Title
Enhancement of thermoelectric properties in the Nb\textsubscript{5}Co\textsubscript{15}Sn half-Heusler/Heusler system through spontaneous inclusion of a coherent second phase

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Half-Heusler XYZ compounds with an 18 valence electron count are promising thermoelectric materials, being thermally and chemically stable, deriving from relatively earth-abundant components, and possessing appropriate electrical transport properties. The typical drawback with this family of compounds is their high thermal conductivity. A strategy for reducing thermal conductivity is through the inclusion of secondary phases designed to minimize negative impact on other properties. Here, we achieve this through the addition of excess Co to half-Heusler NbCoSn, which introduces precipitates of a semi-coherent NbCo2Sn Heusler phase. A series of NbCo1+xSn materials are characterized here using X-ray and neutron diffraction studies and electron microscopy. Electrical and thermal transport measurements and electronic structure calculations are used to understand property evolution. We find that annealing has an important role to play in determining antisite ordering and properties. Antisite disorder in the as-prepared samples improves thermoelectric performance through the reduction of thermal conductivity, but annealing during the measurement degrades properties to resemble those of the annealed samples. Similar to the more widely studied TiNi1+xSn system, Co addition to the NbCoSn phase results in improved thermoelectric performance through a decrease in thermal conductivity which results in a 20% improvement in the thermoelectric figure of merit, zT.

INTRODUCTION

Due to their unique ability to convert a temperature gradient into a voltage differential, thermoelectric materials provide a pathway towards the sustainable harvest of waste heat. The performance of a thermoelectric material is captured by the dimensionless thermoelectric figure of merit, $zT = \frac{S^2}{(\kappa\rho)T}$, where at temperature $T$, $S$ is the Seebeck coefficient, $\kappa$ is the total thermal conductivity, and $\rho$ is the electrical resistivity of a material.1 Various material classes such as main group chalcogenides, 2 silicides, 3 Si–Ge alloys,4 clathrates,5 skutterudites,6 oxides,7 Zintl’s,8 and half-Heusler compounds9 have been explored and optimized for $zT$.

Half-Heusler compounds, in particular, feature large Seebeck coefficients (|S| > 200 µV/K) with appropriate low electrical resistivities, and can be prepared from relatively earth-abundant and available materials, making them attractive candidates for thermoelectric applications.10 Heusler compounds were first synthesized in 1903 by Heusler who discovered that, despite containing no magnetic elements, MnCu2Al exhibited ferromagnetic behavior.11 This led to the discovery of multiple large structural classes of materials, including half-Heusler (hH) and Heusler (H) compounds. Compounds with these structures have unique properties that result in a broad range of applications including magnetic tunnel junctions,12 topological insulators,13 superconductivity,14 magnetocalorics,15 and thermoelectrics.10

The half-Heusler (hH) and Heusler (H) crystal structures are shown in Figure 1, and are described in detail in the caption. hH compounds have the chemical formula XYZ, while the H compounds have the formula XY′YZ, or X’YZ, where X and Y are typically transition metals and Z is a main group element. As X and Z usually have the largest electronegativity difference, these elements form a rock-salt structure with the Y atoms filling the tetrahedral voids of the rocksalt lattice.16 The hH crystal structure can be described as a zinc blende sublattice, formed by Y and Z atoms, where half of tetrahedral vacancies are stuffed by X atoms. Within this perspective, the valence electrons from the electropositive $X^{n+}$ are transferred to the more electronegative ($YZ)^{n-}$ When the total valence electron count (VEC) is eight or eighteen, the compound has a full shell and is expected to be semiconducting.17 These semiconducting hH compounds are valuable compounds for thermoelectric applications, displaying the desirable combination of high Seebeck coefficient, coupled with relatively low electrical resistivities. However, they also exhibit high thermal conductivities $\kappa$ on the order of $\kappa = 10$ W m$^{-1}$K$^{-1}$ in contrast to canonical materials, such as the heavy main group chalcogenides, that can possess values of $\kappa$ that are smaller. Effective methods for lowering $\kappa$, thus improving

