

TECHNISCHE UNIVERSITÄT DARMSTADT

Synthesis, Defect Tuning, and Thermoelectric Properties of NbCoSn and ZrNiSn Half-Heusler Compounds

Ruijuan Yan

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Synthesis, Defect Tuning, and Thermoelectric Properties of NbCoSn and ZrNiSn Half-Heusler Compounds

Dissertation submitted to the Department of Materials and Earth Sciences at Technische Universität Darmstadt

in Fulfilment of the Requirements for the Degree of

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by Ruijuan Yan



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I herewith formally declare that I, Ruijuan Yan, have written the submitted thesis independently pursuant to § 22 paragraph 7 of APB TU Darmstadt. I did not use any outside support except for the quoted literature and other sources mentioned in the paper. I clearly marked and separately listed all of the literature and all of the other sources which I employed when producing this academic work, either literally or in content. This thesis has not been handed in or published before in the same or similar form.

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Abstract

Due to the direct interconversion of heat and electricity, thermoelectrical materials have attracted much scientific attention. Half-Heusler compounds with 18 valence electrons are one of the promising thermoelectric materials due to their excellent electrical properties, thermal stability, and affordable elements. In this dissertation, the half-Heusler compounds NbCoSn and ZrNiSn were exemplarily investigated, including crystal and defect structure, microstructure, electronic band structures, thermoelectric properties, and correlations between them.

Half-Heusler compound NbCoSn was predicated as both promising *n*-type and *p*-type thermoelectric candidates, making it possible to use for both legs of one thermoelectric device. In this work, n-type $NbCo_{1-x}Ni_xSn$ and p-type $Nb_{1-x}Sc_xCoSn$ samples were successfully synthesized. The phase structure and microstructure analysis revealed that the arc-melted desired NbCoSn phase always contained excessive Co, occupying not only the 4c position but also the part of the vacant 4d position. Due to this phenomenon, when Ni was introduced, it occupied both 4c and 4d positions as well, which has been confirmed by formation energy calculations. Furthermore, the electronic band structure calculations indicated that in-gap states were formed due to the existence of the excessive Ni/Co, leading to the largely increased charge carrier concentration. With the suppression of thermal conductivity due to point defects from Ni and the interfaces between the half-Heusler and the full-Heusler phases, an evident enhancement of ZT was achieved. For Nb_{1-x}Sc_xCoSn, p-type semiconductors were realized with $Sc \ge 0.05$. Thermal conductivity was reduced because of the stronger mass and strain field fluctuations induced by the radius and the interatomic coupling force differences between Nb and Sc. However, due to the existence of excessive Co in the samples, the improvement in ZT of p-type NbCoSn was undermined. Besides, the half-Heusler compound ZrNiSn has the same dynamic interstitial defects as the NbCoSn compound. In this work, ZrNiCu_xSn samples were synthesized as well to investigate the occupation and distribution of Cu atoms, which have an important impact on thermoelectric properties. It was found that Cu atoms occupied both 4c and 4d positions, leading to the increase in charge carrier concentrations. Simultaneously, the thermal conductivity of Cu-excessive ZrNiSn samples was reduced because of the interstitial defects and the interfaces after Cu introduction. Therefore, the ZT achieved an obvious improvement in ZrNiSn-based samples.

The obtained results demonstrated that utilizing interstitial defects is a promising approach to enhance the thermoelectric performance of n-type half-Heusler compounds. While to optimize the thermoelectric properties of p-type half-Heusler compounds, the interstitial defects should be controlled.

Kurzfassung

Durch die direkte Umwandlung von Wärme und Elektrizität haben thermoelektrische Materialien große wissenschaftliche Aufmerksamkeit auf sich gezogen. Halb-Heusler Verbindungen mit 18 Valenzelektronen sind eine der vielversprechendsten thermoelektrischen Materialien aufgrund ihrer hervorragenden elektrischen Eigenschaften, ihrer thermischen Stabilität sowie ihrer kostengünstigen Elemente. In dieser Arbeit wurden die Halb-Heusler-Verbindungen NbCoSn und ZrNiSn exemplarisch untersucht, einschließlich der Kristall- und Defektstruktur, der Mikrostruktur, der elektronischen Bandstrukturen, der thermoelektrischen Eigenschaften und der Korrelationen zwischen ihnen.

