was prepared by a melt quench annealing (MQA) synthesis method to compare to its MS + SPS counterpart. For the MQA preparation, the initial two-step induction process detailed for the MS + SPS processed samples described above was followed. The melt was then broken into chunks and flame sealed in a carbon coated quartz tube under a reduced atmosphere of 10\textsuperscript{−3} Torr and annealed at 973 K for 1 week. The annealed sample was then hand ground, cold pressed, and annealed under the same reduced atmosphere and temperature for an additional week.

Finally, a preliminary study was conducted to understand whether the chosen sintering technique affected the electrical and thermal transport properties of the resulting billets. The other pressure sintering technique employed for this study was uniaxial hot pressing (HP). Hence, a MS + SPS sample is compared to a MS + HP sample. The HP conditions consisted of a similar heating rate and the same

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>EPMA composition</th>
<th>Syn. Tech.</th>
<th>$a$ (Å)</th>
<th>$d$ (%)</th>
<th>$n \times 10^{20}$ (cm\textsuperscript{-3})</th>
<th>$\rho$ (mΩ·cm)</th>
<th>$\mu_H$ (cm\textsuperscript{2}/V·s)</th>
<th>$\alpha$ (µV/K)</th>
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<td>9.046</td>
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<td>38.5</td>
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<td>Ca\textsubscript{0.08}Co\textsubscript{0.92}Sb\textsubscript{12.05}</td>
<td>MS + SPS</td>
<td>9.071</td>
<td>100</td>
<td>4.5</td>
<td>0.98</td>
<td>62.2</td>
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<td>Ca\textsubscript{0.05}Co\textsubscript{0.95}Sb\textsubscript{12.15}</td>
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<td>MS + SPS</td>
<td>9.048</td>
<td>99</td>
<td>3.6</td>
<td>0.43</td>
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</table>

\textsuperscript{a}References 12 and 14.
\textsuperscript{b}Reference 17.
maximum sintering temperature of 650 °C as the SPS, but a greater pressure of 160 MPa and only a 2 min hold time were employed by the HP technique. Billets consolidated by HP have the same dimensions and roughly the same density, 99% theoretical, as those from the SPS.

Characterization techniques

Phase identity and purity were assessed by powder x-ray diffraction (PXRD) on the billets using a D8-Advance DaVinci diffractometer with Cu Kα radiation. Lattice parameters were determined by applying Rietveld refinement using Topas software.22 Electron probe microanalysis (EPMA) was performed to determine the element ratios of each sample. The EPMA derived compositions, as assessed by averaging the atomic ratios determined from eight randomly selected locations, are shown in Table I. This averaging verifies that all the constituent elements were present in each grain, while indicating how homogeneously they are distributed within the sample. The standard deviations for Ca and Ce were significantly higher than the theoretical minimum, revealing that these atoms were not completely evenly distributed among the grains.23 Sample characterization techniques for thermoelectric transport properties are similar to previous reports.17,24 Individual properties were measured to ascertain ZT; therefore, the typical 15% uncertainty is associated with the ZT values reported herein.3,4

RESULTS AND DISCUSSION

Microstructural analysis and composition

All PXRD reflections could be indexed to the skutterudite phase with no evidence of secondary phase for the Ca-Ce double-filled materials. The Ca single-filled material showed weak reflections corresponding to CoSb2, which is also evident in the x-ray maps of Co. A representative XRD pattern showing powdered as-spun ribbons and a SPS consolidated sample from those ribbons is shown in Figures 1(a) and 1(b). Because rapid solidification occurs from a melt whose temperature was above the peritectic decomposition point, the XRD patterns of the ribbons reveal a mixture of Sb, CoSb, and CoSb2 along with the desired CoSb3 skutterudite phase. This result has been observed in other MS filled skutterudites, where the wheel speed (cooling rate) can play a role in both the evolution of the microstructure and the proportion of the various phases seen in the as-spun ribbons.21 Figure 1(c) shows that single-filled Ca and Ca-Ce double-filled samples prepared for this study obey Vegard’s law as has been demonstrated in the literature for MQA Ca containing single-filled skutterudites. This indicates that despite the different preparation routes, Ca and Ce are filling the crystallographic voids.14,25

