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Enhanced thermoelectric properties of n-type NbCoSn half-Heusler by improving phase purity

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Here we report the thermoelectric properties of NbCoSn-based n-type half-Heuslers (HHs) that were obtained through arc melting, ball milling, and hot pressing process. With 10% Sb substitution at the Sn site, we obtained enhanced n-type properties with a maximum power factor reaching \(\sim 35 \, \mu W cm^{-1} K^{-2}\) and figure of merit (ZT) value \(\sim 0.6\) in NbCoSn\(_{0.9}\)Sb\(_{0.1}\). The ZT is doubled compared to the previous report. In addition, the specific power cost (\(S W^{-1}\)) is decreased by \(\sim 68\%\) comparing to HfNiSn-based n-type HH because of the elimination of Hf.

The demand for energy is dramatically increasing, putting a heavy burden on modern society. Meanwhile, most of the energy generated from burning fossil fuels is dissipated as waste heat. Thus it is of great importance to recover some of the wasted heat and convert it into useful energy. This can be done by using the thermoelectric principle, where the heat-to-power conversion efficiency is determined by the average of the figure of merit (ZT) over the operating cold and hot side temperatures,\(^1\)

\[
\eta = \frac{T_H - T_C}{T_H} \cdot \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}},
\]

\[ZT = \frac{PF}{\kappa_{tot}} T,\]

\[PF = S^2 \sigma,\]

\[\kappa_{tot} = \kappa_L + \kappa_e,\]

where \(PF, T, \kappa_{tot}, S, \sigma, \kappa_L,\) and \(\kappa_e\) are the power factor, absolute temperature, total thermal conductivity, Seebeck coefficient, electrical conductivity, lattice thermal conductivity, and electronic thermal conductivity, respectively. Higher ZT leads to higher conversion efficiency for thermoelectric materials.

Good ZT values have been reported in HfNiSn-based n-type\(^2\)\(^\endnote{2}{2}\)\(^\endnote{6}{6}\) and HfCoSb-based p-type\(^7\)\(^\endnote{7}{7}\)\(^\endnote{\text{11}}{11}\) half-Heusler (HH) materials. However, the use of Hf is unfavorable due to its high cost.\(^12\) Recently NbFeSb-based p-type materials have been reported to possess ZT \(\sim 1.0\) at 700 °C\(^13\) and \(\sim 1.5\) at 923 °C\(^14\) and high power factor (PF) \(\sim 106 \, \mu W cm^{-1} K^{-2}\) at room temperature.\(^15\) These findings significantly advance the applications of half-Heusler materials in mid-to-high temperature range. However, there are no competitive n-type materials which are Hf-free.

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NbCoSn is a half-Heusler material with 18 valance electrons; its thermoelectric properties have been studied by several groups. Undoped NbCoSn is intrinsically n-type. Kiruma et al. reported the effects of increasing Co concentration up to NbCo$_{1.1}$Sn and obtained a Seebeck coefficient of about $\sim 250 \, \mu V/K$ and peak ZT of 0.3 at $\sim 1000 \, K$ in NbCo$_{1.05}$Sn.$^{16}$ Kawaharada et al. reported the TE properties with partial substitution of Nb by Hf, Ti and Mo, and Sn by Sb.$^{17,18}$ They found Hf and Ti are weak p-type dopants and the resulting Seebeck coefficient is very low. Meanwhile, Mo and Sb are strong n-type dopants, resulting in better TE performance than Hf or Ti doped p-type NbCoSn. Similar studies were also performed by Ono et al. and the ZT $\sim 0.3$ was reported in NbCoSn$_{0.9}$Sb$_{0.1}$.$^{19}$ However, these reported compositions possess many secondary phases such as NbCo$_2$Sn, Sn, Nb$_2$Sn, etc., which deteriorates TE performance, especially the electron transport properties. To investigate the properties of compositions with better purity, we studied NbCoSn$_{1-x}$Sb$_x$ with $x = 0–0.15$ by arc melting, ball milling, and hot pressing. As widely reported,$^{2,3,7–9}$ this approach effectively helps getting pure phase because arc melting prompts the reaction efficiency by heating the elements into liquid states, while high energy ball milling crushes the compounds into nano particles, guarantees the uniformity during the following sintering process. As a result, the purity is improved when comparing with other approaches.$^{16–19}$ Electron transport significantly benefits from phase purifcation, leading to simultaneous enhancement of electrical conductivity and Seebeck coefficient. The highest power factor obtained by this method is $\sim 34 \, \mu W\,cm^{-1}\,K^{-2}$, which is 80% higher than Ono’s reported value. As a result, a peak ZT of $\sim 0.6$ was achieved. Even though the ZT is still lower than 1.0 like other good HfNiSn-based n-type HHs, the calculated specific power cost ($W^{-1}$) is much lower due to elimination of Hf in the composition.