Die Halb-Heusler-Verbindung NbCoSn wurde als vielversprechender Kandidat als n-Typ und p-Typ für die Thermoelektrik klassifiziert, so dass sie für beide Schenkel eines thermoelektrischen Elements verwendet werden kann. In dieser Arbeit wurden *n*-Typ NbCo_{1-x}Ni_xSn und *p*-Typ Nb_{1-x}Sc_xCoSn Proben erfolgreich synthetisiert. Die Phasenstruktur- und Mikrostrukturanalyse ergab, dass die im Lichtbogen geschmolzenen NbCoSn-Proben immer überschüssiges Co enthielten, welches, nicht nur auf der Co 4c Position, sondern auch teilweise auf der freien 4d-Position sitzt. Aufgrund dieses Phänomens besetzt auch hinzugefügtes Ni die 4c und 4d Position, welches durch Berechnungen der Bildungsenergie bestätigt wurde. Darüber hinaus zeigen die Berechnungen der elektronischen Bandstruktur, dass sich aufgrund des übermäßigen Ni/Co Anteils Zustände in der Bandlücke bilden, die zu einer stark erhöhten Ladungsträgerkonzentration führen. Durch die Unterdrückung der Wärmeleitfähigkeit aufgrund von Punktdefekten von Ni und den Grenzflächen zwischen der Halb-Heusler- und der Voll-Heusler-Phase wurde eine deutliche Erhöhung der ZT erreicht. Nb_{1-x}Sc_xCoSn wird mit Sc ≥ 0.05 ein *p*-Typ-Halbleiter. Wärmeleitfähigkeit Gleichzeitig wurde die aufgrund der stärkeren Massenund Dehnungsfeldfluktuationen, die durch den Radius und die interatomaren Kopplungskraftunterschiede zwischen Nb und Sc verursacht werden, verringert. Aufgrund des überschüssigen Co-Gehalts in den Proben wurde die Verbesserung der ZT des p-Typ NbCoSn jedoch unterminiert. Außerdem weist die Halb-Heusler-Verbindung ZrNiSn die gleichen dynamischen Zwischengitterdefekte auf wie die NbCoSn-Verbindung. In dieser Arbeit wurden ZrNiCu_xSn-Proben synthetisiert, um die Besetzung und Verteilung von Cu-Atomen zu untersuchen, die einen wichtigen Einfluss auf die thermoelektrischen Eigenschaften haben. Es wurde festgestellt, dass Cu-Atome sowohl die 4c- als auch die 4d-Position besetzen, was zu einer Erhöhung der Ladungsträgerkonzentration führt. Gleichzeitig wurde die Wärmeleitfähigkeit der ZrNiSn-Proben mit überschüssigem Cu aufgrund der Zwischengitterdefekte und der Grenzflächen nach der Cu-Einbringung reduziert. Daher konnte die ZT in den auf ZrNiSnbasierenden Proben deutlich verbessert werden.

Die gewonnenen Ergebnisse zeigen, dass die Nutzung von Zwischengitterdefekten ein vielversprechender Ansatz zur Verbesserung der thermoelektrischen Leistung von *n*-Typ-Halb-Heusler-Verbindungen ist. Um die thermoelektrischen Eigenschaften von *p*-Halb-Heusler-Verbindungen zu optimieren, sollten jedoch die Zwischengitterdefekte kontrolliert werden.