EPMA results indicate that all the initial constituent elements (Ca, Ce, Co, and Sb) were present in each grain of the samples. A couple key microstructural and compositional differences are noticeable between materials with the same nominal compositions prepared by either the MS + SPS or MQA routes as is shown for Ca0.1Ce0.1Co4Sb12 in Figure 2. First as seen in Figure 2(b), the white regions in the Ca and Ce x-ray maps indicate high concentrations of these elements, which also correlate to elevated oxygen levels in the corresponding regions of the oxygen x-ray map. Thus, the grain boundary regions show higher levels of CaO and CeO2 in the MQA sample as compared to the MS + SPS sample. Second, the MS + SPS sample achieves a much higher filling fraction as compared to the MQA sample for the same starting nominal composition. Please refer to Table I for compositional details. For the samples shown in Figure 2, approximately twice the amount of Ca and three times the amount of Ce are incorporated in the skutterudite phase when the MS + SPS synthesis route is used. In previous
reports on MQA Ca-filled skutterudites, large amounts of excess Ca, ~0.40, were needed to approach the theoretical FFL of ~0.25. A measured filling fraction of ~0.20 has been achieved using the MQA synthesis method. The formation of CaO during the synthesis was hypothesized by others to prevent the complete utilization of the Ca to fill the skutterudite voids because the ubiquitous oxide is sequestering potential fillers. Shown here, the MS + SPS process more effectively incorporates Ca fillers into the voids than the MQA approach where MS + SPS Ca0.25Co4Sb12 achieves comparable Ca filling to MQA Ca0.4Co4Sb12. The reduced amounts of CaO and correspondingly higher Ca content in the MS + SPS skutterudite result in greater than a 100% improvement in ZT as compared to previously reported values, see discussion below.

### Electrical and thermal transport properties

The $R_H$ for all samples were negative over the entire temperature range investigated indicating electron dominated electrical transport consistent with the negative sign of the $\alpha$ observed for all samples. The room temperature values of $n$ and $\mu_H$ are listed in Table I. The inset of Figure 3(a) shows the temperature dependence of $n$ for all the samples. The Ca and Ca-Ce filled MS + SPS samples have $n$ that are akin to optimized Ba-Yb filled skutterudites, which also have ZT values in excess of unity at 773 K. The MQA Ca0.1Ce0.1Co4Sb12 sample had much lower $n$ and $\mu_H$. All the samples produced by MS + SPS show increasing $n$ with increasing filling fraction consistent with previous findings. Above 100 K, $\mu_H$ has a $T^{-3/2}$ temperature dependence indicating that the main carrier scattering mechanism is from acoustical phonons (Figure 3(a)). This is further supported by the carrier dependence of $\mu_H$, which most closely follows
the trend seen in MQA Ba$_x$Ce$_y$ filled n-type skutterudites, see Figure 3(b). Evident from the data presented in Table I and Figure 3(b), for optimal carrier concentrations of about $\sim 3 \times 10^{20} \text{cm}^{-3}$ the $\mu_l$ of MQA Ca only filled samples in the literature are an order of magnitude lower than those presented here for MS + SPS samples. Hence, when Ca only filled skutterudites are prepared by MS + SPS with minimal amounts of secondary oxide, they do in fact behave as one expects where $\mu_l$ of the n-type skutterudite depends solely on $n$ and is independent of the filler atoms identity.

The temperature dependence of $\rho$ from 4 to 800 K of all samples investigated is presented in Figure 4. The inset of Figure 4 shows the very large difference in the low temperature values and temperature dependence of $\rho$ for Ca$_{0.1}$$Ce_{0.1}$Co$_4$Sb$_{12}$ prepared by MQA and MS-SPS. The significant result is that all the MS + SPS samples with either Ca only or Ca and Ce dual fillers show heavily doped degenerate semiconducting behavior in $\rho$ that is typically observed in optimally doped filled skutterudites in contrast to previous reports. Shown in Table I, skutterudite filling species being electropositive elements contribute a larger number of carriers as the filling concentration increases, and this is correlated to the decreasing $\rho$.

Figure 5 shows the temperature dependence of $a$ for all samples investigated. The approximately linear increase in $a$ with temperature is also behavior typical for degenerate semiconductors and has been observed with similar magnitudes for highly filled MQA Ca$_{0.1}$Co$_4$Sb$_{12}$ skutterudites. For the Ca$_{0.1}$$Ce_{0.1}$Co$_4$Sb$_{12}$ samples prepared by MQA ($) and MS + SPS (X), the difference in magnitude is a reflection of the filling fraction and carrier concentration. The $a$ versus $n$ values given in Table I possess an $n^{-1/3}$ trend, as shown by the inset in Figure 5. This concurs with others’ findings that heavily doped Ca containing double-filled skutterudites features $n$ between $5 \times 10^{19}$ and $5 \times 10^{20} \text{cm}^{-3}$ and agrees with the predicted behavior for the rigid band approximation.17

Figure 6 shows the power factor of the MQA sample ($) which agrees with previous reports, but when this composition is processed by MS + SPS, data denoted as X in the graph, it improves by over 100%. Also the MS + SPS sample single-filled with Ca (O) has a greater power factor ($\sim 50 \mu W/cm K^2$ at 773 K) than previously reported for MQA materials determined to have similar EPMA compositions ($\sim 20–30 \mu W/cm K^2$ at 773 K). These improvements in power factor along with those of the double-filled MS + SPS Ca-Ce samples are attributable to reduction in $\rho$, which is hypothesized to be the result of more careful processing, lower oxide content, and improved sample quality. Hence, the MS + SPS process benefits the electrical transport properties of samples that have some amount of Ca filler.

