Thermoelectric properties of n-type half-Heusler compounds ($\text{Hf}_{0.25}\text{Zr}_{0.75}$) $_{1-x}\text{Nb}_x\text{NiSn}$

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Abstract

A series of Nb doped ($\text{Hf}_{0.25}\text{Zr}_{0.75}$) $_{1-x}\text{Nb}_x\text{NiSn}$ ($x = 0-0.03$) samples were synthesized and studied by arc-melting the elements to first form ingots, then ball-milling the ingots to obtain fine powders, and finally hot-pressing the fine powder to form bulk samples. Instead of the conventional Sb doping on the Sn site of the n-type half-Heusler, it was found that Nb is also an effective dopant. When the carrier concentration is optimized at 2.2% Nb, a power factor of $\sim 47 \mu\text{W cm}^{-1} \text{K}^{-2}$ is achieved at and above 600 °C, and a peak ZT ~ 0.9 is achieved at 700 °C with Nb doping from 1.8 at% to 2.2 at%. An output power density of $\sim 22 \text{ W cm}^{-2}$ and a leg efficiency of $\sim 12\%$ are calculated for the Nb doped samples.

Keywords: Half-Heusler, Thermoelectric, Full-Heusler nanoinclusions, Nb doping, Output power density

1. Introduction

Thermoelectric materials which can harvest waste heat and convert it directly into electricity have been gaining intensive attentions for its potential applications in energy conversion technologies [1]. The energy conversion efficiency of a thermoelectric material is governed by the Carnot efficiency and the dimensionless figure of merit (ZT), in which ZT is defined as $ZT = (S^2\sigma/\kappa)T$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature [2]. To achieve high conversion efficiency, large ZT value is required, that means high Seebeck coefficient, high electrical conductivity, and low thermal conductivity are favorable. However, these parameters are interrelated so it is difficult to change one individual parameter without affecting the others [3, 4]. Great efforts have been devoted to improve the thermoelectric properties of the existing materials. Enhanced ZT values have already been achieved in materials such as Bi_2Te_3 based materials which are used for applications near room temperature [5], lead chalcogenides and skutterudites for middle temperature power generation [6-9], and SiGe for high temperatures [10].

Half-Heusler compounds attract research interests for its potential applications in power generation in the middle to high temperature range from 500 °C to 800 °C [11, 12]. It is well-known for its non-toxicity, high thermal stability, and strong mechanical strength. Half-Heuslers refer to the ternary compounds with a general composition XYZ where X and Y are transition metals and Z is a main group element. They crystallize in a MgAgAs -like structure with $F\bar{4}3m$ space group. Both theoretical and experimental work have been done on a series of half-Heusler

compounds with valence electron count of 18 which are narrow band gap semiconductors [13-16] and some compounds with valence electron counts of 19 [17-19]. But until now, the most widely studied half-Heuslers are still MNiSn based compositions as n-type and the MCoSb based ones as p-type, where M refers to Hf, Zr, Ti or their combination. Different approaches have also been adopted to improve the thermoelectric performance of the MNiSn based n-type half-Heuslers. For instance, carrier concentrations can be optimized by doping with the adjacent elements such as Sb for Sn, Ta for M, and so on [20-23]. Ternary alloying of M by Hf, Zr, and Ti can reduce the lattice thermal conductivity by introducing point defects scattering [24, 25]. What's more, nanostructuring approach can also effectively suppress the lattice thermal conductivity by increasing the grain boundary scattering to increase the ZT [26, 27].