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Abbreviations & Symbols

TE	Thermoelectric
HH	Half-Heusler
FH	Full-Heusler
XRD	X-ray diffraction
SR-PXRD	Synchrotron radiation powder X-ray diffraction
SEM	Scanning electron microscope
EDX	Energy-dispersive X-ray spectroscopy
XPS	X-ray photoemission spectroscopy
LFA	Laser flash Analyzer
DSC	Differential Scanning Calorimetry
SPS	Spark plasma sintering
PF	Power factor
ZT	Dimensionless thermoelectric figure of merit
DOS	Electronic density of state
DFT	Density functional theory
APT	Atom probe tomography
FIB	Focused ion beam
η	Thermal conversion efficiency of thermoelectric materials
Т	Absolute temperature
S	Seebeck coefficient
π	Peltier coefficient
β	Thomson coefficient
Q	Heat
Ι	Electrical current
σ	Electrical conductivity
ρ	Electrical resistivity
κ	Thermal conductivity
κ_c	Carrier (electrons κ_e and phonons κ_p) contribution to thermal conductivity

$\kappa_{ m L}$	Lattice contribution to thermal conductivity
d_s	Density of bulk samples
d_t	Thickness of bulk samples
k_B	Boltzmann constant
h	Planck constant
E_F	Femi energy
Ε	Carrier energy
r	Scattering factor
t	Time
<i>n</i> (<i>n</i> _H)	Electron carrier concentration
р (рн)	Hole carrier concentration
μ ($\mu_{ m H}$)	Mobility of charge carriers
$R_{ m H}$	Hall constant
е	Elemental electronic charge
E_g	Band gap
<i>m</i> *	Effective mass
m_b^*	Band effective mass
m_d^*	DOS effective mass
N_{v}	Band degeneracy
L	Lorenz number
ED	Resonant level
Г	Width of the resonant state
τ	Phonon relaxation time
Cv	Isochoric specific heat capacity
C_p	Isobaric specific heat capacity
Ν	The number of atoms in one formula
\mathcal{V}_{g}	Group velocity
D	Thermal diffusivity
$ heta_D$	Debye temperature
λ	Wavelength of the incident X-ray beam
ω	Phonon angular frequency
Vs	Sound speed

V	Volume per atom
Γ_S	Strain disorder scattering parameters
Γ_M	Mass disorder scattering parameters
Γ_{exp}	Experimental disorder scattering parameters
γ	Grüneisen constant
М	Average atomic mass/Molar mass
E_{def}	Deformation potential
v_l	Longitudinal sound velocity
d_g	Grain size

Chapter 1 Introduction

1.1 Thermoelectric Background

The energy demand is increasing drastically due to the growth of the population on earth. According to the British Petroleum (BP) report about Statistical Review of World Energy in 2020 [1], fossil fuels (oil, natural gas, coal) are still dominant in energy consumption and considerably utilized in the global power sectors. The considerable consumption of these non-renewable resources directly causes the global energy crisis as well as the growth of carbon emissions (about 1.1 % per year in the past 10 years). From a long-term perspective, these problems need to be solved by developing alternative and environmentally friendly energy sources like renewable resources (solar energy, geothermal, hydroelectric). However, in a short-term perspective, the best strategy that can be taken is to recover the waste heat and improve the energy efficiency [2,3].

Large amounts of heat are dissipated in almost every energy conversion process [4]. If the dissipated heat can be reused, it would positively influence the total energy efficiency. Thermoelectric (TE) technologies enable the direct inter-conversion between heat and electrical energy by the carrier conduction, making it possible to reduce heat losses. TE devices can be easily utilized on a small and large scale without long-term maintenance since they are reliable, noiseless, and emissions-free [5]. Due to the interconversion of heat and electricity, TE materials can be used in power generation and refrigeration fields. TE power generation devices can use all kinds of heat energy, such as the heat from the sun, industrial processes, automobile exhaust, and even home heating. Efforts are already underway to mount TE generators on artificial satellites, detectors, and navigation lights [6,7]. In addition, refrigeration devices can be an alternative for traditional chemicals (Freon) and applied in refrigerators and air conditioners, which will become more important with climate change [8].