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count. NbCoSn has been explored for thermoelectric properties and was selected due to its 18 valence electron count. NbCoSn has been explored for thermoelectric applications by Ono et al., who investigated the effect of Sb-doping on the thermoelectric properties, while Kimura et al. explored biphasic NbCo$_{1+x}$Sn, $x = 0.00, 0.05, 0.10, 0.15, 0.20$ samples were prepared, as described in more detailed below. Compositions were selected to be in the biphasic regime between the $h$H and $H$ phases to maximize thermoelectric properties as illustrated by previous work on the Ti–Ni–Sn system. Samples were characterized through X-ray and neutron powder diffraction, microscopy, and thermoelectric property measurements. Density functional theory (DFT) calculations were performed to examine the electronic band structure for the possible origins of the high Seebeck coefficient, as well as to approximate the value of the minimum thermal conductivity $\kappa_{\text{min}}$ of NbCoSn, following Clarke’s treatment.

To determine the effect of annealing on the structural and thermoelectric properties, samples were prepared using two different approaches, indicated as “as-prepared” (AP) and “annealed” (An). The AP samples were first arc-melted in an Ar atmosphere from a stoichiometric ratio of the pure elements: Nb foil (99.8%, Sigma Aldrich), Co powder (99.9%, Sigma Aldrich), and Sn shot (99.8%, Sigma Aldrich). The samples were flipped between each melt, and melted a total of three times to ensure homogeneity. The mass loss during melting was less than 2% for all samples. The An samples were then wrapped in Ta foil, placed in an evacuated fused silica ampoule, and submitted to an additional annealing step at 1123 K for 1 week. Both AP and An samples were subsequently pulverized in a WC ball-mill for 5 min, and powders were then loaded in a 20 mm diameter die for further consolidation by spark plasma sintering (SPS). Samples were pressed in the SPS for 5 minutes at 50 MPa at 1123 K. The resulting samples were approximately 7 g in mass. Electrical discharge machining was used to section samples to appropriate dimensions for measurements.

Room temperature synchrotron X-ray diffraction (XRD) data were acquired for all samples at the Advanced Photon Source at the 11-BM beamline at Argonne National Laboratory. Samples were placed in Kap-
ton capillaries and a wavelength of 0.4592 Å was selected to avoid resonant Sn absorption. Room temperature neutron diffraction data were acquired on the POWGEN diffractometer at Oak Ridge National Laboratory for $x = 0.00$ AP and $x = 0.00$, 0.15 An samples. Samples were loaded into 6 mm vanadium cans and data was collected for approximately 2 h per sample. Refinement of all diffraction data was completed using the Rietveld method as implemented in the GSAS-EXPGUI suite of programs.\textsuperscript{31,32} Sn occupancy was held at 1 while allowing the Co and Nb site occupancies to vary. Crystal structures were visualized using VESTA.\textsuperscript{33}

The microstructure of each sample was examined by removing a small piece from the bulk sample, mounting it in epoxy, and polishing with SiC and then with diamond suspension, finishing with 0.25 μm diamond suspension. Scanning electron microscopy (SEM) studies were carried out on a FEI XL30 Siron FEG microscope equipped with a backscattered-electron (BSE) detector. Energy dispersive X-ray (EDX) analysis assisted in phase identification. TEM lamella were prepared using a focused ion beam (FIB, Helios, FEI). Detailed investigation of microstructure was conducted in Tecnai G2 sphera TEM (FEI) operating at 300 keV.

Electrical transport properties (electrical conductivity and Seebeck coefficient) were measured on 2 mm × 2 mm × 8 mm bars on an ULVAC ZEM-3 instrument under 0.1 atm of He from room temperature to 873 K and back to room temperature. Measurements were performed twice to verify results. A Netzsch LFA 457 instrument was employed to measure thermal diffusivity using the laser flash method, between room temperature and 1123 K. Dense pellets were used for the measurements and a graphite spray was applied before measuring to minimize emissivity errors. As the electrical and thermal transport properties were measured at different temperature intervals, $z\Gamma$ was calculated by interpolation of the thermal conductivity to the same temperatures as the electrical transport measurement.

