Stronger phonon scattering by larger differences in atomic mass and size in p-type half-Heuslers Hf$_{1-x}$Ti$_x$CoSb$_{0.8}$Sn$_{0.2}$

Xiao Yan,$^a$ Weishu Liu,$^a$ Hui Wang,$^a$ Shuo Chen,$^a$ Junichiro Shiomi,$^{bc}$ Keivan Esfarjani,$^b$ Hengzhi Wang,$^a$ Dezhi Wang,$^a$ Gang Chen$^{ab}$ and Zhifeng Ren$^{ab}$

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High lattice thermal conductivity has been the bottleneck for further improvement of the thermoelectric figure-of-merit (ZT) of half-Heuslers (HHs) Hf$_{1-x}$Zr$_x$CoSb$_{0.8}$Sn$_{0.2}$. Theoretically, the lattice thermal conductivity can be reduced by exploring larger differences in the atomic mass and size in the crystal structure, leading to higher ZT. In this paper, we experimentally demonstrated that a lower thermal conductivity in p-type half-Heuslers can be achieved when Ti is used to replace Zr, i.e., Hf$_{1-x}$Ti$_x$CoSb$_{0.8}$Sn$_{0.2}$, due to larger differences in the atomic mass and size between Hf and Ti compared with Hf and Zr. The highest ZT peak, \( \sim 1.0 \) at 800 °C, in the Hf$_{1-x}$Ti$_x$CoSb$_{0.8}$Sn$_{0.2}$ (x = 0.1, 0.2, 0.3, and 0.5) system was achieved using Hf$_{0.8}$Ti$_{0.2}$CoSb$_{0.8}$Sn$_{0.2}$, which makes this material useful in power generation applications.

Introduction

Thermoelectric (TE) materials can convert heat, such as that in the vehicle exhaust systems$^{1,2}$ and that generated from solar radiations,$^{3,4}$ into electric power in an environmentally friendly and less costly way. PbTe$^6$ and skutterudites$^8$ are suitable materials for medium temperature (300–500 °C) applications whereas SiGe$^9$ alloys are used for high temperature power generation applications (500–800 °C). Despite the advantages of non-toxicity, high thermal stability, and low cost compared to PbTe, skutterudites and SiGe alloys, half-Heuslers,$^{a}$ another class of thermoelectric materials, have been much less explored, owing to the low thermoelectric figure-of-merit (ZT). By definition, ZT = \( \frac{S^2 \sigma}{w \kappa} T \), where S is the Seebeck coefficient, \( \sigma \) is the electrical conductivity, \( \kappa \) is the thermal conductivity and \( T \) is the absolute temperature. Historically, peak ZT values of p-type half-Heuslers remain low at \(~0.5\), which is mostly attributed to the high thermal conductivity.\(^{13}\) Only recently, a peak ZT of 0.8 at 700 °C has been achieved in a p-type half-Heusler system by using a nanostructure approach,\(^{13}\) revealing the potential of half-Heuslers (HH) as promising candidates for high-temperature power generation applications. In this report, we found that larger differences in the atomic mass and size between Hf and Ti compared with Hf and Zr can further reduce the lattice thermal conductivity, leading to a peak ZT of \( \sim 1.0 \) in p-type HH materials, which make HHs potential materials for consideration in power generation applications in the temperature range up to 800 °C, possibly replacing the much more expensive SiGe alloys.$^{9,10}$

Alloy scattering, resulting from differences in the atomic mass and size, may effectively lower the lattice thermal conductivity.$^{14}$ In the case of p-type half-Heuslers with the formula MCoSb, where M is Ti,

Broader context

How to scavenge vast amounts of waste heat has increasingly become a major concern. It is possible that thermoelectrics can provide an economical and environmentally friendly way to achieve this. High thermoelectric figure-of-merit (ZT) materials are preferred for efficient performances. Historically, PbTe and skutterudites have been considered as candidates for medium temperature applications owing to their good ZT values. However, their uses are limited due to either toxicity or low thermal stability. In the same temperature range, half-Heuslers are chemically non-toxic and thermally stable, compared with PbTe and skutterudites, but the ZT peak of p-type half-Heuslers has remained around 0.5 for quite a long time until our recent work improved the ZT to 0.8. In this study, we achieved a ZT value of about 1 for a p-type half-Heusler, which makes it useful for medium to high temperature power generation applications, such as waste heat recovery in car exhaust systems. Specifically, the ZT enhancement comes mainly from the reduction of thermal conductivity, which arises partly from the enhanced alloy scattering, due to larger differences in the atomic mass and size of Hf and Ti compared with Hf and Zr, and partly from enhanced boundary scattering due to various nanostructures.
Experimental procedure

Alloyed ingots with Hf$_{1-x}$Ti$_x$CoSb$_{0.8}$Sn$_{0.2}$ ($x = 0.1, 0.2, 0.3$, and $0.5$) compositions were first formed by arc melting a mixture of an appropriate amount of the individual elements according to the stoichiometry. To prevent oxidation during the arc melting, the chamber was continuously streamed with Ar gas throughout the operation. Normally the ingot would be re-melted twice, flipping the ingot over each time to ensure the homogeneity of the ingot. We repeated the experiments numerous times and have confirmed no noticeable impurity phases were observed. A close scrutiny revealed that XRD peaks shift towards higher angles with increasing Ti, suggesting that Ti replaces Hf to form alloys.