Numerous TE materials with high performance have been investigated until now. The *ZT* values as a function of temperature for these TE materials are plotted in Figure 1.1. Traditional TE materials Bi-Te systems, PbTe, and Si-Ge alloys are suitable for relatively low-temperature (T < 473 K), moderate temperature (700 K - 1000 K), and high temperature (T > 1000 K) applications, respectively [9]. However, the *ZT* values of these materials have been under unity for almost a decade, and PbTe and

Bi-Te materials cannot be applied for large scales due to the high toxicity of Pb as well as the weak mechanical strength. As the development of TE fundamentals, more and more promising TE materials have been discovered and extensively studied, such as Skutterudites (CoSb₃) [10], Clathrates (Sr₈Ga₁₆Ge₃₀ [11], Ba₈Ga₁₆Ge₃₀ [12]), Zintl phase (BaCu₂Te₂ [13], Yb₁₄MnSb₁₁ [14]), lead-free Chalcogenides (BiOCuSe [15], Cu₂Se [16] and SnSe [17]) and half-Heusler compounds ((Ti,Zr,Hf)NiSn [18,19], (Ti,Zr,Hf)Co(Sb,Sn) [20,21], NbFeSb [22], ZrCoBi [23] etc.). In addition, some new strategies like low dimensionality have been applied to improve the density of state near the Femi level and further the figure of merit [24]. In the future, combining new approaches and new materials will be a promising perspective to study TE materials. Nowadays, most TE devices are assembled by Bi₂Te₃-based materials, but it only works at room temperature (Figure 1.1). For mid/high-temperature applications, HH compounds are one of the most promising TE materials due to the larger bandgap than Bi₂Te₃ compounds.



Figure 1.1 ZT values of thermoelectric materials [25].

1.2 Half-Heusler compounds

Half-Heusler (HH) compounds with general formula *XYZ* (*X*, *Y* = transition metals, *Z* = main group elements) have the cubic MgAgAs type structure ($F\overline{4}3m$, space group 216). As shown in Figure 1.2 (a), *X*, *Y*, and *Z* occupy the Wyckoff positions: *X* is at 4a (0, 0, 0), *Y* is at 4c (1/4, 1/4, 1/4), and *Z* is at 4b (1/2, 1/2, 1/2), leaving the 4d (3/4, 3/4, 3/4) position vacant. While, when the Wyckoff position 4d (3/4, 3/4, 3/4) are full-Heusler (FH) *XY*₂*Z* compounds will be formed (Figure 1.2)

(b)). This crystal structure can be understood by Zintl chemistry [26]: the electropositive cations X^{n_+} fill in the octahedral voids which are formed by the tetrahedral anionic framework $[YZ]^{n_-}$.



Figure 1.2 Crystal structure of half-Heusler (a) and full-Heusler (b) compounds.

Many HH compounds are promising thermoelectric candidates due to their symmetrical crystal structure and special electronic band structure. Firstly, from the crystal structure point of view, since the cubic structure has high crystal symmetry, multiple carrier pockets of one band are degenerated, resulting in a high band degeneracy N_v and further a large effective mass m^* ($m^* = N_v^{2/3} m_b^*$, m_b^* is the band effective mass). Thus, a large Seebeck coefficient can be easily achieved. Moreover, these materials have a tolerance to substitute parent elements without destructing the lattice structure, making it possible to tune the electronic properties and also achieve a low lattice thermal conductivity by exotic elements substitution. Secondly, from the electronic band structure, the d atomic orbitals of electropositive X^{n+} interact with the *d* atomic orbitals of *Y* in the $[YZ]^{n-}$ molecular orbitals, splitting into two states (bonding states and anti-bonding states, shown in Figure 1.3). The energy difference between these two states is the bandgap of HH compounds, which makes HH compounds intermetallic with semiconductor properties. The bandgap value is between 0.2 ~ 1.2 eV, leading to high electrical conductivity. In HH compounds with 18 valence electrons, the bonding states are fully occupied, but the anti-bonding states are empty, resulting in the closed-shell configuration [27]. That is the reason that HH compounds are thermodynamically stable. In addition, these HH compounds normally have low deformation potential energy E_{def} , which means the interaction between the electrons and phonons is weak, and electrons can be easily transported, obtaining a high mobility $\mu_{\rm H}$ in these materials [28,29]. These intrinsic features are favorable for the noticeable high PF in HH compounds. Except for the excellent TE properties, HH compounds possess high mechanical strength, low toxicity, and high thermal stability, thus being attractive for practical TE applications [30,31]. Given these advantages, HH compounds are promising TE candidates.