The electronic structure of hH NbCoSn was calculated using density functional theory (DFT) as implemented in the Vienna \textit{ab initio} Simulation Package (VASP)\textsuperscript{34,35} with projector-augmented wave (PAW) pseudopotentials.\textsuperscript{36,37} For structure optimization and band structure calculations, the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approximation (GGA-PBE) was employed.\textsuperscript{38} The standard primitive unit cell of the conventional face-centered orthorhombic cell was obtained using AFLLOW.\textsuperscript{39} A Γ center $k$-mesh of 8×8×8 was employed. Additional calculations of the density of states (DOS) employed the HSE06 screened hybrid functional.\textsuperscript{40} Calculations of $\kappa_{min}$ were conducted following Clarke\textsuperscript{30} using the Young’s modulus calculated from VASP using the Voigt-Reuss-Hill approximation.\textsuperscript{41}

FIG. 2. (a) PBE electronic band structure displaying an indirect band gap in hH NbCoSn. (b) HSE06 density of states for NbCoSn, showing a gap of almost 1.3 eV.

RESULTS AND DISCUSSION

Computational

The results of first-principles DFT calculations of the electronic structure of hH NbCoSn are displayed in Figure 3, including (a) the band structure, calculated using the PBE functional, and (b) the density of states, calculated using the hybrid HSE06 functional for greater reliability in establishing a band gap. NbCoSn is seen from DFT with GGA approximation to possess an indirect gap close to 1.3 eV. The band structure calculation suggests a band structure with a smaller band gap, closer to 1.0 eV. Given that this compound is n-type (from the Seebeck coefficient, discussed presently), it is relevant to consider the nature of the conduction band, which is largely comprised of Nb d states. The conduction band minimum at the X point is doubly degenerate and relatively flat. As the Seebeck coefficient is related to the effective mass, this result may explain the relatively high Seebeck coefficient.\textsuperscript{1} These results are in contrast with the electronic structure of the more widely studied n-type thermoelectric hH TiNiSn, which has a valence band minimum that is singly degenerate at the X point. DFT calculations estimate a minimum lattice thermal conductivity, $\kappa_{min}$ of 0.86 W m$^{-1}$ K$^{-1}$. This value is lower than experimental measurements $\kappa$ approaching 4 W m$^{-1}$ K$^{-1}$ at 1100 K.

Structural Characterization

In order to understand the thermoelectric properties of these compounds, it is first essential to evaluate them
FIG. 3. Powder synchrotron X-ray diffraction results for the as-prepared (AP) NbCo$_{1+x}$Sn, $x=0.00$ through 0.20 (indicated) samples. Indexed peaks from the refined lattice constants for the $hH F\bar{4}3m$ and $H Fm\bar{5}m$ phases are shown in the top two panels. (220) peaks are shown in detail on the panel to the right, where the evolution of the $H$ phase can be observed with increasing $x$.

from a structural perspective. This was accomplished through the analysis of the average structure of the Nb–Co–Sn series through synchrotron X-ray and neutron diffraction studies. Synchrotron X-ray diffraction provides the high $Q$-space resolution and high signal-to-noise necessary to consider the evolution of the minor $H$ phase and determine impurity phases, while neutron diffraction allows for accurate determination of site occupancies and atomic displacement parameters (ADPs, reported as $U_{iso}$). Together, these techniques can provide a detailed description of the structural phases and atomic parameters of these $hH$–$H$ materials, in particular the average structural disorder and its role on the observed physical properties.

