Synthesis and Properties of $Ce_xCo_4Ge_6Se_6$

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The novel, partially filled compounds $Ce_xCo_4Ge_6Se_6$ were synthesized using two methods: low-temperature interdiffusion and nucleation of ultrathin elemental layers and a bulk, high-temperature technique. The compounds were characterized by differential scanning calorimetry, powder X-ray diffraction, and electron probe microanalysis. The lattice parameters for the samples synthesized using the high-temperature technique were calculated to be 8.30 Å, while the samples synthesized using the elemental deposition technique showed lattice expansion proportional to the amount of incorporated rare earth element, with lattice parameters ranging from 8.30 Å for $x = 0$ up to a lattice parameter of 8.34 Å for $x = 0.2$. Rietveld analysis on X-ray diffraction data for both sets of samples showed incorporation of the rare earth element into the interstitial site, up to 20% occupancy.

Introduction

The skutterudite-like compound, $CoGe_{1.5}Se_{1.5}$, was first synthesized in 1977[1] and since then has been included in the ranks of skutterudite-related phases that have been investigated for thermoelectric applications. Unfilled skutterudites, such as $CoSb_3$, have been found to have thermal conductivity values that are too high for efficient use in thermoelectric applications, and $CoGe_{1.5}Se_{1.5}$ is no exception. Although its room-temperature thermal conductivity, ~6 W m^{-1} K^{-1}, is lower than that of $CoSb_3$, which is ~10 W m^{-1} K^{-1}, and its Seebeck coefficient is somewhat larger than that of $CoSb_3$, its electrical resistivity is nearly 2 orders of magnitude larger, and therefore, $CoGe_{1.5}Se_{1.5}$ has a smaller figure of merit than $CoSb_3$.[2,3] The thermal conductivity decreased significantly when an additional atom was inserted into the large interstitial site in the lattice of both skutterudites and clathrates.[4] Thus far, although many different types of atoms have been inserted into the $CoSb_3$,[5,6] $Co_xFe_{1-x}Sb_3$, and related lattices, there have been no reports of atoms having been successfully inserted into the significantly smaller $CoGe_{1.5}Se_{1.5}$ lattice. Whether this is due to lattice size or electronic effects has not been determined. We have attempted to synthesize filled $CoGe_{1.5}Se_{1.5}$ using two different methods: First, we used low-temperature interdiffusion and nucleation of films consisting of sequentially deposited ultrathin elemental layers; second, we used a typical, high-temperature solid-state synthetic technique. We examined a number of samples from both techniques and carefully characterized their structures, employing X-ray diffraction and Rietveld refinement. We conclusively show that both synthetic techniques can be used in producing samples that are partially "filled" with lanthanides.

Experimental Techniques

The thin-film samples were synthesized in a custom-built ultrahigh vacuum deposition system, described elsewhere.[7] Samples were synthesized in a 10^{-6}–10^{-7} torr atmosphere. Cobalt, germanium, and cerium were alternately deposited from an electron beam gun at a rate of 0.5 Å/s, and selenium was deposited from an effusion cell at a rate of 0.5 Å/s. A computer-controlled quartz crystal monitoring system was used to control layer thicknesses that were on the order of 2–10 Å for each elemental layer. Multiple layers of each element were deposited to yield a sample with a total thickness of approximately 1000 Å. The substrate was a 4 in. diameter silicon wafer previously coated with poly(methyl methacrylate) (PMMA). The substrate was at ambient temperature during the deposition.

After deposition, the sample was removed from the PMMA-coated wafer by dissolving the PMMA off the wafer using acetone. The powder sample was collected by vacuum filtration using a Teflon filter and used for differential scanning calorimetry (DSC) analysis. DSC measurements were conducted on a Netsch DSC 200 PC. The samples weighed approximately 1 mg and were heated from 50 to 550 °C at a rate of 10 °C/min. These annealed powder samples were used for X-ray diffraction (XRD) studies. XRD was conducted using a Scintag XDS-2000 $\theta-2\theta$ diffractometer between $15° \leq 2\theta \leq 85°$. These XRD data were used to identify any crystalline compounds that formed during annealing. XRD scans