Figure 1.3 Schematic illustration of the hybridization of half-Heusler semiconductor [32].

HH compounds with 18 valence electrons attract more interest in the TE field due to the structure stability (anti-bonding states are empty, and bonding states are fully occupied). Figure 1.4 shows the ZT values of most promising HH thermoelectric materials, such as ternary compounds ZrNiSn [33,34], TiCoSb [35], NbCoSn [36], NbFeSb [22], TaCoSn [37] and multi-component compounds (Ti,Zr,Hf)(Co,Ni)(Sb,Sn) [18-21]. Many studies have been carried out to improve the ZT values by substituting other elements to optimize the electrical transport properties and simultaneously suppress the lattice thermal conductivity. Among them, ZT of Sb and Sn co-substituted ZrCoBi (ZrCoBi_{0.65}Sb_{0.15}Sn_{0.2}) reached ~ 1.4 at 1000 K [23] due to the quite low thermal conductivity (~ 2.5 Wm⁻¹K⁻¹ at room temperature). An excellent thermoelectric performance ($ZT_{1200K} = 1.5$) was achieved as well in 12 % Hf substituted p-type NbFeSb compound [38]. Recently, a pioneering method combining 17-electrons HH and 19-electrons HH compounds was employed to obtain high TE performance in the ternary compounds, named double HH by S. Anand [39]. For example, Z. Liu et al. substituted Fe on Ni site, forming TiFe_{0.5}Ni_{0.5}Sb compound [40]. They theoretically demonstrated that the TiFe_{0.5}Ni_{0.5}Sb compound had a large effective mass since the existence of high band degeneracy in the band structure, thereby maintaining the higher Seebeck coefficient. Due to the strong disorder effects between Fe and Ni, a much lower thermal conductivity was obtained as well. Therefore, the TE performance was enhanced. This could be a new pathway to design high-performance TE materials. However, although much higher ZT values have been achieved, most materials have complex compositions and contain the expensive element Hf, which is not favorable for practical applications [33,41]. As for double HH, it is difficult to obtain the HH phase by direct arc melting due to the high formation energy. Thus, some new synthesized methods and conditions need to be explored. In a short term, it is urgent to develop some simple ternary HH compounds without expensive elements, simultaneously utilizing the intrinsic properties to improve the TE performance.



Figure 1.4 State-of-the-art ZT values of half-Heusler materials. $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn_{0.998}Sb_{0.002}$ [34], ZrCoBi_{0.65}Sb_{0.15}Sn_{0.2} [23], ZrNi_{1.03}Sn [33], Nb_{0.88}Hf_{0.12}FeSb [37], Zr_{0.76}Ti_{0.05}Hf_{0.19}CoSb_{0.8}Sn_{0.2} [41], Hf_{0.8}Ti_{0.2}CoSb_{0.8}Sn_{0.2} [42], TiFe_{0.6}Ni_{0.4}Sb [40], NbCo_{0.95}Pt_{0.05}Sn [36], Ta_{0.6}Nb_{0.4}CoSn_{0.94}Sb_{0.06} [37], TiFe_{0.4}Ni_{0.6}Sb [40], TiCo_{0.85}Fe_{0.15}Sb [35], Ti_{0.85}V_{0.15}CoSb [43], Nb_{0.8}Zr_{0.2}CoSn [44].

1.3 Motivation

NbCoSn is a ternary HH compound with a valence electron count (VEC) of 18. Intrinsic NbCoSn is an *n*-type semiconductor with a bandgap value of 0.987 eV in the range of 10 k_BT_0 , leading to good electrical transport properties [45]. Many studies have been carried out to improve the TE properties of NbCoSn compounds, such as NbCoSn with Sb substitution on Sn site [46] and Pt substitution on Co site [36]. Among all the studies, it is noticed that the excessive Co always exists in NbCoSn samples synthesized by high-temperature techniques (arc-melting or induction-melting), despite being designed as the nominal 1:1:1 composition [36,47,48], which makes it possible to tune the defects by controlling the synthesis conditions. A similar manifestation has been observed in the ZrNiSn compound, where the excessive Ni occupying the 4d site (interstitial defects) significantly affected the microstructure and simultaneously changed the electronic band structure [33,49]. This implies that the interstitial defects could have an impact on the TE properties of HH compounds. Y. Kimura et al. reported a formation of NbCo₂Sn in the NbCoSn matrix by adding more Co, but the intrinsic excessive Co was not mentioned in this work [47]. Also, the explanation of TE properties was not associated with these defects. Therefore,

the deeply experimental and computational studies on these intrinsic defects are favored for explaining the microstructure and the TE properties in the *n*-type NbCoSn system.