Synchrotron X-ray diffraction was performed on $x=0.00, 0.05, 0.10, 0.15, 0.20$ AP and $x=0.00, 0.15$ An samples. The results for the AP samples are presented in Figure 3, and the evolution of the $H$ (220) reflection, highlighted in the right panel, corresponds to increases in $x$-content. Rietveld refinement of the X-ray diffraction data indicated small weight fractions of secondary phases, including Nb$_3$Sn, elemental Sn, and an unidentified intermetallic phase. Secondary phases (Sn and Nb$_3$Sn) were less than 2wt%, and were thus not included in the overall fits of the diffraction data. The An samples have a smaller percentage of secondary phases, indicating the additional annealing step results in the dissolution of secondary phases remnant from the melting process. In addition to phase purity, there is a slight decrease in the lattice constant with additional annealing as is indicated by a comparison of the AP and An samples where $x=0.00$ ($a=5.9559(1)$Å for the AP material as compared to $a=5.9510(3)$Å for the An). This lattice contraction suggests the An samples have increased ordering, as will be shown by neutron analysis.

Powder neutron diffraction was completed at room temperature for a subset of samples ($x=0.00$ AP and $x=0.00, 0.15$ An). Results for the An samples are shown with the Rietveld fits in Figure 4. Key crystallographic parameters are compared in Table I. The ADPs, presented as $U_{iso}$, of these compounds are similar at each of these sites, indicating that the individual atomic sites have similar degrees of structural disorder. While completing this analysis, attempts were made to introduce

![Figure 4](image-url)

**FIG. 4.** Fits obtained from the Rietveld refinement of powder neutron diffraction data for the annealed (An) samples of NbCo$_{1+x}$Sn, with (a) $x=0.00$, using a single $hH$ phase, and (b) $x=0.15$ refined with $hH$ and $H$ phases.

<table>
<thead>
<tr>
<th>$x=0.00$, AP</th>
<th>$x=0.00$, An</th>
<th>$x=0.15$, An</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>5.95786(2)</td>
<td>5.95240(2)</td>
</tr>
<tr>
<td>Nb $U_{iso}$</td>
<td>0.0035(5)</td>
<td>0.00288(3)</td>
</tr>
<tr>
<td>Co $U_{iso}$</td>
<td>0.0030(2)</td>
<td>0.0031(2)</td>
</tr>
<tr>
<td>Sn $U_{iso}$</td>
<td>0.0029(4)</td>
<td>0.0032(4)</td>
</tr>
<tr>
<td>Occ. Nb$_N$</td>
<td>0.90(2)</td>
<td>0.97(2)</td>
</tr>
<tr>
<td>Occ. Co$_N$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Occ. Sn$_N$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Occ. Co$_N$</td>
<td>0.10(2)</td>
<td>0.03(2)</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>5.7%</td>
<td>6.2%</td>
</tr>
</tbody>
</table>

**TABLE I.** Structural parameters of the $hH$ phase as obtained from Rietveld refinement of the neutron diffraction data, comparing AP and An samples. Note the greater degree of site-ordering in the An samples.
Co interstitials similar to the Ni interstitials found in vacant tetrahedral sites of the TiNiSn system. However, these attempts resulted in the Co interstitial to have unreasonably large \( U_{iso} \) values, suggesting it to be an unfit model. While both of the \( x = 0 \) compounds have excess Co on the Nb 4\( a \) Wyckoff sites, this substitution is most evident in the \( AP \) sample as compared to the \( An \) samples. Additionally, occupancies of the annealed \( x = 0.15 \) compound indicates that the addition of the secondary \( H \) phase may encourage site ordering. Thus, the \( An \) sample has a higher degree of site ordering (\( i.e., \) Co and Nb are occupying their predicted sites) in addition to having a higher phase purity.

Figure 5 compares the \( hH \) lattice constant, \( H \) lattice constant, and \( H \) mole fraction with respect to \( x \). The synchrotron X-ray data indicates that the lattice constants of both phases are independent of composition in the range studied, indicating that the the addition of extra Co to the \( hH \) phase contributes to the formation of the \( H \) phase and not to the introduction of Co-interstitials in the \( hH \) phase. This result contrasts the lattice constant expansion found in the Ti–Ni–Sn system with the addition of Ni.\(^{21}\) Furthermore, there is no evidence of peak splitting, as found in TiNiSn, that results from an extra phase with Ni interstitials.\(^{23}\) Figure 5(c) compares how the refined mole fraction of the \( H \) phase varies with nominal \( x \). These results indicate that the \( H \) phase emerges near the 1:1 ratio with regards to the nominal compositions.