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(1) Korenstein, R.; Soled, S.; Wold, A.; Collin, G. *Inorg. Chem.* **1977**, *16*, 2344–2346.
(2) Nolas, G. S.; Yang, J.; Ertenberg, R. W. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *68*, 193206.
(3) Morelli, D. T.; Meisner, G. P. *J. Appl. Phys.* **1995**, *77*, 3777–3781.
(4) Nolas, G. S.; Slack, G. A. *Am. Sci.* **2001**, *89*, 136–141.
(5) Nolas, G. S.; Morelli, D. T.; Tritt, T. M. *Annu. Rev. Mater. Sci.* **1999**, *29*, 89.
(6) Uher, C. Skutterudites: Prospective novel thermoelectrics. In *Semiconductors and Semimetals*; Tritt, T. M., Ed.; Academic Press: New York, 2000; Vol. 69, p 139.
(7) Fister, L.; Li, X.-M.; McConnell, J.; Novet, T.; Johnson, D. C. *J. Vac. Sci. Technol., A* **1993**, *11*, 3014–3019.

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Table 1. Percent Filling of the Rare Earth Cation in the Void Positions of the Skutterudite Structure Determined Using Rietveld Refinement of Diffraction Patterns for High-Temperature Samples Prepared Using Direct Synthesis Methods

sample	nominal composition	percent filling (Rietveld) (±2%)
A	$Ce_{0.05}Co_4Ge_6Se_{6.5}$	6% Ce
B	$Ce_{0.4}Co_4Ge_6Se_{6.5}$	13% Ce
C	$Yb_{0.3}Co_4Ge_6Se_{6.5}$	14% Yb
D	$Eu_{0.25}Co_4Ge_6Se_{6.5}$	11% Eu

that were used for Rietveld analysis had extended count times, usually a total of 12 h for the entire angle range. Reitveld analysis (using the EXPGUI program) was conducted on the sample series of X-ray data to calculate the lattice parameter and the amount of cerium filling.

Chemical composition information on the samples was obtained through a Cameca S-50 electron probe microanalysis (EPMA) instrument using a beam current of 20 nA and beam voltages of 8, 12, and 16 keV. All of the compositions were normalized to full occupancy of the cobalt site.

The high-temperature set of samples was synthesized by mixing high-purity reactants inside boron nitride crucibles that were sealed inside fused quartz ampoules under a nitrogen atmosphere. The reactants included a slight excess of selenium and the filler elements cerium, europium, and ytterbium. The excess Se was added to account for a vapor pressure of selenium in the ampule at the reaction temperature. These samples were reacted at 700 °C for 72 h. The products were ground to fine powders inside a nitrogen atmosphere dry box, cold-pressed into pellets, and sintered at 700 °C for several more days. The resulting pellets were ground again inside a dry box, and the powders were analyzed using XRD, as described previously.

Results and Discussion

High-Temperature Samples. We synthesized a series of samples with several different filler atoms in varying quantities (see Table 1 for a summary of the samples) and analyzed them using high-angle XRD. Samples of the powders were hot-pressed into pellets and analyzed using EPMA to determine the composition of the products.

The unfilled samples were found to be Se-poor, because of the relatively high vapor pressure of selenium.[2] They were also Co-rich overall, compared to the ideal ratio of 3:1 pnictide:metal atom, with compositions of $CoGe_{1.452}Se_{1.379}$ and $CoGe_{1.431}Se_{1.385}$. Despite the overall Co-rich composition, these samples showed only the skutterudite peaks in the XRD patterns (see Figure 1). All of the unfilled samples had lattice sizes of 8.306 ± 0.008 Å,[2] which is comparable to the single-crystal samples synthesized by Korenstein et al.[1]

The diffraction patterns of the series of samples with the filler atoms in varying quantities revealed the formation of the skutterudite structure, with no or only weak extra diffraction lines present from apparent impurity phases in the diffraction patterns. Surprisingly, there was no expansion of the lattice parameter (see Figure 2) even with significant nominal compositions of the rare earth filler atoms. With further examination of the XRD data, we noted decreased intensities in the first skutterudite peaks compared to the (*310*) peak, which usually indicates the presence of atoms in the interstitial site of the crystal lattice (see Figure 2). To determine the occupancy of the interstitial site, we performed additional XRD scans on these samples, using much longer count times and much larger angle ranges than previously collected and performed Rietveld analysis on the resulting data. Rietveld refinement confirmed that there was no expansion in the lattice and also revealed that the decreased intensity of the first three peaks [with Miller indices (*011*), (*002*), and (*112*)] compared to the unfilled sample was consistent with the incorporation of "filler" atoms in the structure during synthesis. Refined occupancies for the filler atoms ranged from 6 to 14% as summarized in Table 1. We were unable to increase the filling amount above ∼14% even when we incorporated larger equivalents of the filler atom in the initial reaction mix.