A total 10 grams of elements (Nb pieces 99.99% and Co shavings 99.9%, Atlantic Metals and Alloy; Sn granules 99.9% and Sb broken rod 99.9%, Alfa Aesar) for each batch were weighed according to the stoichiometry. In order to reduce Sb evaporation, we first melted Sb with Sn to form alloys, then the other elements were added and melted together 3–4 times with flipping the sample over each time to form a more uniform ingot. The ingot was then crushed into nano-powders by a high energy ball milling (SPEX 8000M Mixer/Mill) machine for 2 h. The powders were then consolidated into disks by hot pressing at 1000 $^\circ C$ and 80 MPa for 2 min.

A PANalytical multipurpose diffractometer with an X’celerator detector (PANalytical X’Pert Pro) was used to characterize the phases. Morphology and elemental distributions of the samples were characterized by a scanning electron microscope (SEM, LEO 1525) and an energy dispersive x-ray spectroscope (EDS), respectively. An Electron Probe Micro-Analysis (EPMA, JXA-8600) was used to characterize the phases. Morphology and elemental distributions of the samples were characterized by a transmission electron microscope (TEM, JEOL 2010F) was used to observe the detailed microstructures.

The thermal conductivity was calculated as a product of thermal diffusivity ($D$), specific heat ($c_P$), and density, measured by a laser flash system (LFA457, Netzsch), a differential scanning calorimeter (DSC, 404 C), and an Archimedes’ kit, respectively. Bar shaped samples ($\sim 2 \times 2 \times 10 \, mm^3$) were used to measure electrical conductivity and Seebeck coefficient on a ZEM-3 machine (ULVAC). Carrier concentrations ($n_H$) were measured using a physical properties measurement system (PPMS, Quantum Design) under a 3 T magnetic field. The Hall mobility $\mu_H$ was calculated based on $\mu_H = \sigma R_H$, where $R_H$ is the Hall coefficient. The uncertainty for electrical conductivity is 3%, Seebeck coefficient 5%, and thermal conductivity 6%, so the combined uncertainty for power factor and ZT is 10% and 12%, respectively. To increase the readability, we did not plot error bars on the curves.

The band structure and density of states (DOS) are obtained from density functional theory (DFT) calculations within the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form for the exchange-correlation function.$^{20}$ The electronic transport coefficients are computed by solving the Boltzmann transport equation for electrons using the intrinsic contribution from the electron-phonon interaction to the electron relaxation time calculated within the electron-phonon-averaged (EPA) approximation.$^{21}$

Due to the similar atomic size and masses, all samples possess similar densities (Table I). Figure 1 shows the X-ray diffraction (XRD) spectrum of NbCoSn$_{1-x}$Sb$_x$ when $x = 0, 0.01, 0.02, 0.05, 0.1,$ and 0.15. All samples show pure half-Heusler (HH) phase, indicating good solubility of Sb at the Sn site. Also, the energy dispersive spectroscopy (EDS) mapping on a polished surface of NbCoSn$_{0.9}$Sb$_{0.1}$ shows uniform elemental distribution (see supplementary material Figure S1$^{22}$).
TABLE I. Nominal, actual compositions, and measured mass densities of NbCoSn$_{1-x}$Sb$_x$ by electron probe micro-analysis (EPMA).

| Nominal     | EPMA          | Density (g cm$^{-3}$) |
|-------------|---------------|-----------------------|
| NbCoSn      | NbCo$_{1.01}$Sn$_{0.98}$ | 8.35                  |
| NbCoSn$_{0.99}$Sb$_{0.01}$ | NbCo$_{1.01}$Sn$_{0.98}$Sb$_{0.01}$ | 8.48                  |
| NbCoSn$_{0.98}$Sb$_{0.02}$ | NbCo$_{1.00}$Sn$_{0.96}$Sb$_{0.02}$ | 8.48                  |
| NbCoSn$_{0.95}$Sb$_{0.05}$ | NbCo$_{1.02}$Sn$_{0.94}$Sb$_{0.05}$ | 8.48                  |
| NbCoSn$_{0.85}$Sb$_{0.15}$ | NbCo$_{1.01}$Sn$_{0.84}$Sb$_{0.14}$ | 8.52                  |

no phase segregation is observed. The electron probe micro-analysis (EPMA) results are shown in Table I with the actual composition of the final product very close to the nominal composition.