From these results, it is concluded that, regardless of annealing, as \( x \) is increased, the \( H \) phase will form as a second phase alongside the \( hH \) phase. Additionally, the extra annealing step in preparation of the \( An \) samples increases the site ordering of the \( hH \) phase as shown through a decrease in lattice constant and the degree of substitution of Co on the Nb sites. These results contrast the interstitial defects found in the TiNiSn system, exemplifying the variable forms of structural disorder that may appear within the Heusler family.

**Microscopy**

In addition to exploring the proportions of the phases and ordering in \( hH \) and \( H \) compounds, the microstructure of this biphasic compound has been studied to evaluate the interfaces between the two phases. Representative SEM micrographs are given in Figure 6, where it is apparent that the \( x = 0.00 \) \( An \) compound is entirely the \( hH \) phase, as shown in frame (a). Regions of Sn impurities can be identified by their bright appearance. Particles of \( H \) evolve with Co addition, as shown in frame (b) evaluating the \( x = 0.15 \) \( An \) sample. Dark regions of micrographs are pores that formed during sample preparation. These \( H \) inclusions become large in the \( x = 0.20 \) \( AP \) sample. Intermediate compositions (\( x = 0.05, 0.10 \)) show similar \( H \) features as \( x = 0.15 \), but are less frequent. Comparison of \( An \) to \( AP \) samples indicates a reduction in impurity phases, such as Nb\(_3\)Sn and Sn upon the introduction of the annealing step.

The TEM image of lamella taken from the two-phase region indicated in Figure 6(c) is shown in Figure 7 and clearly reveals the presence of precipitates with sizes
ranging from the nanometer to micron scale. A range of precipitate size will scatter phonons at a range of wavelengths, maximizing the reduction of $\kappa$. The brighter particle is confirmed by EDX to be the $H$ phase and the darker matrix as $hH$. The bright field TEM, Figure 7, is labeled to indicate the location for diffraction analysis. Selected area electron diffraction pattern (SAED) taken from the $H$ phase, the $hH$ phase, and the interface between the two indicates the same crystallographic orientation. This demonstrates a cube-on-cube orientation relationship between the $H$ precipitates and the $hH$ matrix with semi-coherent interfaces, which is expected due to their similar crystal structure and lattice parameter 3% misfit. Coherent interfaces are shown to significantly reduce the thermal conductivity without affecting the electrical conductivity, which is critical in designing a highly efficient thermoelectric material.

Physical Properties

To determine the thermoelectric properties of the biphasic materials, a series of high temperature transport measurements were completed. The electrical resistivity ($\rho$), shown in panel (a) of Figure 8, indicates metallic behavior for all samples, as shown by the positive slope in the temperature dependence of the resistivity. This is in contrast to the semiconducting behavior of the $hH$ compound as predicted through DFT. Since these calculations were performed on a perfectly ordered system, discrepancies can be attributed to the varying amounts of site ordering evidenced by the analysis of the diffraction data. A similar antisite disorder effect was proposed by Ono et al., who also predicted semiconducting behavior but observed metallic conductivity for samples of NbCoSn$_{1-x}$Sb$_x$. Additionally, we can observe that resistivity generally decreases with increasing $x$. In addition to compositional effects, an increase in the temperature dependence of the resistivity was observed for both $An$ samples, in particular, the $x = 0.00$ $An$ sample has a comparatively high electrical resistivity to the rest of the series. These observations can be attributed to the high degree of ordering present in the $An$ sample, allowing it to be closer to its theoretical semiconducting state.

The Seebeck coefficient $S$ is illustrated in panel (b) of Figure 8. The magnitude of the Seebeck coefficient decreases with increasing $H$ content. The $x = 0.00$ $An$ (no $H$ phase) sample shows the largest magnitude in Seebeck coefficient, particularly when compared with the $AP$ sample. This can be explained by the higher degree of ordering in the $An$ sample as indicated by the structural characterization of these compositions.