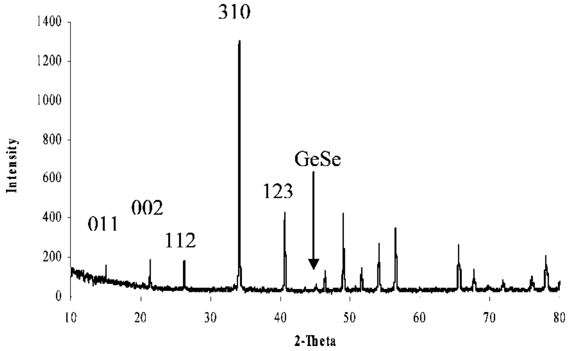

Figure 1. XRD scan of the $CoGe_{1.5}Se_{1.5}$ sample synthesized using the high-temperature method.

The lack of expansion in the lattice parameter has previously been taken to mean that no filling has occurred. However, our results are consistent with results found by Takizawa et al.,[8] who used high-pressure synthesis to insert germanium and silicon into the $CoSb_3$ lattice and observed a decrease in intensity in the first few skutterudite peaks but not an increase in the lattice size. To further explore the ability to incorporate filler atoms into the structure of $Co_4Ge_6Se_6$, a low-temperature approach was explored.

Low-Temperature Samples. The low-temperature technique used herein has been successful in the past for increasing the amount of interstitial filling of skutterudites compared to high-temperature techniques.[9] We began our investigation of low-temperature synthesis of the title compounds by exploring the effect of composition on the formation kinetics of the $Co_4Ge_6Se_6$ host matrix. A series of samples were synthesized with Ge/Co ratios ranging from 0.76 to 2.63 and Se/Co ratios ranging from 0.94 to 2.00, with an ideal ratio of 1.5 for both. The thicknesses of the individual elemental layers were on the order of 2–10 Å, and approximately 80 layers were sequentially deposited to yield a total film thickness of 1000 Å. All of the samples showed exothermic peaks in DSC analysis. These DSC samples were analyzed with XRD, and in all cases, crystalline products were formed after annealing. For samples with Ge/Co and Se/Co ratios above 2.0 and below 1.0, exotherm peak temperatures were observed at approximately 400 °C and no skutterudite phase formed after annealing according to

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(8) Takizawa, H.; Miura, K.; Ito, M.; Suzuki, T.; Endo, T. *J. Alloys Compd.* **1999**, *282*, 79–83.

(9) Hornbostel, M. D.; Hyer, E. J.; Thiel, J. P.; Johnson, D. C. *J. Am. Chem. Soc.* **1997**, *119*, 2665–2668.

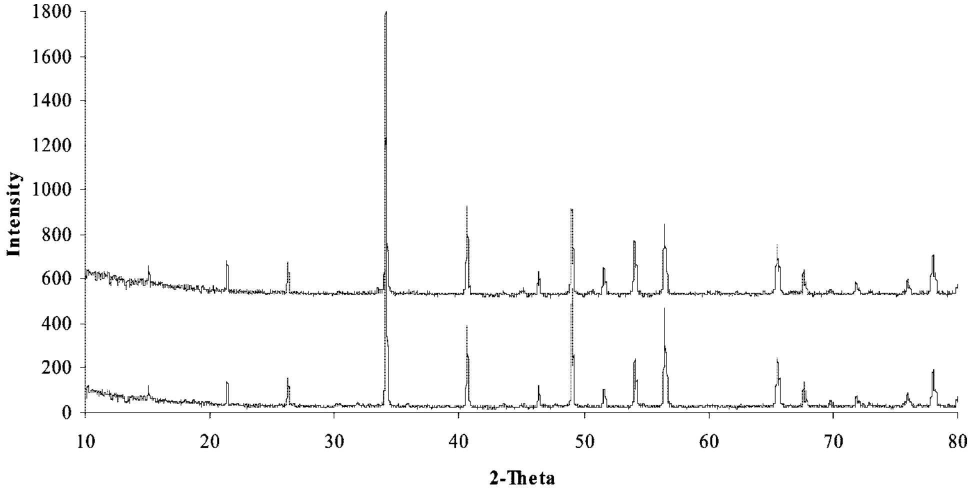

Figure 2. Top diffraction scan is that obtained on an unfilled $CoGe_{1.5}Se_{1.5}$ sample. The bottom scan is that obtained for sample C. The relative intensities of the first three skutterudite peaks compared to the (310) reflection in the diffraction data for sample C have reduced intensities compared to that obtained for the unfilled $CoGe_{1.5}Se_{1.5}$ sample.