Figure 2(a) shows the scanning electron microscopic (SEM) images of sample with nominal composition NbCoSn$_{0.9}$Sb$_{0.1}$, demonstrating grain size from $\sim$250 to $\sim$800 nm. It has to be mentioned that there are still some minor impurities which cannot be detected by XRD or EDS. Figs. 2(b) and 2(c) are the low and high resolution TEM images of NbCoSn$_{0.9}$Sb$_{0.1}$, which show there are some minor defects or precipitates. Thus to completely remove the impurities seems unrealistic. However, the phase purity is much higher than the previously reports.16–19

Figures 3(a)-3(h) show the thermoelectric properties of NbCoSn$_{1-x}$Sb$_x$ with $x$ up to 0.15. For comparison, we also plotted the literature data of NbCoSn$_{0.9}$Sb$_{0.1}$19 (thick black line) and NbCoSb$^{23}$ (dotted line), the latter is an unusual half-Heusler thermoelectric material that has 19 valance electrons. Figures 3(a) and 3(b) plot the electric conductivity and the Seebeck coefficient, respectively. Higher Sb concentration results in higher conductivity and lower Seebeck coefficient. For NbCoSn$_{0.9}$Sb$_{0.1}$, both the conductivity and Seebeck coefficient are higher than Ono’s reported values,19 which resulted in much higher power factors (Fig. 3(c)) with a peak value of $\sim$34 $\mu$W cm$^{-1}$ K$^{-2}$ in NbCoSn$_{0.9}$Sb$_{0.1}$ at 873 K, $\sim$80% higher than Ono’s result.

Figs. 3(d)–3(f) show the total thermal conductivity ($\kappa_{\text{tot}}$), specific heat ($c_P$), and thermal diffusivity ($D$), respectively. It is interesting to note that the thermal conductivity of the base composition NbCoSn is $\sim$8.2 W m$^{-1}$ K$^{-1}$ at room temperature (Fig. 3(d)), but even 1% Sb doping increased the value to $\sim$9.7 W m$^{-1}$ K$^{-1}$. The mechanism of the enhancement is not completely clear at the moment since the increased electronic contribution cannot account for all of the increase. For samples with more Sb doping, the thermal conductivity keeps decreasing as a result of the decreased lattice thermal conductivity ($\kappa_L$) (Fig. 3(g)). It should be mentioned that the decrease in $\kappa_L$ is not due to point defect scattering because the $\kappa_L$ of ternary NbCoSb$^{23}$ is smallest among all the NbCoSn$_{1-x}$Sb$_x$ samples. The electron-phonon interaction possibly dominates the phonon

FIG. 1. X-ray diffraction (XRD) spectra of NbCoSn$_{1-x}$Sb$_x$ with $x$ = 0, 0.01, 0.02, 0.05, 0.1, and 0.15.
FIG. 2. (a) SEM image of NbCoSn$_{0.9}$Sb$_{0.1}$, indicating grain size from $\sim$250 to $\sim$800 nm, (b) low resolution, and (c) high resolution TEM image of NbCoSn$_{0.9}$Sb$_{0.1}$. The white arrows in (b) and white curve in (c) indicate there are still some minor impurities. (d) Lattice constant of $\sim$5.94 Å is for NbCoSn$_{0.9}$Sb$_{0.1}$ and the inset in (d) is its FFT image.

scattering because of the increased carrier concentration (Fig. 4(a)) or the stronger phonon-phonon interaction with higher concentration of Sb. As a result, the $ZT$ values reaches $\sim$0.6 (Fig. 3(h)) in NbCoSn$_{0.9}$Sb$_{0.1}$, which is about double of the $ZT$ value reported by Ono et al. with the same composition.

The relation of the Hall concentration ($n_H$, solid square) and mobility ($\mu_H$, open circle) with Sb concentration is shown in Figure 4(a). The measured carrier concentration increases almost linearly with Sb concentration for all the Sb partially substituted compositions; however, the undoped composition has $n_H$ value even higher than that of 2% Sb doping. This could be qualitatively explained by the two-band model in which $n_H$ could be written as

$$n_H = \frac{1}{qR_H}$$

$$R_H = \frac{1}{q} \frac{p - nb^2}{(p + nb)^2},$$

where $q$ is positive value of carrier charge, $R_H$ is the Hall coefficient, $p$ and $n$ are the real concentration of electrons and holes, respectively; $b$ is defined as the carrier mobility ratio between electrons and holes usually in the order of unity. Thus,
FIG. 3. Thermoelectric properties: (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) total thermal conductivity, (e) specific heat, (f) thermal diffusivity, (g) lattice thermal conductivity, and (h) ZT of NbCoSn$_{1-x}$Sb$_x$ with $x = 0, 0.01, 0.02, 0.05, 0.1, and 0.15$. The reference data of NbCoSn$_{0.9}$Sb$_{0.1}$ and NbCoSb are taken from Ref. 19 (thick black line) and Ref. 23 (dashed line), respectively.