Additionally, R. He et al. calculated the band structure and the density of state of the NbCoSn compound, shown in Figure 1.5 [46]. Notably, an obvious even higher valley degeneracy occurred at the valence band edge where both the L and the W points contributed to the hole concentration. This fact indicated that NbCoSn could be a good *p*-type semiconductor as well if substituting suitable elements. Also, it was calculated that both *n*-type and *p*-type NbCoSn compounds could achieve high PF [50,51], allowing the usage of similar material for both legs in one TE device to remain good application compatibility. Therefore, studying *p*-type NbCoSn has profound meaning for practical applications. Until now, a few efforts have been implemented to obtain the *p*-type NbCoSn. Ti, Mo, and Hf were initially described as weak *p*-type dopants [52,53]. Later, Zr and Ti were chosen to substitute Nb and a positive Seebeck coefficient was obtained. However, the still lower electrical conductivity hindered the formation of heavily hole-doped NbCoSn and the attainment of the predicated high TE performance in the *p*-type NbCoSn [44]. Thus, more effective elements should be identified to contribute more holes, which drives the exploration of other elements, achieving higher TE performance in *p*-type NbCoSn.



Figure 1.5 Band structure (a) and density of state (b) of NbCoSn. The yellow region indicates the bandgap [42].

According to the studies about the interstitial defects on the NbCoSn HH compound, we noticed that the interstitial defects have an important impact on the phase structure and the TE properties. It would be interesting to survey the interstitial defects in other HH compounds. Therefore, in Chapter 6, the ZrNiSn compound was chosen as an example due to the intrinsic higher TE performance [54-57]. The interstitial defects have been put forward in the ZrNiSn compound, but at the beginning, it was believed

that the off-stoichiometric phenomenon was caused by the Zr/Sn antisite and Ni/vacancy disorders [58,59]. Until 2012, the high-resolution synchrotron radiation powder X-ray diffraction (SR-PXRD) was employed to determine the disorders in the ZrNiSn compound [60]. The results revealed that excessive Ni was suggested to be present in the structure, partly occupying the vacant 4d position in the HH structure. It is similar to the excessive Co in NbCoSn compounds [36,47,48]. According to the density functional theory (DFT) calculations, these excessive Ni defects can induce the in-gap states between the conduction band and the valence band, leading to a reduction in the bandgap [61]. It can explain why the experimental bandgap is always much smaller than the calculated one in the ZrNiSn system. However, the impact of this effect on thermal and electrical transport properties has not been deeply investigated from the experiments. Therefore, it is meaningful to study this effect in the ZrNiSn system, providing a general understanding of interstitial defects on the TE properties of HH compounds.

1.4 Overview of this thesis

This thesis consists of seven chapters and is structured as follows. The first chapter is the general introduction part. The second chapter describes the fundamental of thermoelectricity, including three TE effects, TE physical parameters, and optimization strategies of TE performance. The third chapter is the experimental part, where the sample preparation and synthesis methods, the applied measurements and characterization techniques, and all devices and equipment in use are described. Some further detailed technical parameters are also presented in the following corresponding chapters. Chapters 4, 5, and 6 discuss the material synthesis, crystal structure, and microstructure, as well as the results of the high temperature ($300 \text{ K} \sim 1100 \text{ K}$) transport properties of NbCoSn with Ni introduction, *p*-type NbCoSn with Sc substitution, and ZrNiSn with Cu introduction, respectively. Last but not least, chapter 7 summarizes all the research work and gives some suggestions for further studies on HH compounds.