In this paper, we study the effects of Nb doping on the thermoelectric properties of $\text{Hf}_{0.25}\text{Zr}_{0.75}\text{NiSn}$ based compounds. Nb has one more valence electron than Hf/Zr so it can increase the carrier concentration for this n-type half-Heusler compound. In fact, Hiroaki Muta *et al.* did Nb doping in ZrNiSn and TiNiSn before and the maximum ZT value of 0.6 was obtained for $\text{Zr}_{0.98}\text{Nb}_{0.02}\text{NiSn}$ at 800 K [28]. Most recently, Julia Krez *et al.* reported Nb doping in the phase separated n-type $\text{Ti}_{0.3}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ compound and peak ZT value around 0.7 at 900 K was achieved [29]. Here we investigate the effects of Nb doping in the nanostructured $\text{Hf}_{0.25}\text{Zr}_{0.75}\text{NiSn}$ compounds. The carrier concentration is optimized by different concentrations of Nb doping and the thermal and electrical properties of these samples are discussed accordingly. It is interesting to note that some full-Heusler nanoinclusions are found within the half-Heusler matrix by SEM and TEM analysis, which could also play a positive role in the improvement of the thermoelectric properties. Power factor of $\sim 47 \mu\text{W cm}^{-1} \text{ K}^{-2}$ and peak ZT of ~ 0.9 are achieved with Nb doping from 1.8% to 2.2% at 700 °C. The output power density and

leg efficiency of all the samples are also calculated based on the engineering power factor $(PF)_{eng}$ and engineering figure of merit $(ZT)_{eng}$.

2. Experimental details

$(Hf_{0.25}Zr_{0.75})_{1-x}Nb_xNiSn$ ($x = 0, 0.005, 0.01, 0.012, 0.014, 0.016, 0.018, 0.02, 0.022, 0.025, \text{ and } 0.03$) ingots were firstly synthesized by arc-melting the Hf chips (99.7%, Alfa Aesar), Zr slug (99.5%, Alfa Aesar), Nb foil (99.97%, Alfa Aesar), Ni slug (99.98%, Alfa Aesar), and Sn shot (99.99+%, Alfa Aesar) according to the stoichiometry under Ar atmosphere. The ingots were arc-melted at least three times, each time flipped over to ensure homogeneity. Subsequently the alloyed ingots were put into the stainless steel jar with grinding balls and ball-milled for 5-9 hours to make nanopowders (SPEX 8000M Mixer/Mill). Finally the nanopowders were hot-pressed in a graphite die to form bulk samples. The disks of 12.7 mm in diameter and around 2 mm in thickness were obtained for measurements. The volumetric densities of the samples were measured by Archimede's method. The densities for $(Hf_{0.25}Zr_{0.75})_{1-x}Nb_xNiSn$ samples ($x = 0, 0.005, 0.01, 0.012, 0.014, 0.016, 0.018, 0.02, 0.022, 0.025, \text{ and } 0.03$) are 8.479 g/cm³, 8.415 g/cm³, 8.427 g/cm³, 8.431 g/cm³, 8.431 g/cm³, 8.430 g/cm³, 8.451 g/cm³, 8.431 g/cm³, 8.426 g/cm³, 8.461 g/cm³, and 8.420 g/cm³, respectively. The thermal diffusivities of the disks were measured on a laser flash equipment (LFA457, Netzsch). The specific heat capacity measurements were carried out on a differential scanning calorimeter (DSC 404 C, Netzsch). Samples were also cut into $2 \times 2 \times 12$ mm bars for electrical conductivity and Seebeck coefficient measurements from room temperature to 700 °C on a commercial equipment (ZEM-3, Ulvac). Hall measurements were performed on a Physical Property Measurement System (Quantum design) to get the carrier concentrations of these samples at room temperature. The

Hall mobility μ_H is calculated by the equation $\mu_H = \sigma / (n_H e)$, where σ , n_H , and e are electrical conductivity, Hall carrier concentration, and elementary charge, respectively. The samples were also characterized by XRD (X'pert PRO PANalytical diffractometer with a Cu K α radiation source), SEM (LEO 1525), and TEM (JEOL 2100F). The uncertainties were estimated to be 3% for thermal diffusivity, specific heat capacity, and electrical conductivity, and 5% for Seebeck coefficient, which results in an uncertainty of 11% for ZT. To increase the readability of all the curves, all the figures are plotted without the error bars.