The ingot was then loaded into a ball milling jar with grinding balls, inside an argon-filled glove box and then subjected to a mechanical ball-milling process to produce nanopowders. Finally bulk samples were obtained by consolidating the nanopowders into cylinders with a diameter of 12.7 mm and a height of 13 mm, using the direct current induced hot-pressure method, to measure the properties in the same direction. A combination of Hf and Ti is thought to be more effective in reducing the lattice thermal conductivity than that of Hf and Zr, considering the larger differences in the atomic mass and size of Hf and Ti. This concept has been validated experimentally in n-type (Ti, Zr, Hf)NiSn half-Heusler systems. However, there is lack of knowledge about the effect of (Hf, Ti) combinations on the thermal conductivity and ZT of p-type half-Heuslers. Our initial motivation was that enhanced alloy scattering of phonons by larger atomic mass and size differences, in combination with the enhanced boundary scattering from a nanocomposite approach, could further reduce the still large lattice part of the thermal conductivity without a large penalty on the electronic properties, thereby enhancing the ZT. Our investigation on the thermolectric properties of Hf$_{1-x}$Ti$_x$CoSb$_{0.8}$Sn$_{0.2}$ ($x = 0.1, 0.2, 0.3$, and $0.5$) proves that Hf$_{0.8}$Ti$_{0.2}$CoSb$_{0.8}$Sn$_{0.2}$ has a lower thermal conductivity of $\sim 2.7$ W m$^{-1}$ K$^{-1}$, leading to a higher ZT value of $\sim 1.0$ at 800 °C.

Results and discussion

Fig. 1a shows the XRD patterns of the as-pressed Hf$_{1-x}$Ti$_x$CoSb$_{0.8}$Sn$_{0.2}$ ($x = 0.1, 0.2, 0.3$, and $0.5$) samples. The diffraction peaks of all the samples are well-matched with those for cubic half-Heusler phases. No noticeable impurity phases were observed. A close scrutiny revealed that XRD peaks shift towards higher angles with increasing Ti, suggesting that Ti replaces Hf to form alloys. We have also estimated the lattice parameter $a$ of all the samples with different Hf/Ti ratios and plotted the results with respect to the Ti fraction $x$ in Fig. 1b. As expected, the lattice parameter decreases linearly with increasing Ti, following Vegard’s law.

The SEM image of the as-pressed Hf$_{0.8}$Ti$_{0.2}$CoSb$_{0.8}$Sn$_{0.2}$ sample is displayed in Fig. 2a, from which we can see that the grain sizes are in...
According to each composition. For the whole temperature range, the thermal conductivities of the $\text{Hf}_{0.8}\text{Ti}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$, $\text{Hf}_{0.8}\text{Ti}_{0.3}\text{CoSb}_{0.8}\text{Sn}_{0.2}$, and $\text{Hf}_{0.5}\text{Ti}_{0.3}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ samples are similar to each other and are much lower than that of $\text{Hf}_{0.5}\text{Ti}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$. The thermal conductivity of $\text{Hf}_{0.8}\text{Ti}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ changes very little with increasing temperature and the minimum value is 2.7 W m$^{-1}$ K$^{-1}$. To get a clear view of how the Hf/Ti ratio affects the lattice heat transport, we estimated the lattice thermal conductivity ($\kappa_l$) by subtracting both the electronic contribution ($\kappa_e$) and the bipolar contribution ($\kappa_{bipolar}$) from the total thermal conductivity ($\kappa$) while $\kappa_e$ was obtained using the Wiedemann–Franz law. The temperature-dependent Lorenz number was calculated from the reduced Fermi energies, which were estimated from the Seebeck coefficients with consideration of the two-band model. Similar to the total thermal conductivity, the lattice thermal conductivities of the $\text{Hf}_{0.8}\text{Ti}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$, $\text{Hf}_{0.7}\text{Ti}_{0.3}\text{CoSb}_{0.8}\text{Sn}_{0.2}$, and $\text{Hf}_{0.5}\text{Ti}_{0.3}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ samples are similar to each other and are much lower than that of $\text{Hf}_{0.5}\text{Ti}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ (Fig. 3e). As Ti is gradually introduced into the HfCoSb$_{0.8}$Sn$_{0.2}$ system, the lattice thermal conductivity experiences a sharp suppression from $x = 0.1$ to $x = 0.2$ and then becomes almost saturated above $x = 0.2$. The theoretical calculations on $\text{Hf}_{1-x}\text{Ti}_x\text{CoSb}$, using molecular dynamic (MD) simulations via the harmonic and cubic force interatomic constants obtained from first principles calculations, predicted such thermal conductivity decreases. The lattice thermal conductivities of the $\text{Hf}_{1-x}\text{Ti}_x\text{CoSb}_{0.8}\text{Sn}_{0.2}$ ($x = 0.1$, $0.2$, $0.3$, and $0.5$) samples at room temperature are plotted in the inset of Fig. 3e in comparison with the calculations. It is very encouraging to see that our experimental data and the theoretical calculations are in very good agreement.