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Chapter 2 Fundamentals of Thermoelectricity

2.1 The thermoelectric effects

Thermoelectric materials are based on two fundamental effects: the Seebeck effect and the Peltier effect, and one supplementary description of the Peltier effect: the Thomson effect. The Seebeck effect, firstly discovered by Thomas Johann Seebeck in the 1800s, is for power generation. In contrast, the Peltier effect is a reverse phenomenon of the Seebeck effect and can be used for cooling.

2.1.1 Seebeck effect

Seebeck effect is built up between two conductors with a temperature difference, resulting in charge carrier diffusion from the hot side to the cold side, therefore generating voltage difference ΔV , as shown in Figure 2.1. The value of ΔV is described as

$$\Delta V = S \Delta T, \tag{2.1}$$

where *S* is the relative Seebeck coefficient between these two conductors, namely $S = \Delta V / \Delta T$. Apparently, the Seebeck effect results from the charge carrier diffusion. Thus, the sign of *S* is determined by the dominant charge carriers in this material. A positive value of *S* indicates that the major carriers are holes, whereas a negative value of *S* indicates that electrons are the dominant carriers.



Figure 2.1 Schematic diagram of the Seebeck effect.

2.1.2 Peltier effect

The Peltier effect is defined as a temperature difference created by applying a voltage between two connected semiconductors (shown in Figure 2.2). When an electrical current (I) passes through them, heat (Q) is generated or absorbed in the joints between these two semiconductors. The Peltier coefficient (π) is defined as

$$\pi = Q/I. \tag{2.2}$$

The Peltier effect originates from the carrier voltage difference in the circuit. When carriers flow from conductor \mathbf{a} to conductor \mathbf{b} , the energy exchange between the lattices happens at the junction, generating or absorbing heat.



Figure 2.2 Schematic diagram of the Peltier effect.

2.1.3 Thomson effect

The Seebeck effect and the Peltier effect are generated between two conductors, while the Thomson effect is defined as a conversion of heat and electricity in a single conductor with a temperature gradient. As illustrated in Figure 2.3, when the electrical current (*I*) flows through one conductor with a temperature difference, it emits or absorbs heat except for Joule heat. Thus, the Thomson coefficient (β) can be defined by the following formula:

$$\beta = Q/I \,\Delta T. \tag{2.3}$$

When the direction of current is consistent with that of the temperature gradient, the conductor absorbs heat, and then the β is positive. Otherwise, it is negative. The Thomson effect is similar to the Peltier effect. The main difference between them is that the voltage gradient originates from the carrier potential energy difference of these two conductors in the Peltier effect, but it results from the carrier temperature

gradient in the Thomson effect. Compared to the Seebeck effect and the Peltier effect, the Thomson effect has a minor contribution to the energy conversion and thus usually is ignored in designing TE devices.



Figure 2.3 Schematic diagram of the Thomson effect.

2.2 Thermoelectric Conversion Efficiency and parameters

The thermoelectric conversion efficiency of a thermoelectric generator is determined by the Carnot efficiency and materials performance as [1]:

$$\eta = (\frac{T_{hot} - T_{cold}}{T_{hot}}) \frac{\sqrt{1 + ZT_{avg}} - 1}{\sqrt{1 + ZT_{avg}} + (\frac{T_{cold}}{T_{hot}})},$$
(2.4)

where T_{hot} is the hot-side temperature, T_{cold} is the cold-side temperature, and ZT_{avg} is the average dimensionless thermoelectric figure of merit, which is a critical measurement for materials' performance and is a function of several parameters:

$$ZT = \frac{S^2 \sigma}{\kappa} T = \frac{S^2 \sigma}{\kappa_c + \kappa_L} T , \qquad (2.5)$$

