Effects of partial substitution of Ni by Pd on the thermoelectric properties of ZrNiSn-based half-Heusler compounds

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We report on the effects of partial substitution of nickel by palladium on the thermoelectric properties of ZrNiSn-based half-Heusler compounds. It is shown that the substitution of palladium for nickel results in a significant, beneficial reduction of the thermal conductivity. The Seebeck coefficient also decreases, but only by a small amount. In the $Hf_{0.5}Zr_{0.5}Ni_{0.8}Pd_{0.2}Sn_{0.99}Sb_{0.01}$ compound, a power factor of 22.1 $\mu W\,K^{-2}\,cm^{-1}$ and a thermal conductivity as low as 4.5 W/m K are measured at room temperature. The dimensionless figure of merit *ZT* increases with increasing temperature and reaches a maximum value of 0.7 at about 800 K. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1425459]

ZrNiSn-based half-Heusler compounds are a subset of a much larger family of compounds possessing the cubic MgAgAs-type structure, which has the space group $F\bar{4}3m$. The compounds are semiconductors with band gaps of about 0.21–0.24 eV.[1–3] The large Seebeck coefficients *S*, due to the heavy conduction band and modestly large electrical conductivity, make them ideal candidates for thermoelectric optimization.[4–7] In the past, we introduced phonon mass-fluctuation scattering by alloying Hf (atomic mass = 179) on the Zr (atomic mass = 91) site, which leads to an overall reduction of the total thermal conductivity κ;[5] we also explored the effect of less than 1 at. % Sb doping on the Sn site, which results in several orders of magnitude lowering of the resistivity ρ without significantly reducing *S*, leading to large power factors (S^2/ρ) comparable to that of state-of-the-art materials.[5] Our previous high temperature transport properties study[3] found a peak power factor in excess of 35 $\mu W/cm\,K^2$ over a broad temperature range between 675 and 875 K for the $Zr_{0.5}Hf_{0.5}NiSn_{0.99}Sb_{0.01}$ sample. The peak figure of merit (*ZT*) value was ~0.5 at around 800 K. Despite the high S^2/ρ, κ of this sample is about 6 W/m K, still 3–4 times higher than that of state-of-the-art materials. In this letter, we explore the effect of isoelectronic alloying of Pd on the Ni site, trying to further reduce κ of these compounds.

We prepared our samples by a solid state reaction method. The powder mixture of the high purity constituents was heated to 1173 K under a flowing argon atmosphere for 96–168 h. Then, a spark plasma sintering technique was used at 1123 K for 25 min to consolidate the obtained powders. It is well established that both the solid state reaction method and the combined arc melting and annealing method[3–5] produce high quality samples that exhibit almost identical properties.[1] Thermal conductivity was measured by a laser flash technique (Shinkuriko: TC-7000) in vacuum over the temperature range of 300–1000 K using a disk-shaped specimen. Graphite and stainless specimens were used as the standard samples for calibration in the thermal conductivity measurements. Details of the other measurement techniques can be found elsewhere.[8,9] Our x-ray powder diffraction and electron microprobe analysis show that all samples are of single phase and stoichiometric.

Figure 1 displays the temperature dependence of ρ of ZrNiSn-based half-Heusler compounds. Doping 1 at. % of Sb on the Sn site reduces the room temperature ρ by a factor of 4–6 and profoundly changes the temperature dependence of ρ from an activated behavior (for the undoped samples) to a metal-like one (for the doped samples). ρ of the doped samples are actually very close to each other and are smaller than those of the undoped samples over the entire temperature range. As the temperature increases, ρ approaches a common value comparable to that reported in Ref. 5, indicating that the materials are entering the intrinsic conduction region.

Figure 2 shows the temperature dependence of *S* for all the ZrNiSn-based half-Heusler compounds. For each sample, there are two distinct regions of behavior. $|S|$ increases as temperature increases from room temperature, indicating that the conduction is dominated by extrinsic charge carriers excited from the impurity state. At about 700 K, $|S|$ reaches a

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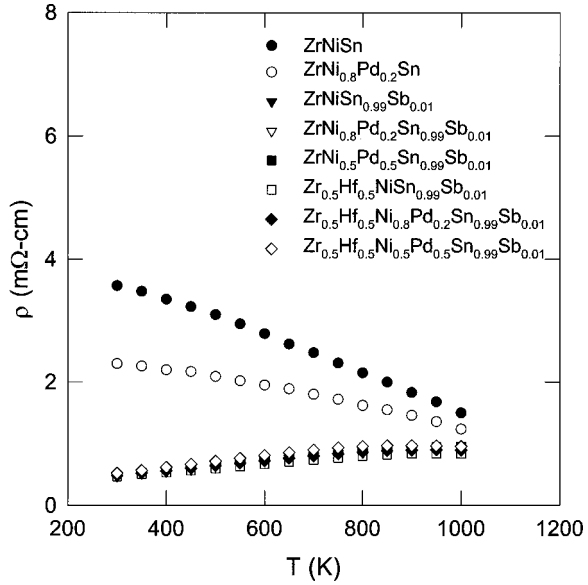