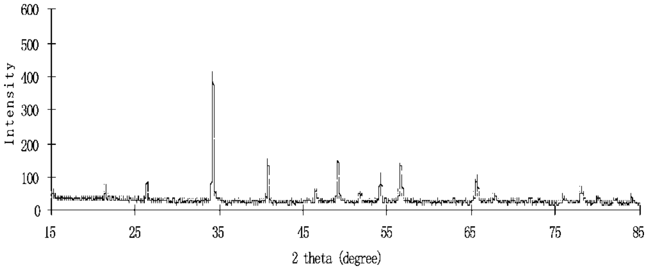

Figure 3. X-ray pattern of sample $CoGe_{1.36}Se_{1.47}$ prepared using the low-temperature interdiffusion of deposited layers.

Table 2. Composition Data, Exotherm Temperatures, and Phases Identified in the Post-DSC Diffraction Patterns for Representative Samples in the Co–Ge–Se System Prepared Using Low-Temperature Interdiffusion of Deposited Layers[a]

sample	composition (EPMA)	DSC peak, °C (±0.1 °C)	phases formed
A1	$CoGe_{2.07}Se_{1.40}$	404	none
A2	$CoGe_{2.63}Se_{1.68}$	402	none
B1	$CoGe_{1.39}Se_{1.30}$	433	$CoGe_{1.5}Se_{1.5}$
B2	$CoGe_{1.31}Se_{1.26}$	431	$CoGe_{1.5}Se_{1.5}$
C1	$CoGe_{1.96}Se_{1.63}$	419, 426	$CoGe_{1.5}Se_{1.5}$, other
C2	$CoGe_{1.84}Se_{1.50}$	416, 427	$CoGe_{1.5}Se_{1.5}$, other

[a] Ge and Se are normalized to one Co.

Table 3. Composition Data, Exotherm Temperatures, Fractional Ce Occupancy, and Lattice Parameters Calculated for Samples in the $Ce_xCo_4Ge_6Se_6$ System Prepared Using Low-Temperature Interdiffusion of Deposited Layers

sample number	composition from EPMA (±0.1)	DSC peak, °C (±0.1 °C)	Ce from Rietveld (±0.02)	parameter, Å (±0.005 Å)
1	$Co_4Ge_{5.4}Se_{5.9}$	428.1	0	8.302
2	$Ce_{0.2}Co_4Ge_{5.4}Se_{5.8}$	439.0	0.09	8.321
3	$Ce_{0.4}Co_4Ge_{6.0}Se_{6.0}$	445.1	0.15	8.327
4	$Ce_{0.6}Co_4Ge_{5.4}Se_{5.7}$	454.4	0.07	8.312
5	$Ce_{0.6}Co_4Ge_{5.5}Se_{5.9}$	453.9	0.11	8.326
6	$Ce_{0.6}Co_4Ge_{5.8}Se_{5.5}$	454.0	0.17	8.332
7	$Ce_{0.7}Co_4Ge_{5.5}Se_{5.5}$	459.3	0.21	8.339
8	$Ce_{1.1}Co_4Ge_{5.8}Se_{6.3}$	459.3	0.12	8.324
9	$Ce_{1.0}Co_4Ge_{5.5}Se_{6.1}$	461.9	0.10	8.320

the observed diffraction patterns. For samples with Ge/Co and Se/Co ratios between 1.5 and 2.0 and 1.3 and 2.0, respectively, we observed a mixed phase sample containing skutterudite and an unidentified impurity phase with exotherm peak temperatures of approximately 430 °C, with an additional small peak in the DSC data at approximately 420 °C. Samples with Ge/Co and Se/Co ratios of 1.3 ± 0.1 had a single exotherm peak at approximately 430 °C, and we observed single-phase skutterudite in the XRD data after heating past the exotherm (see Figure 3). Diffraction data collected just before the exotherm indicated that the sample was X-ray-amorphous. Note that Figures 2 and 3 look very similar, apart from differences in overall peak intensities.