3. Results and discussion

All the Nb doped $(\text{Hf}_{0.25}\text{Zr}_{0.75})_{1-x}\text{Nb}_x\text{NiSn}$ samples ($x = 0-0.03$) obtained by arc-melting, ball-milling, and hot-pressing have single half-Heusler phase in the detection limit of the XRD machine, shown in Fig. 1. All the peaks are indexed as the cubic half-Heusler phase.

Fig. 2 shows the microstructures of the $(\text{Hf}_{0.25}\text{Zr}_{0.75})_{0.978}\text{Nb}_{0.022}\text{NiSn}$ samples. The SEM image of the freshly fractured surface in Fig. 2a indicates that the sample is densely packed polycrystalline. The relative density of the sample is calculated to be 99.3% (experimental density of 8.426 g/cm³ vs. the theoretical density of 8.482 g/cm³), which also demonstrates the high compaction. The grain size of the sample ranges from 200 nm to micrometers. The wide distribution of the grain size may be ascribed to the non-uniform grinding during ball-milling and high hot-pressing temperature for which the nanoparticles grow rapidly. Fig. 2b is the low-magnification TEM image that confirms the grain size distribution from hundred nanometers to micrometers and the grain boundaries. Furthermore, some small particles on the scale of several nanometers can be seen on the surface of the grains as shown in the SEM image in Fig. 2a, and this can also be noticed in the low-magnification TEM image with some black spots on the

individual grain (Fig. 2b). High-magnification TEM image is taken on one of those nanoinclusions and is shown in Fig. 2c. This nanoinclusion is about 20 nm. The electron diffraction pattern is taken on the nanoinclusion and presented in Fig. 2d. This electron diffraction pattern can be indexed as full-Heusler structure (space group $Fm\bar{3}m$) oriented along the [101] zone axis. On the other hand, split spots can be noticed in the electron diffraction pattern that originates from the half-Heusler matrix with similar diffraction pattern along [101] zone axis. As full-Heusler has slightly larger lattice constant than half-Heusler, for the split spots, the part closer to the transmission spot belongs to the full-Heusler and the farther part belongs to the matrix. By measuring the split diffraction spots, we get about 2% differences of the lattice parameters between full-Heusler and half-Heusler. Therefore, full-Heusler nanoinclusions are distributed in this half-Heusler sample. In addition, samples with other doping concentrations ($x = 0, 0.01$) were also found to have such nanoparticles on the grains in their SEM images shown in Supplementary Fig. S1, so we believe that the full-Heusler nanoinclusions exist in all of our half-Heusler samples. Although we start our experiments by arc-melting the elements in stoichiometry, higher nickel concentration around 38 at% compared to the stoichiometric value of 33 at% is found in the final hot-pressed samples by EDS. Such Ni/interstitial site intrinsic disorder is also reported by others in $ZrNiSn$ and about 5% excess of Ni was found [30, 31]. Reports of calculations, synchrotron x-ray and neutron scattering studies pointed out that rather than a statistical distribution, the excess Ni atoms tend to come close to each other and form full-Heusler nano-clusters within the half-Heusler matrix [32, 33], which is consistent with our observations of the full-Heusler nanoinclusions. It is reported that excess Ni on interstitial sites can produce in-gap electronic states near the Fermi energy and the nanoinclusions can also act as

phonon scattering centers to reduce lattice thermal conductivity [34-37], both of which are beneficial for the improvement of thermoelectric properties.