Due to the low thermal conductivity and high power factor achieved by partially substituting Hf with Ti, the ZT of $\text{Hf}_{0.8}\text{Ti}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ reached 1.0 at 800 °C and 0.9 at 700 °C (Fig. 3f), showing promise for p-type materials as an option in high-temperature applications.

We also show the specific heat (Fig. 4a) and thermal diffusivity (Fig. 4b) of the $\text{Hf}_{1-x}\text{Ti}_x\text{CoSb}_{0.8}\text{Sn}_{0.2}$ ($x = 0.1$, $0.2$, $0.3$, and $0.5$) samples. The specific heat of all the samples increases steadily with temperature. For the same temperature, the specific heat increases with increasing Ti. To be thorough, we measured the specific heat of $\text{Hf}_{0.8}\text{Ti}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$, which has the highest ZT at high temperatures, using both a high-temperature DSC instrument (404C, Netzsch Instruments, Inc.), which can measure the sample beyond 800 °C, and a low-temperature DSC instrument (200-F3, Netzsch Instruments, Inc.), which can only reach up to 600 °C. The measurements from the two different DSC instruments agree with each other within 3%. On the other hand, thermal diffusivity of all the samples precisely follows the trend of decreasing with increasing Ti.

We plotted the temperature-dependent TE properties of the nanostructured bulk $\text{Hf}_{0.8}\text{Ti}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ sample in comparison with that of $\text{Hf}_{0.8}\text{Zr}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ (ref. 13) in Fig. 5. Both samples have been subjected to the same ball milling and hot pressing conditions to minimize the size effect on the transport properties. The electrical conductivity of $\text{Hf}_{0.8}\text{Zr}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ is higher than that of $\text{Hf}_{0.8}\text{Ti}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ for the whole temperature range and the difference becomes smaller with increasing temperature (Fig. 5a). In contrast, the Seebeck coefficient of $\text{Hf}_{0.8}\text{Ti}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ is almost the same as that of $\text{Hf}_{0.8}\text{Zr}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ for all the temperatures (Fig. 5b). As a result of the reduced electrical conductivity, the power factor of $\text{Hf}_{0.8}\text{Ti}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ is lower than that of

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**Fig. 2** (a) SEM image and (b-d) TEM images of the as-pressed $\text{Hf}_{0.8}\text{Ti}_{0.2}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ sample.
Hf$_{0.5}$Zr$_{0.5}$CoSb$_{0.8}$Sn$_{0.2}$ from 100 $^\circ$C to 700 $^\circ$C (Fig. 5c). However, this reduced power factor is compensated by the much reduced thermal conductivity (Fig. 5d), which yields an enhanced ZT, especially at higher temperatures (Fig. 5f). The total thermal conductivity of Hf$_{0.8}$Ti$_{0.2}$CoSb$_{0.8}$Sn$_{0.2}$ is ~17% lower than that of Hf$_{0.5}$Zr$_{0.5}$CoSb$_{0.8}$Sn$_{0.2}$ (Fig. 5d), indicating that the combination of Hf and Ti is more effective in reducing the thermal conductivity compared with the Hf and Zr combination. The origin of the thermal conductivity reduction achieved in Hf$_{0.8}$Ti$_{0.2}$CoSb$_{0.8}$Sn$_{0.2}$ in comparison with Hf$_{0.5}$Zr$_{0.5}$CoSb$_{0.8}$Sn$_{0.2}$ comes from two parts: the