The lattice parameter of the skutterudite phase was calculated to be 8.300 ± 0.005 Å and did not change significantly as a function of changing the Ge/Se ratio in the range where single-phase X-ray samples were observed, which is in good agreement with previous, high-temperature studies and the high-temperature samples investigated in this study.[1,2] A representative set of low-temperature $Co_4Ge_6Se_6$ samples is summarized in Table 2.

Using the knowledge of the compositions required to form the host matrix, we explored the filling of this structure with cerium by adding increasing amounts of Ce in the initial reactants. XRD analysis showed that for Ge/Co and Se/Co ratios of 1.5–1.8, multiple phases formed. In addition to the skutterudite phase, these samples formed crystalline germanium and, in some cases, an unidentified impurity phase. For Ge/Co and Se/Co ratios of 1.3 ± 0.1, the samples formed single-phase skutterudites with respect to XRD, regardless of the amount of cerium included in the sample. The amount of cerium in this system varied between $x = 0$ and 1.1. Table 3 shows the compositions of cerium-containing samples in which single-phase skutterudites were formed. All Ce-filled samples that formed single-phase skutterudites had exotherm peak temperatures of approximately 440–460 °C, somewhat higher than the unfilled samples as observed previously in comparable situations.[10] For the samples that formed only the pure skutterudite phase, the DSC exotherm peak temperatures increased linearly with the increase in the amount of cerium (see Figure 4).

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(10) Sellinschegg, H.; Smalley, A.; Yoon, G.; Johnson, D. C.; Nolas, G. S.; Kaeser, M.; Tritt, T. M. *Proc. Int. Conf. Thermoelectr.* **1999**, 352–355.

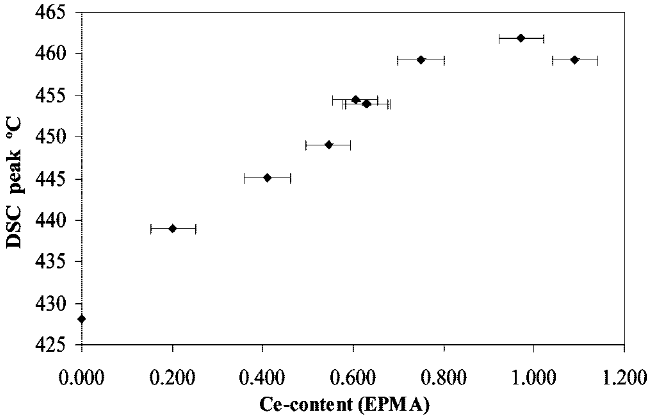

Figure 4. Change in the DSC exotherm temperature of films prepared by depositing layers of the elements as a function of the cerium content of the sample from EPMA.

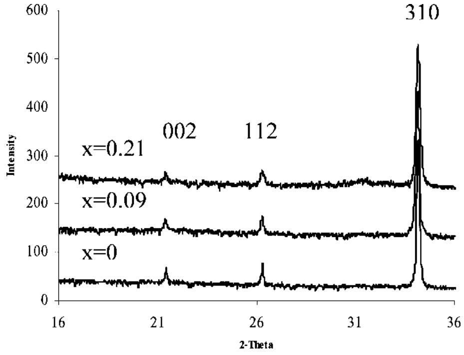

Figure 5. XRD patterns of samples in the Ce$_x$Co$_4$Ge$_6$Se$_6$ system with varying amounts of cerium. The Miller indices are noted on the first three skutterudite peaks visible.

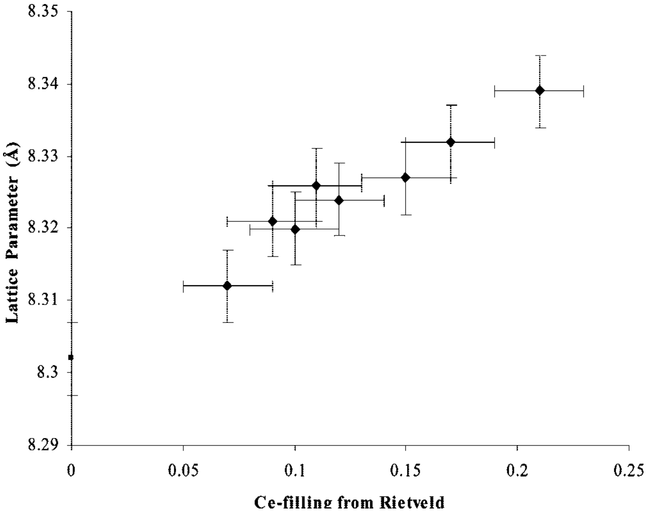

Figure 6. Correlation between the lattice parameter and the amount of cerium filling determined using Rietveld refinement for samples prepared by low-temperature interdiffusion of deposited layers.