FIG. 1. Temperature dependence of the electrical resistivity of ZrNiSn-based half-Heusler compounds. The data points for some of the samples are not visible due to being blocked by other symbols.

maximum and starts to decrease with increasing temperature. This is due to the excitation of electron–hole pairs across the energy gap, and the opposing contribution to S from the two carriers reduces the observed $|S|$. From Fig. 2 we see that not only Sb doping on the Sn site but also alloying Pd on the Ni site reduces $|S|$. The former effect was reported in Ref. 6 and is believed to be due to increased carrier concentration upon Sb doping. We do not know the exact physical reason for the latter, but we speculate that it might be related to the crucial role of the Ni site in forming the energy band gap in ZrNiSn.[10] Despite $|S|$ reduction upon alloying Pd on the Ni site, large values of $|S|$ are obtained due to the heavy electron mass of the conduction band.[5,11] S^2/ρ for all the samples are plotted in the inset of Fig. 2. Large values of S^2/ρ (over 20 μW/cm K^2) are observed for a number of Sb-doped samples over the whole temperature range. The maximum S^2/ρ is 34.4 μW/cm K^2 for $ZrNiSn_{0.99}Sb_{0.01}$. These large values of

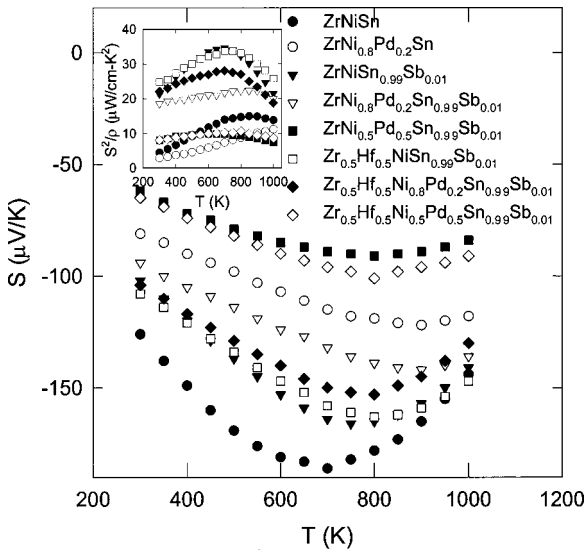

FIG. 2. Temperature dependence of the Seebeck coefficient and the power factor (insert) of ZrNiSn-based half-Heusler compounds.

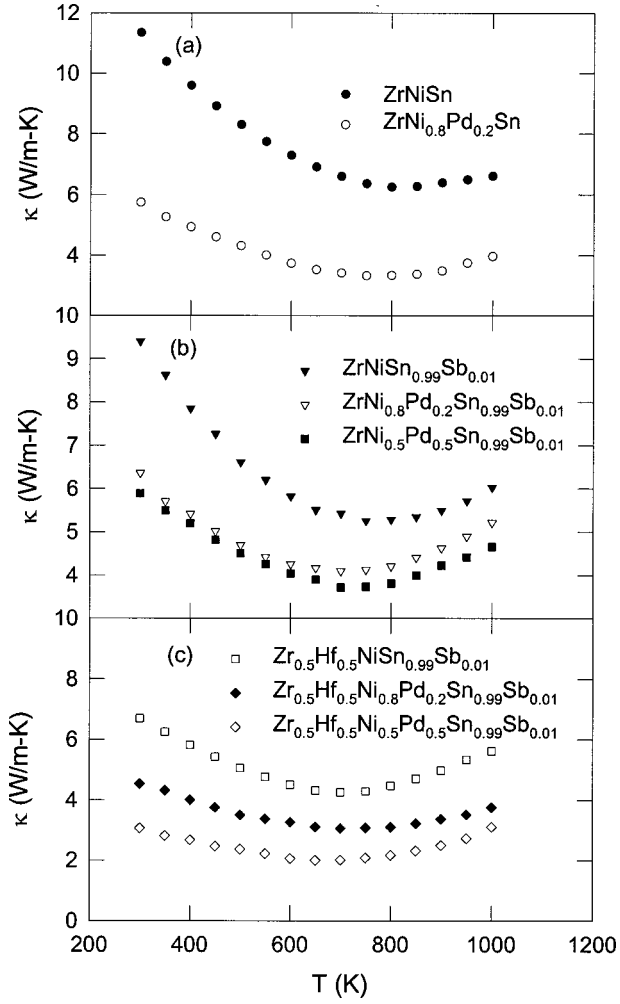

FIG. 3. The effect of Pd alloying on the Ni site on the thermal conductivity of ZrNiSn-based half-Heusler compounds: (a) undoped samples, (b) Sb-doped samples, and (c) Sb-doped samples with Hf alloying on the Zr site.