Fig. 3 Temperature-dependent (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) thermal conductivity, (e) lattice thermal conductivity and (f) ZT of the Hf$_{1-x}$Ti$_x$CoSb$_{0.8}$Sn$_{0.2}$ ($x = 0.1, 0.2, 0.3$ and $0.5$) samples. The lattice thermal conductivities of the Hf$_{1-x}$Ti$_x$CoSb$_{0.8}$Sn$_{0.2}$ ($x = 0.1, 0.2, 0.3$ and $0.5$) samples at room temperature are plotted in comparison with molecular dynamics (MD) calculations on Hf$_{1-x}$Ti$_x$CoSb in the inset of (e).$^{28}$

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Fig. 4 Temperature-dependent (a) specific heat and (b) thermal diffusivity of the Hf$_{1-x}$Ti$_x$CoSb$_{0.8}$Sn$_{0.2}$ ($x = 0.1, 0.2, 0.3$ and $0.5$) samples.
electronic part and the lattice part. Specifically, the $\kappa_e$ of Hf$_{0.8}$Ti$_{0.2}$CoSb$_{0.8}$Sn$_{0.2}$ is about 13–31% lower than that of Hf$_{0.5}$Zr$_{0.5}$CoSb$_{0.8}$Sn$_{0.2}$. The lattice thermal conductivity of Hf$_{0.8}$Ti$_{0.2}$CoSb$_{0.8}$Sn$_{0.2}$ is about 11–19% lower than that of Hf$_{0.5}$Zr$_{0.5}$CoSb$_{0.8}$Sn$_{0.2}$ (Fig. 5e), consistent with more thermal conductivity reduction by the Hf and Ti combination in an n-type half-Heusler system. Our experimental results clearly show that thermal conductivity can be most effectively reduced with the combination of Hf and Ti, owing to the larger difference in the atomic mass and size for this combination. However, the lattice part still dominates the total thermal conductivity. If more alloy scattering and/or more boundary scattering by even smaller grains can be achieved, thermal conductivity is expected to be reduced further. It is clearly shown in Fig. 5f that the ZT of Hf$_{0.8}$Ti$_{0.2}$-CoSb$_{0.8}$Sn$_{0.2}$ is comparable to that of Hf$_{0.5}$Zr$_{0.5}$CoSb$_{0.8}$Sn$_{0.2}$ at low temperatures and exceeds that of Hf$_{0.5}$Zr$_{0.5}$CoSb$_{0.8}$Sn$_{0.2}$ at temperatures above 500 °C, demonstrating promise for high temperature applications. The data from p-type silicon germanium (SiGe), another promising p-type material for high temperature applications, is also included for comparison (Fig. 5f). Hf$_{0.8}$Ti$_{0.2}$-CoSb$_{0.8}$Sn$_{0.2}$ may also have cost advantages over SiGe due to the extremely high cost of Ge.

The data we report here are representative results from many runs. A few typical $ZT$ vs. $T$ curves of Hf$_{0.8}$Ti$_{0.2}$CoSb$_{0.8}$Sn$_{0.2}$ are shown in Fig. 6 to demonstrate the repeatability. We have not only made many parallel batches under similar conditions (samples 1 and 2) but also did...
the thermal stability test by measuring the same sample up to 800 °C again after the first measurement (sample 1 and 1re). In fact, the results are repeatable within 10% from batch to batch and there is no observable degradation in either the individual properties or the ZT after re-measurement to 800 °C. The good repeatability and thermal stability of the Hf0.8Ti0.2CoSb0.8Sn0.2 sample further strengthens its promising candidacy for high temperature applications.

Although we have optimized the binary Hf1−xTiCoSb0.8Sn0.2 composition by tuning the Hf/Ti ratio and demonstrated the feasibility of the thermal conductivity reduction and ZT enhancement, there still remains much room for further improvement. First, a ternary combination of Ti, Zr, and Hf at the M site has given rise to a ZT value of 0.92 in an n-type MnNiPdSnSb system.29 However, there is little understanding about the influence of a ternary combination of Ti, Zr and Hf on the transport properties of p-type half-Heuslers, which deserves further investigation. Second, boundary scattering can be further enhanced by preserving the nanosize of the precursor nanopowders during hot pressing. By combining the enhanced alloying scattering along with the enhanced boundary scattering, the thermal conductivity is expected to be further lowered and the ZT is expected to increase even more.

Conclusions

Larger differences in the atomic mass and size between Hf and Ti compared with Hf and Zr at the M site of p-type half-Heuslers, MCoSb, are proven to be effective in reducing the lattice thermal conductivity by stronger phonon scattering, which leads to a lower thermal conductivity of 2.7 W m−1 K−1 in Hf0.8Ti0.2CoSb0.8Sn0.2. As a result, a peak ZT for Hf0.8Ti0.2CoSb0.8Sn0.2 reached 1.0 at 800 °C, which paves the way for practical uses of HHs for power generation applications.

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