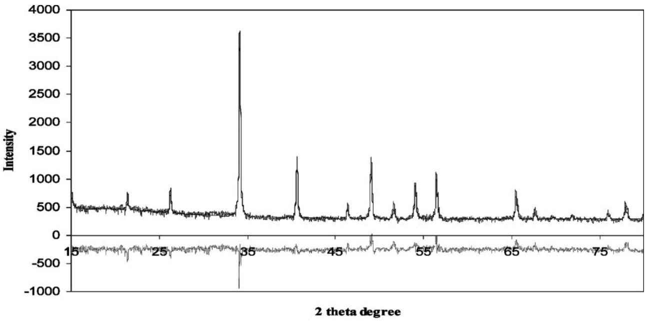

Figure 7. X-ray Rietveld refinement profile for sample 9, fitted as Ce$_{0.10}$Co$_4$Ge$_6$Se$_6$. The lattice parameter was $a = 8.320$ Å; the residuals were $R_{wp} = 0.0965$, $R_p = 0.0745$, and $X^2 = 3.498$.

When we examine the lattice parameters and XRD data for these samples, we note two significant features. First, we again see that two of the low-angle peaks [those with Miller indices (*002*) and (*112*)] showed decreased intensity when compared to the unfilled sample (see Figure 5). Second, the lattice parameters for the samples that included cerium were calculated to be between 8.31 and 8.34 Å. These unit-cell values are larger than those of the unfilled structure (8.30 Å). The expansion of the lattice and the decrease in intensity of low-angle XRD peaks independently confirm that we have incorporated cerium into the interstitial site in the crystal.[8] Neither indicates the amount of filling, however.

To determine the amount of cerium that was incorporated into the interstitial site, we used Rietveld analysis on the XRD data. We modeled the system after CoSb$_3$, with 50% occupancies of both Ge and Se in the Sb position and with Ce at the (0, 0, 0) position and refined the XRD data to calculate both the lattice parameter and amount of Ce filling. Although we did not actually have exactly 50% occupancy of both Ge and Se on the pnictide site, our XRD data were not of sufficient quality to be able to reliably refine the occupancies of the pnictide site. This accounts for a small amount of error in the data fit. When we refined the occupancy of the cerium site, we found that the best fit for our data included a Ce occupancy ranging from $x = 0.07$–0.2. We also found that the lattice parameter increased linearly with increasing Ce content for the range of $x = 0$–0.2 (see Figure 6). A sample Rietveld fit is shown in Figure 7, as well as typical residuals for the fits. Table 3 contains a list of the samples, their stoichiometries as intended, and the actual amount of cerium filling. As can be seen, the amount of cerium that was actually incorporated into the interstitial site is not strongly correlated with the amount present in the sample. The impurity phase that contains the excess Ce is either amorphous, present as very small grains, or present in a volume fraction that is below the XRD detection limits.

Although the lattice parameter and the DSC temperature both increased linearly with an increasing cerium content, they do not correlate with each other. The DSC temperature was graphed with respect to the actual cerium content of the sample, whereas the lattice parameter was compared to the amount of cerium that was incorporated into the lattice. On the surface, it still appears that these two quantities should correlate: we expect that the samples in which more cerium was included during synthesis should incorporate more cerium into the interstitial site. Instead, we find that the system has a more complicated relationship.