The temperature dependent electrical conductivity of the undoped $\text{Hf}_{0.25}\text{Zr}_{0.75}\text{NiSn}$ and the Nb doped $(\text{Hf}_{0.25}\text{Zr}_{0.75})_{1-x}\text{Nb}_x\text{NiSn}$ samples are presented in Fig. 3a. For the undoped and 0.5% Nb doped samples, the electrical conductivity increases when the temperature increases showing the typical behavior of semiconductors. When the samples are doped with more than 1.2% Nb, the electrical conductivity decreases with increasing temperature which exhibits characteristics of degenerate semiconductors. Comparing all the doped samples, the higher the doping level, the larger the electrical conductivity is. The Hall carrier concentrations and Hall mobility at room temperature of all the samples are measured and listed in Table 1. Since Nb has one more valence electron than Hf/Zr, it acts as an electron donor. Therefore, when the amount of Nb doping increases, the Hall carrier concentration increases leading to the enhancement of the electrical conductivity. Fig. 3b shows the temperature dependent Seebeck coefficient. Without any doping, the absolute value of Seebeck coefficient decreases with increasing temperature because of the thermal excitation of both electrons and holes. After Nb doping, the absolute value of Seebeck coefficient increases as temperature increases at first, and then it begins to decrease or stops increasing at higher temperatures which is due to the excitation of intrinsic charge carriers, known as bipolar effects. With Nb doping concentration increases, the Seebeck coefficient decreases at any fixed temperature. When the doping concentration is higher than 2% the Seebeck coefficient shows continuous increase in the whole temperature range from room temperature to 700 °C, which means that the bipolar effects can be suppressed by higher concentrations of extrinsic charge carriers. With the optimized carrier concentration, the power factors of the Nb doped samples have significant improvement in comparison with the undoped

one in the whole temperature range, as shown in Fig. 3c. Fig. 3d presents the values of power factors at 600 °C and 700 °C with different Nb doping levels. As the doping concentration increases, the power factor increases at first and then decreases when the carrier concentration becomes too large. The highest power factor of $\sim 47 \mu\text{W cm}^{-1} \text{K}^{-2}$ is achieved at 600 °C with Nb doping of 2.2% and this is about 37% enhancement over the undoped sample.

Fig. 4 gives the temperature dependent thermal diffusivity (a), specific heat capacity (b), total thermal conductivity (c), and lattice thermal conductivity (d) of the undoped and Nb doped samples. With increasing temperature, the thermal diffusivity decreases at first and then increases at high temperatures due to the bipolar effects especially for the undoped samples and the ones doped with low concentration. The suppression of bipolar effects can also be clearly noticed as the upturn of thermal diffusivity happens at higher temperatures when the Nb doping concentration increases. The specific heat capacity (C_p) of the samples doped with 1.2% and 2.2% Nb is measured and are shown in Fig. 4b. The C_p values of the two samples are almost the same and the minor difference is within the measurement error of DSC, so we use the C_p of 1.2% doped sample for all the doped samples. The thermal conductivity in Fig. 4c is calculated by multiplying the density, the specific heat capacity, and the thermal diffusivity. It turns out that thermal conductivities of all the doped samples are much larger than the undoped one and increase with doping concentration.

The total thermal conductivity is the sum of the lattice thermal conductivity and the electronic thermal conductivity from the charge carriers and bipolar effects. The electronic thermal conductivity can be obtained using the Wiedemann-Franz relation, $\kappa_e = L\sigma T$, where L is the Lorenz number. The Lorenz number can be calculated according to the following equation,

$$L = \left(\frac{k_B}{e} \right)^2 \left(\frac{(r+7/2)F_{r+5/2}(\xi)}{(r+3/2)F_{r+1/2}(\xi)} - \left[\frac{(r+5/2)F_{r+3/2}(\xi)}{(r+3/2)F_{r+1/2}(\xi)} \right]^2 \right) \quad (1)$$

where r is the scattering parameter, and F_n is the Fermi integral given by,

$$F_n(\xi) = \int_0^\infty \frac{\chi^n}{1+e^{\chi-\xi}} d\chi \quad (2)$$

Based on a single parabolic band model, the reduced Fermi energy ξ can be deduced from the Seebeck coefficient as,

$$S = \pm \frac{k_B}{e} \left(\frac{(r+5/2)F_{r+3/2}(\xi)}{(r+3/2)F_{r+1/2}(\xi)} - \xi \right) \quad (3)$$

In this calculation, we assumed that the acoustic phonon scattering dominates in the carrier scattering mechanism. The calculated Lorenz numbers are presented in the Supplementary Fig. S2. Accordingly, the lattice thermal conductivity of all the samples is calculated from room temperature to 400 °C right before the bipolar effects occur by subtracting the electronic thermal conductivity from the total thermal conductivity. As shown in Fig. 4d, the lattice thermal conductivity decreases with increasing temperature. There is not too much difference of the lattice thermal conductivity among all the samples. This is probably because the doping concentrations for our samples are pretty low (only 3%), so the point defect scattering caused by the dopants is small and is not the dominant phonon scattering mechanism here.