\[ n_H = \frac{(p + nb)^2}{p - nb^2}. \]

For heavily doped semiconductors (SCs), it satisfies $p \gg n$ or $n \gg p$, thus $n_H \approx p$ or $n$. However, for low level doping around the intrinsic region, the values of $p$ and $n$ are close to each other,
FIG. 4. (a) Carrier concentration (left vertical axis) and mobility (right vertical axis) of NbCoSn\textsubscript{1-x}Sb\textsubscript{x}. (b) Seebeck coefficient vs. carrier concentration, showing an increased effective mass from 5.7 m\textsubscript{e} to 7.1 m\textsubscript{e} with higher concentration of Sb.

thus, the denominator in the expression of n\textsubscript{H} could be quite small and result in an artificially large n\textsubscript{H}.

With Sb concentration increasing from 0.01 to 0.15, n\textsubscript{H} increases almost linearly to \(>2 \times 10^{21}\) cm\textsuperscript{-3}, which is quite high for TE materials. Huang et al. reported an even higher carrier concentration of \(6 \times 10^{21}\) cm\textsuperscript{-3} for NbCoSb.\textsuperscript{23} On the other hand, the measured carrier mobility increases significantly from \(0.2\) to \(11\) cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} with Sb concentration up to 0.05, then it decreases to \(8.8\) cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} with Sb concentration reaching 0.15 (Fig. 4(a) right). It is necessary to point out that the Hall mobility (\(\mu\textsubscript{H}\)) with Sb concentration below 0.05 is underestimated due to, as explained, the overestimation of Hall concentration (n\textsubscript{H}). Fitting with the Pisarenko relation using the compositions with Sb concentration higher than 0.05 by the single parabolic band model, the electron density of states (DOS) effective mass (m*) is found to gradually increase from 5.7 m\textsubscript{e} to 7.1 m\textsubscript{e} with Sb concentration up to 1.0. The enhanced effective mass accounts for the decreased carrier mobility when Sb concentration is higher than 0.05 (Fig. 4(a)).

Figures 5(a) and 5(b) show the band structure and density of states (DOS) calculated using density functional theory (DFT). The base composition NbCoSn is semiconducting, but the samples NbCoSn\textsubscript{1-x}Sb\textsubscript{x} behave like metal due to heavy doping Sb on Sn site. The indirect band gap is around 1 eV with the conduction band minima (CBM) at X points and the valence band maxima (VBM) at L and W points. The CBM consists of two bands thus giving a high valley degeneracy (\(N_v = 6\)). High valley degeneracy is widely proven to be beneficial to thermoelectric performance.\textsuperscript{24–29} More interestingly, we notice that an even higher valley degeneracy occurs at the

FIG. 5. (a) Band structure and (b) density of states (DOS) of NbCoSn calculated within DFT using the PBE exchange-correlation function. The yellow region indicates the bandgap.
VBM, where the L and W points both contribute to the hole transport, thus higher TE performance of p-type NbCoSn is expected. This part is still under investigation.

Figures 6(a)-6(d) show the electronic transport coefficients of NbCoSn calculated within the electron-phonon-averaged (EPA) approximation. Calculations are performed for the base composition, NbCoSn, and the doping is treated within the rigid-band approximation. The calculated values of the electronic transport coefficients show a good agreement with the experimental results shown in Fig. 3. For instance, the calculations at $T = 973$ K and $n = 0.05$ yield $\sigma = 0.80 \times 10^5$ $\Omega^{-1}$ m$^{-1}$, $S = -190$ $\mu$V K$^{-1}$, $PF \sim 29$ $\mu$W cm$^{-1}$ K$^{-2}$, and $\kappa_e = 0.90$ W m$^{-1}$ K$^{-1}$ (see Fig. 6) while the measurements at $T = 973$ K and $x = 0.05$ give $\sigma = 0.64 \times 10^5$ $\Omega^{-1}$ m$^{-1}$, $S = -213$ $\mu$V K$^{-1}$, $PF \sim 29$ $\mu$W cm$^{-1}$ K$^{-2}$, and $\kappa_e = 1.00$ W m$^{-1}$ K$^{-1}$ (see Fig. 3). The deviations between theory and experiment in $\sigma$ at low temperatures are due to extrinsic scattering mechanisms (ionized impurities and grain boundaries) not included in EPA calculations. The deviations in $S$ in the low doping limit are possibly resulted from the difference between the carrier concentration $n$ and the Sb concentration $x$.