Rather than a correlation between Ce from EPMA and Ce in the interstitial site, we found a correlation between the Ge/Se ratio and the amount of Ce that was incorporated into the interstitial site of the skutterudite. The actual degree of Ce insertion increased when we increased the ratio of Ge/Se (see Figure 8). This is not necessarily a linear relationship but illustrates that changing the ratio of Ge/Se changes the

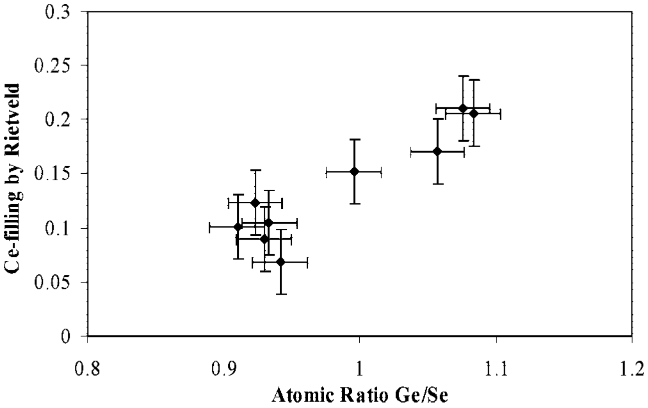

Figure 8. Relationship between the amount of Ce filling determined from Rietveld analysis of the diffraction data and the Ge/Se ratio determined using electron probe microanalysis.

amount of cerium that is incorporated into the interstitial site. Excess Ge allowed more Ce to be incorporated, while excess Se resulted in smaller amounts of Ce incorporated into the interstitial site. We explain this by looking at the bonding of the compound. Because Ge has fewer electrons for bonding than Se, it is likely that this is due to electronic stability; when there is excess Ge, additional Ce can be incorporated to add extra electrons for bonding, but with additional Se, there are already excess electrons, so there is less of a need for Ce to be included for electronic stability. What we are doing here is basically what has been done in filled samples that are doped on the metal site: charge compensation. We suggest that it might be possible to further increase the Ge/Se ratio to improve the amount of cerium incorporated into the interstitial site of the skutterudite.

In both the low- and high-temperature samples, we have observed successful partial filling of the interstitial site and there are similarities and differences in what we observe between the two synthesis methods. In the low-temperature samples, although the Ce filling increased with the amount of Ce added, the actual amount incorporated into the interstitial site saturated at 20% filling, even though we had included stoichiometric amounts of Ce sufficient for 100% filling. In the high-temperature samples, we observed a similar trend: the maximum filling amount was approximately 15%, regardless of the amount of filler atom included. We attempted to synthesize several samples with higher amounts of filler atom using the high-temperature method, but the skutterudite phase was of poor quality and we observed impurity phases in the XRD data; therefore, we concluded that these samples likely did not incorporate additional amounts of the filler atom into the interstitial site.

There are several factors that could have limited the amount of Ce filling in both synthesis methods. First, because $CoGe_{1.5}Se_{1.5}$ is an electronically stable compound, adding an element into the interstitial site adds extra electrons that are not needed for bonding. For the isoelectronic compound $CoSb_3$, only a small amount of Ce could be incorporated using high-temperature synthesis methods.[11] This result is comparable to the ~15% filling that we incorporated into our high-temperature $CoGe_{1.5}Se_{1.5}$ samples. Therefore, it is reasonable that this percentage incorporation represents the limit of electronic stability for these compounds.[11]

On the other hand, a much greater amount of Ce was able to be incorporated into the $CoSb_3$ lattice using the thin-film synthesis method that we used.[10] Because we were unable to include more than ~20% cerium into our low-temperature samples, another potential explanation is needed. It is possible that the crystal lattice simply cannot expand any further to include additional filling atoms. Takizawa et al.,[12] who used high-pressure to synthesize filled skutterudites, observed that the maximum lattice parameter for any filled $CoSb_3$ compound, regardless of the actual amount of filler atom incorporated, was 9.10–9.12 Å.[12] They attributed this plateau in lattice size to the inability of the Sb–Sb bonds to stretch further while still maintaining the bond. The percent increase in lattice size for these samples was 0.94% for the fully filled $CoSb_3$ compound. These results compare favorably to our own in the $Ce_xCo_4Sb_{12}$ system. The maximum lattice parameter that we observed was 9.11 Å for the fully filled compound, which is 0.84% larger than the unfilled lattice parameter of 9.034 Å.[13] The largest increase in the lattice parameter in the filled $CoGe_{1.5}Se_{1.5}$ samples compared to unfilled was 0.05 Å, which corresponds to a percent increase of 0.60%. Given that the $CoGe_{1.5}Se_{1.5}$ lattice is significantly smaller than the $CoSb_3$ lattice, it is reasonable to expect that the maximum lattice expansion possible would be less than that for $CoSb_3$.