Measured heat capacity ($C_p$) data from 348–773 K of all the samples were similar in trend and magnitude, and they agreed with the Dulong-Petit limit, within $\pm 0.01 \text{ J/(g K)}$. Hence, the measured $C_p$ values used to calculate $\kappa$ were considered reasonable. The total $\kappa$ and the $\kappa_L$ of all samples are shown in Figures 7(a) and 7(b), respectively. As expected, MS + SPS Ca-Ce filled materials show a trend of decreasing $\kappa_L$ as filling fraction increases. Also at low temperatures, a reduction in the peak $\kappa_L$ is observable as first the MS + SPS samples transition from single-filled Ca (O) to double-filled Ca-Ce (X, $\Box$, -) and then as the Ca-Ce filler concentrations...
increase. One possible explanation for such behavior would be increased point defect scattering from the higher filling ratio and the heavier Ce filler species. The conjecture that the MS + SPS synthesis route is beneficial for the TE properties of Ca-filled skutterudites is bolstered by the result that the $\kappa_L$ of the MS + SPS Ca-filled sample presented here (O) reaches a minimum value of $\kappa_L \approx 1.4$ W/mK, whereas previous reports for similar compositions prepared by MQA have higher values of $\kappa_L \approx 2.2$ W/mK. Comparing these $\kappa_L$ values should be valid since the same Lorenz number, $L_0 = 2.45 \times 10^{-8}$ V$^2$/K$^2$, has been reported or assumed to be the same as those used in the literature for these materials.\textsuperscript{12,17} Hence, the MS + SPS synthesis route has reduced the Ca-filled skutterudites $\kappa_L$ by 40% likely through an increased filler concentration. It is doubtful that nanograins of oxide are the contributing factor for this reduction as has been found in other skutterudites because the oxide grains are micron sized in the Ca-filled skutterudites.\textsuperscript{31} In summary, we have demonstrated that through careful control of synthesis conditions, the oxidation of Ca fillers can be suppressed allowing it to be incorporated into the skutterudite where it reduces $\kappa_L$ and behaves as an n-type dopant typical of other filler species.

Shown in Figures 4, 5, and 7(a) the transport properties remained quite similar for the Ca$_{0.15}$Ce$_{0.075}$Co$_4$Sb$_{12}$ samples produced via MS + SPS (•) or MS + HP (▲). Also as previously discussed, XRD shows both these samples to be phase pure. Hence, it appears that typical solid state reactions and diffusion processes are occurring with either sintering mechanism, and the most significant improvements in transport properties, which are likely due to reduced amounts of secondary oxide phases, are arising from the MS portion of the MS + SPS process.

Figure 8 shows the ZT curves of all the samples. In order to construct the high temperature data set, a polynomial fit was performed on the $\kappa$ data. Then, $\kappa$ was calculated from the fit for the same temperatures at which $\rho$ and $\sigma$ were measured enabling the determination of ZT above 300 K. In accord with all the transport data presented thus far, the Ca-filled skutterudite when prepared by MS + SPS shows a 80–100% improvement in ZT over previously published values.\textsuperscript{12,17} Likewise, a 100% improvement was observed in double-filled Ca-Ce containing skutterudites as compared to previously published results.\textsuperscript{18} The ZT values shown here for the best performing sample, MS + SPS Ca$_{0.15}$Ce$_{0.075}$Co$_4$Sb$_{12}$ (•), are confidently stated by the authors. This is possible because upon observing the increased performance of this material due to the MS + SPS process, the authors synthesized a second batch of MS ribbons of the same nominal composition to internally confirm these results, then external verification of high temperature (>300 K) transport properties was performed at a separate lab, ORNL. The similar ZT performance of the Ca or Ca-Ce-filled MS + SPS skutterudites presented in this study is a strong indicator that Ca behaves as one usually envisages for the typical filler element, such as Yb, Ce, or Ba, in a skutterudite.

**SUMMARY AND CONCLUSIONS**

A synthesis route, MS + SPS, has been described that leads to twofold improvement in the thermoelectric performance of the lower cost formulations such as Ca or Ca-Ce filled n-type skutterudites, which can be an alternative to Yb-Ba filled skutterudites. MS + SPS samples displayed homogeneous microstructure with visibly less CaO and Ce$_2$O$_7$ appearing at the grain boundaries than observed in MQA samples. EPMA data also suggested that the MS + SPS synthesis technique had a more efficient filling rate for Ca than the MQA technique leading to more optimally doped...
materials with lower lattice thermal conductivity. In conclusion, Ca behaves similarly to other fillers leading to heavily doped semiconductor trends in resistivity and Seebeck coefficient. We also find that reductions in the amount of Ca and Ce oxide lead to improved carrier mobilities, increased carrier concentration, and reduced lattice thermal conductivity as compared to previously published results.12,14,16,18 These results suggest that there are likely no band structure features that lead to unusual transport properties in MQA Ca-filled n-type skutterudites; instead, the irregularities can be ascribed to deleterious secondary phases.

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