Fig. 5 presents the temperature dependent figure of merit ZT values of all the samples. Compared to the undoped sample, the samples doped with x from 0.5% to 2.2% Nb show enhanced ZT values in the whole temperature range from room temperature to 700 °C. When the doping concentration is higher than 2.2%, the ZT values begin to decrease because the carrier concentration is too large. As a result, the highest ZT of ~0.9 is achieved at 700 °C in samples

doped with Nb from 1.8% to 2.2%. Since the conventional ZT and power factor only indicate the performance of a material at a specific temperature, Kim *et al.* defined an engineering figure of merit $(ZT)_{\text{eng}}$ and an engineering power factor $(PF)_{\text{eng}}$ which are associated with the temperature boundaries and gradient and will provide a more accurate prediction of the maximum efficiency of a material by accounting for cumulative temperature dependent properties [38]. The engineering power factor $(PF)_{\text{eng}}$ and engineering figure of merit $(ZT)_{\text{eng}}$ of the undoped sample and all the Nb doped samples are calculated assuming a leg length of 2 mm, a cold side temperature of 50 °C and a hot side temperature ranging from 75 °C to 700 °C (Supplementary content). The results of $(PF)_{\text{eng}}$ and $(ZT)_{\text{eng}}$ as a function of hot side temperature are presented in Fig. 6a and Fig. 6b, respectively. All the Nb doped samples show an obvious enhancement of $(PF)_{\text{eng}}$ compared to the undoped sample. For $(ZT)_{\text{eng}}$, the highest values are obtained in samples doped with 0.5% Nb. The output power density and leg efficiency are calculated using $(PF)_{\text{eng}}$ and $(ZT)_{\text{eng}}$, respectively, by also taking into account the Thomson effect (Supplementary content). As shown in Fig. 6c, the output power density increases with the increase of Nb doping concentration till 2.2%. At the hot side temperature of 700 °C, the maximum output power density of $\sim 22 \text{ W cm}^{-2}$ is achieved in the sample doped with 2.2% Nb which is about 70% higher over the undoped sample. For the leg efficiency shown in Fig. 6d, it decreases slowly as the Nb doping concentration increases beyond 0.005 but the leg efficiency of all the doped samples are higher than the undoped sample. The maximum efficiency is about 12% at hot side temperature of 700 °C in 0.5% Nb doped sample and this is about 37% higher than the undoped sample.

We have shown in this work that the thermoelectric performance of the nanostructured n-type half-Heusler $\text{Hf}_{0.25}\text{Zr}_{0.75}\text{NiSn}$ can be enhanced by Nb doping. Both the power factor $\sim 47 \mu\text{W cm}^{-1} \text{ K}^{-2}$ and peak ZT ~ 0.9 are comparable to the reported best n-type half-Heuslers with ZT

around 1 that are doped with Sb [24, 25]. The advantage of Nb over Sb doping is that the experiments are more controllable, since Sb has high vapor pressure and evaporates a lot during arc-melting and Nb doesn't have such problems. What's more, the higher output power density of 22 W cm^{-2} with a leg length of 2 mm, a cold side temperature of $50 \text{ }^{\circ}\text{C}$ and a hot side temperature of $700 \text{ }^{\circ}\text{C}$ indicates that our samples are promising thermoelectric materials for higher power generation applications.