We observed that, in the low-temperature system, we were able to incorporate more cerium when we increased the Ge/Se ratio. This "tuning" of the doping into the pnictide site is analogous to the more common doping that is performed on the metal site to incorporate more filler atom. It seems likely that we could employ this method of tuning to the amount of each element doped into the pnictide site to increase the amount of cerium incorporated into the interstitial site of the lattice.

Electrical measurements were made on both an unfilled sample and a sample with ~10% Ce incorporation into the lattice to gauge the change in properties resulting from filling the void site. The temperature dependence of the electrical resistivity of the Ce incorporation shows behavior typical of a semiconductor, increasing from 9.6×10^{-6} Ω m at room temperature to 3.2×10^{-2} Ω m at 100 K. Room-temperature Seebeck measurements gave Seebeck values of -40 μV/K, indicating that the incorporation of Ce into the $CoGe_{1.5}Se_{1.5}$ matrix results in the majority of carriers being electrons. For a comparison, the electrical resistivity of the undoped sample $Co_4Ge_{5.8}Se_{5.8}$ was 2 orders of magnitude higher, increasing from 8.7×10^{-4} Ω m at room temperature to 1.1×10^{-1} Ω m at 100 K. Room-temperature Seebeck measurements on the unfilled sample yielded a Seebeck coefficient of -86 μV/K, which is considerably smaller than the high Seebeck values of -550 and 341 μV/K reported for bulk samples with compositions of $CoGe_{1.452}Se_{1.379}$ and $CoGe_{1.431}Se_{1.385}$,

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(11) Morelli, D. T.; Meisner, G. P.; Chen, B.; Hu, S.; Uher, C. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1997**, *56*, 7376–7383.

(12) Takizawa, H.; Okazaki, K.-i.; Uheda, K.; Endo, T.; Nolas, G. S. *Mater. Res. Symp. Proc.* **2002**, *691*, 37–47.

(13) Caillat, T.; Borshchevsky, A.; Fleurial, J.-P. *J. Appl. Phys.* **1996**, *80*, 4442–4449.

respectively.[2] This prior report emphasized that the electrical behavior depends very sensitively upon the ratio of Ge and Se in these compounds. The room-temperature electrical resistivities of both the filled and unfilled samples are significantly lower than that previously reported for the unfilled pseudobinary compound.[2] This probably results from a significantly higher carrier concentration in the samples prepared in this study, which is also responsible for the much lower Seebeck coefficients reported here compared to the previously reported bulk samples.[2]

The total thermal conductivity at room temperature for both Ce-filled (1.1 W m^{-1} K^{-1}) and unfilled (1.2 W m^{-1} K^{-1}) samples are similar, and both are a factor of 6 smaller than the prior thermal conductivity measurement of $CoGe_{1.5}Se_{1.5}$.[2] This decrease in thermal conductivity with a corresponding increase in electrical conductivity is unusual, because most mechanisms that decrease thermal conductivity also decrease electrical conductivity. While the decrease in the thermal conductivity of the partially filled sample was expected from measurements on other filled skutterudites, the significant reduction in the thermal conductivity of the unfilled sample suggests that another mechanism must be responsible for the observed decrease. The percent of crystalline skutterudite in an undoped powder sample that was single-phase with respect to X-ray analysis was determined using the Rietveld refinement method by adding standard reference material NIST 640c Si powder. This indicated that 80% by weight in this sample was the crystalline skutterudite compound and 20% was amorphous. Because the crystalline skutterudite phase forms from an amorphous precursor in the low-temperature synthesis technique used, the low thermal conductivity could be a result of amorphous grain boundary regions between the crystalline grains.

Conclusions

Because of the decreased intensity in the first three peaks in the skutterudite pattern of the XRD and our Rietveld refinements of those data, we can conclude that we have successfully synthesized partially filled $CoGe_{1.5}Se_{1.5}$ skutterudites using both high-temperature and low-temperature synthesis techniques. In the case of the low-temperature samples, we have further confirmed the presence of cerium in the samples by the expansion of the unit cell. We observed a correlation of the amount of Ce incorporated in the structure with the Ge/Se ratio. This suggests that it may be possible to optimize the electrical resistivity and Seebeck coefficient of the filled skutterudite for optimum thermoelectric performance by varying the Ge/Se ratio at a fixed Ce concentration. For both the filled and unfilled samples prepared in this study, a significantly lower thermal conductivity was measured.

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