S^2/ρ are expected in light of the reduced ρ due to Sb doping and the modest value of S.

Another crucial factor that determines the thermoelectric properties of these compounds is κ. Because the thermoelectric figure of merit ZT is given by $ZT=S^2T/\rho\kappa$, where T is the absolute temperature, it is clear that one needs to reduce κ to achieve higher ZT. The half-Heusler compound ZrNiSn has a room temperature κ between 10 and 15 W/m K. It was shown that isoelectronic alloying on the Zr site reduces the room temperature κ to about 6 W/m K.[5,12,13] The effect of alloying Pd on the Ni site on κ is shown in Fig. 3. Panel (a) shows the temperature dependence of κ of the undoped samples. The room temperature κ of the ZrNiSn sample is 11.4 W/m K, comparable to that reported in the literature.[5,12,13] Upon alloying 20 at. % of Pd on the Ni site, there is a reduction of κ by about a factor of 2 over the entire temperature range. This is the result of the phonon mass-fluctuation scattering between Ni (atomic mass=58.7) and Pd (atomic mass=106.4). Further reduction of κ is accomplished by alloying more (50 at. %) Pd on the Ni site, as illustrated by panels (b) and (c) for Sb-doped samples and Sb-doped samples with 50 at. % Hf alloying on the Zr site, respectively. The room temperature κ for the $Zr_{0.5}Hf_{0.5}Ni_{0.8}Pd_{0.2}Sn_{0.99}Sb_{0.01}$ and $Zr_{0.5}Hf_{0.5}Ni_{0.5}Pd_{0.5}Sn_{0.99}Sb_{0.01}$ samples is 4.5 and 3.1 W/m K,

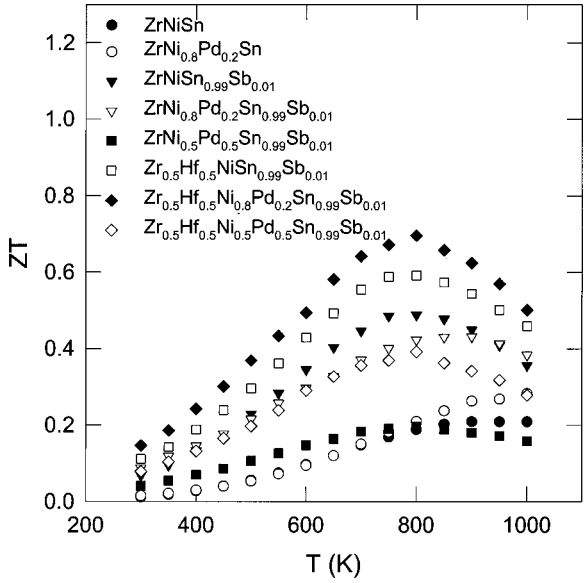

FIG. 4. Thermoelectric figure of merit *ZT* for all the samples between 300 and 1000 K.

respectively. These values are lower than the reported 6 W/m K for the $Zr_{0.5}Hf_{0.5}NiSn_{0.99}Sb_{0.01}$ samples.[5] It is interesting to point out that κ for the $ZrNi_{0.8}Pd_{0.2}Sn_{0.99}Sb_{0.01}$ sample is higher than that of the $ZrNi_{0.8}Pd_{0.2}Sn$ sample, and the difference increases with increasing temperature. We attribute this to the larger electronic component of κ for the doped sample, while the lattice components of the two are very close. Alloying 50 at. % of Hf on the Zr site reduces significantly the lattice component of κ, and therefore reduces κ over the entire temperature range as indicated in Fig. 3 by $Zr_{0.5}Hf_{0.5}Ni_{0.8}Pd_{0.2}Sn_{0.99}Sb_{0.01}$.

Figure 4 shows *ZT* for all the samples between 300 and 1000 K. We observe $ZT=0.7$ at 800 K for the $Zr_{0.5}Hf_{0.5}Ni_{0.8}Pd_{0.2}Sn_{0.99}Sb_{0.01}$ sample. This is the highest *ZT* value for any half-Heusler compound reported so far.[1] At 800 K, *ZT* values are about 0.55 and 1.1 for SiGe alloys (traditional thermoelectric materials) and skutterudites[14] (newly discovered thermoelectric materials), respectively. Future improvement will have to come from further reduction of the thermal conductivity. Increasing the boundary scattering of charge carriers and phonons by preparing samples with smaller grain size may be worthwhile to explore.[15]

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