4. Conclusions

Nb doped $(\text{Hf}_{0.25}\text{Zr}_{0.75})_{1-x}\text{Nb}_x\text{NiSn}$ samples ($x = 0, 0.005, 0.01, 0.012, 0.014, 0.016, 0.018, 0.02, 0.022, 0.025, \text{ and } 0.03$) are successfully synthesized by ball-milling the arc-melted ingot to form nanopowder and then hot-pressing the nanopowder to get nanostructured bulk samples. With Nb doping, the carrier concentration increases as well as the electrical conductivity indicating that Nb is an effective electron donor in this n-type half-Heusler. With optimized carrier concentration, a peak $ZT \sim 0.9$ at $700 \text{ }^{\circ}\text{C}$ is achieved in samples with Nb doping from 1.8 at% to 2.2 at%. The calculations of the output power density and leg efficiency demonstrate that the maximum output power density around 22 W cm^{-2} and highest leg efficiency around 12% can be obtained in Nb doped samples.

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Fig. 1. XRD patterns of $(\text{Hf}_{0.25}\text{Zr}_{0.75})_{1-x}\text{Nb}_x\text{NiSn}$ samples ($x = 0, 0.005, 0.01, 0.012, 0.014, 0.016, 0.018, 0.02, 0.022, 0.025, \text{ and } 0.03$).

Fig. 2. SEM image (a) and the low magnification TEM image (b) of sample $(\text{Hf}_{0.25}\text{Zr}_{0.75})_{0.978}\text{Nb}_{0.022}\text{NiSn}$, high resolution TEM image (c) and the electron diffraction pattern (d) of the full Heusler nanoinclusion. In image (d), the spots covered by the stopper are marked as yellow dashed circles.

Fig. 3. Temperature dependent electrical conductivity (a), Seebeck coefficient (b), power factor (c), and power factor at 600 $^{\circ}\text{C}$ and 700 $^{\circ}\text{C}$ (d) of $(\text{Hf}_{0.25}\text{Zr}_{0.75})_{1-x}\text{Nb}_x\text{NiSn}$ samples ($x = 0, 0.005, 0.01, 0.012, 0.014, 0.016, 0.018, 0.02, 0.022, 0.025, \text{ and } 0.03$).

Fig. 4. Temperature dependent thermal diffusivity (a), specific heat capacity (b), thermal conductivity (c), and lattice thermal conductivity (d) of $(\text{Hf}_{0.25}\text{Zr}_{0.75})_{1-x}\text{Nb}_x\text{NiSn}$ samples ($x = 0, 0.005, 0.010, 0.012, 0.014, 0.016, 0.018, 0.020, 0.022, 0.025, \text{ and } 0.030$).

Fig. 5. Temperature dependent ZT of $(\text{Hf}_{0.25}\text{Zr}_{0.75})_{1-x}\text{Nb}_x\text{NiSn}$ samples ($x = 0, 0.005, 0.01, 0.012, 0.014, 0.016, 0.018, 0.02, 0.022, 0.025$, and 0.03).

Fig. 6. Calculated $(PF)_{\text{eng}}$ (a), $(ZT)_{\text{eng}}$ (b), output power density (c), and efficiency (d) as a function of hot side temperature for $(\text{Hf}_{0.25}\text{Zr}_{0.75})_{1-x}\text{Nb}_x\text{NiSn}$ samples ($x = 0, 0.005, 0.01, 0.012, 0.014, 0.016, 0.018, 0.02, 0.022, 0.025, \text{ and } 0.03$) with cold side at $50\text{ }^{\circ}\text{C}$ and leg length of 2 mm .

Table 1. Hall carrier concentration and Hall mobility at room temperature of $(\text{Hf}_{0.25}\text{Zr}_{0.75})_{1-x}\text{Nb}_x\text{NiSn}$ samples ($x = 0, 0.005, 0.01, 0.012, 0.014, 0.016, 0.018, 0.02, 0.022, 0.025$, and 0.03).

Nb doping level (at%)	0	0.5	1	1.2	1.4	1.6	1.8	2	2.2	2.5	3
Carrier concentration (10^{20} cm^{-3})	0.17	0.96	1.76	2.16	2.7	3.05	3.28	3.31	3.92	4.72	5.85
Mobility (cm^2 $\text{V}^{-1} \text{ S}^{-1}$)	37.5	39.7	36.7	36.2	33.2	32.9	33.9	36.5	33.5	33.0	29.7