The electrical resistivity is proportional to the magnitude of the Seebeck coefficient as both are dependent on carrier concentration. This phenomenon is evident in this material system by observing that the sample with the lowest resistivity ($x = 0.20$ $AP$) is also the one with the lowest magnitude in Seebeck coefficient. Conversely, the sample with the highest resistivity ($x = 0.00$ $An$) has the largest magnitude in Seebeck coefficient. Therefore, as shown in Figure 9, varying $x$ results in a limited change in the Power Factor, $S^2\rho^{-1}$.

Trends in the thermal conductivity, $\kappa$, as a function of temperature for $x = 0.00$, 0.15 ($An$, $AP$) are summarized in Figure 10.

The lattice contribution to thermal conductivity is shown for $x = 0.00$ $An$ and $x = 0.15$ $AP$, as determined by subtracting the electronic contribution to thermal conductivity, as calculated by the Widemann-Franz law, from the experimental thermal conductivity.
FIG. 9. The thermoelectric power factor, $S^2\rho^{-1}$ displayed for the different $AP$ and $An$ samples, as a function of temperature. At the highest temperature measured, there is a general trend towards a high power factor, suggesting that the decreased resistivity with increasing $x$, both for the $AP$ and $An$, plays a greater role than changes in the Seebeck coefficient.

FIG. 10. Thermal conductivity ($\kappa$) for $x = 0.00, 0.15$ samples as (a) a function of temperature and (b) a function of $x$ at 800 K. It is observed that both the absence of the additional annealing step and the inclusion of the secondary $H$ phase reduces $\kappa$.

The $zT$ metric ($zT = S^2/(\kappa\rho)T$) for $x = 0.00, 0.15$ ($An$, $AP$) is shown in Figure 11. It is observed that $zT$ reaches a maximum of 0.122 at 822 K for the $x = 0.15$ $AP$ sample. As the power factors for all studied materials are similar at this temperature, the enhanced $zT$ is attributed primarily to the reduction of $\kappa$. Comparing the maximum $zT$ of the annealed, thermally stable, samples indicates 20% improvement in the thermoelectric figure of merit upon the introduction of NbCo$_2$Sn inclusions. This confirms that the addition of a secondary phase is an effective method for optimizing the thermal aspects of the thermoelectric performance of these $hH-H$ systems.

CONCLUSION

In summary, we have shown that $hH$ compound NbCoSn will develop a biphasic structure with $H$ NbCo$_2$Sn through the introduction of excess Co. TEM shows the resulting interface is semi-coherent in nature. Two different preparation approaches, one which included a high temperature anneal, permitted the examination of antisite defects and their influence on trans-
port properties relevant to thermoelectric performance. In contrast to TiNiSb, results indicate that additional Co does not sit in the tetrahedral vacancies of the hH lattice, but may occupy Nb sites without a high temperature anneal. The annealed, highly ordered, compounds exhibit electrical resistivity closer to theoretical temperature anneal. The annealed, highly ordered, compounds exhibit electrical resistivity closer to theoretical temperature anneal. The annealed, highly ordered, compounds exhibit electrical resistivity closer to theoretical temperature anneal. The annealed, highly ordered, compounds exhibit electrical resistivity closer to theoretical temperature anneal. The annealed, highly ordered, compounds exhibit electrical resistivity closer to theoretical temperature anneal. The annealed, highly ordered, compounds exhibit electrical resistivity closer to theoretical temperature anneal. The annealed, highly ordered, compounds exhibit electrical resistivity closer to theoretical temperature anneal. The annealed, highly ordered, compounds exhibit electrical resistivity closer to theoretical temperature anneal. The annealed, highly ordered, compounds exhibit electrical resistivity closer to theoretical temperature anneal. The annealed, highly ordered, compounds exhibit electrical resistivity closer to theoretical temperature anneal.

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