Even though the NbCoSn-based HH does not have the same ZT as the HfNiSn-based n-type HHs, such as Hf$_{0.25}$Zr$_{0.75}$NiSn$_{0.99}$Sb$_{0.01}$, it is much cheaper since it does not contain Hf. Table II lists the prices of the relevant elements from which the calculated prices are $126$ kg$^{-1}$ for Hf$_{0.25}$Zr$_{0.75}$NiSn$_{0.99}$Sb$_{0.01}$ but only $26$ kg$^{-1}$ for NbCoSn$_{0.9}$Sb$_{0.1}$, which is only $\sim 1/5$, thus a much lower $S$ W$^{-1}$ is expected for NbCoSn.

Based on the equations derived by Kim et al., we calculated the conversion efficiency and output power density assuming a leg length of 2 mm and cold side temperature of 323 K (Fig. 7).
TABLE II. The price of relevant elements in the year 2010.\textsuperscript{12}

| Elements | Hf | Zr | Ti | Ni | Sn | Sb | Nb\textsuperscript{a} | Co |
|----------|----|----|----|----|----|----|----------------|----|
| Prices (\textdollar \ kg\textsuperscript{-1}) | 563 | 99.8 | 10.7 | 21.8 | 27.3 | 8.8 | 14.3 | 46 |

\textsuperscript{a}The price of Nb is in year 2005.

Not surprisingly, both the power density (Fig. 7(a)) and the conversion efficiency (Fig. 7(b)) of NbCoSn\textsubscript{0.9}Sb\textsubscript{0.1} are lower than Hf\textsubscript{0.25}Zr\textsubscript{0.75}NiSn\textsubscript{0.99}Sb\textsubscript{0.01}, but the specific power cost (\textdollar \ W\textsuperscript{-1}) is much lower as well (Fig. 7(c)), when the hot side temperature ($T_H$) is 873 K, it is \textasciitilde0.012 \textdollar \ W\textsuperscript{-1} for Hf\textsubscript{0.25}Zr\textsubscript{0.75}NiSn\textsubscript{0.99}Sb\textsubscript{0.01}, but \textasciitilde0.004 \textdollar \ W\textsuperscript{-1} for NbCoSn\textsubscript{0.9}Sb\textsubscript{0.1}. This specific power

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7}
\caption{The calculated power density (a), efficiency (b), and specific power cost (\textdollar \ W\textsuperscript{-1}) (c) of Hf\textsubscript{0.25}Zr\textsubscript{0.75}NiSn\textsubscript{0.99}Sb\textsubscript{0.01} and NbCoSn\textsubscript{0.9}Sb\textsubscript{0.1}.}
\end{figure}
cost is also much lower than that of the reported HfCoSb based p-type material.\textsuperscript{9} 0.024 $W^{-1}$K\textsuperscript{-1} for Hf\textsubscript{0.44}Zr\textsubscript{0.12}CoSb\textsubscript{0.8}O\textsubscript{0.2} and 0.012 $W^{-1}$K\textsuperscript{-1} for Hf\textsubscript{0.19}Zr\textsubscript{0.76}Ti\textsubscript{0.05}CoSb\textsubscript{0.8}Sn\textsubscript{0.2} (with $T_H$ at 873 K). Thus NbCoSn could be competitive with HfNiSn-based n-type half-Heusler for large-scale applications.

Sb doping could effectively enhance the thermoelectric performance of NbCoSn-based n-type half-Heuslers by eliminating the impurity phases. Both the electrical conductivity and Seebeck coefficient are higher, resulting in a higher power factor. The peak power factor is $\sim 34 \mu W cm^{-1}K^{-2}$ at 873 K in NbCoSn$_{0.9}$Sn$_{0.1}$, which is 80\% higher than the previously reported data with the same composition. A peak ZT of $\sim 0.6$ was achieved at 973 K, which is about double the previously reported value with the same composition. Most importantly, the specific power cost of NbCoSn-based HH is much lower than the HfNiSn-based HHSs.

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