where *S* is the Seebeck coefficient, σ the is electrical conductivity, κ_c and κ_L is the electron and lattice component of thermal conductivity κ ($\kappa = \kappa_c + \kappa_L$), and *T* is the absolute temperature. The term $S^2\sigma$ is referred to the thermoelectric power factor (PF). In principle, the higher the *ZT* is, the higher the thermoelectric conversion efficiency we can achieve. Figure 2.4 shows the energy conversion efficiency calculated by Equation (2.4), and the measured thermoelectric efficiencies for some promising materials are also plotted for comparison. At present, the reported efficiencies are around 12 % for bismuth
telluride/skutterudite segmented modules [2], which is lower than the existing advanced heat engines. According to Equation (2.4), the efficiency can be effectively improved by enhancing the dimensionless figure of merit ZT. Therefore, the practical application of thermoelectric materials critically depends on the enhancement in ZT. From Equation (2.5), a material with a high figure of merit should have a large Seebeck coefficient and a high electric conductivity as well as a low thermal conductivity. These three TE parameters are described specifically below.



Figure 2.4 Relationship between the temperature difference between the cold-side and the hot-side, materials' ZT_{avg} , and Carnot efficiency with reported materials [3].

2.2.1 Seebeck coefficient S

The Seebeck coefficient *S* is also called thermopower. It is positive for *p*-type materials while negative for *n*-type materials. A typical value is the order of $1 \,\mu\text{V/K}$ for metals and $100 \,\mu\text{V/K}$ for semiconductors [4]. According to the relaxation time approximation, if non-degenerate semiconductors are exposed to an electric field and a temperature gradient, the *S* can be described by Boltzmann equations as [5]:

$$S = \pm \frac{k_B}{e} \left[\frac{E_F}{k_B T} - \left(r + \frac{5}{2} \right) \right], \tag{2.6}$$

where k_B is the Boltzmann constant, E_F is the Femi energy, and r is the scattering factor, depending on scattering mechanisms (r = -1/2 for acoustic scattering, r = 1/2 for optical scattering, and r = -3/2 for impurity scattering).

For metals or degenerate semiconductors with a parabolic band, the S can be denoted as [5]:

$$S = \pm \frac{\pi^2}{3} \frac{k_B}{e} \frac{\left(s + \frac{3}{2}\right)}{\frac{E_F}{k_B T}}$$
(2.7)

and then can be simplified by Mahan-Sofo theory [6]

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m_d^* T(\frac{\pi}{3n})^{\frac{2}{3}}.$$
 (2.8)

Obviously, the *S* is proportional to DOS effective mass m_d^* and inversely proportional to charge carrier concentration *n* (or *p*). The charge carriers (electrons and holes) are all contributed to the Seebeck coefficient. When electrons and holes coexist, the whole Seebeck coefficient *S* is weighted by relative contributions of electrons and holes, namely [7]

$$S = \frac{\sigma_n S_n + \sigma_p S_p}{\sigma_n + \sigma_p},$$
(2.9)

where σ_n and S_n are electrical conductivity and Seebeck coefficient of electrons, σ_p and S_p are electrical conductivity and Seebeck coefficient of holes.

2.2.2 Electrical conductivity σ

Electrical conductivity is an important property for TE materials. It is derived from the following equation:

$$\sigma = n e \mu, \tag{2.10}$$

where *e* is the elementary charge, and μ is the charge carrier mobility. Variations in the electrical conductivity depend on the change carrier concentration and the charge carrier mobility. Generally, it is difficult to improve these two parameters simultaneously. It is found that the optimum range of electrical conductivity for thermoelectric materials is from 5×10^4 to 10^5 S/m [8].

2.2.3 Thermal conductivity *κ*

Heat energy can be transmitted in solids via carriers (electrons or holes), lattice waves (phonons), electromagnetic waves, and so on. The ability to transport the heat is defined as thermal conductivity κ :

$$\kappa = -\frac{\dot{Q}}{\vec{\nabla}T},\tag{2.11}$$

where \vec{Q} is the heat flow rate vector across a unit cross-section perpendicular to \vec{Q} and *T* is the absolute temperature.

The thermal conductivity consists of three distinct contributions in semiconductors: carrier thermal conductivity κ_c , lattice thermal conductivity κ_L and bipolar diffusion thermal conductivity κ_b ($\kappa = \kappa_c + \kappa_L + \kappa_b$). In general, the bipolar diffusion may be a noticeable contribution to the thermal conductivity when the values of the carrier concentration and the mobility are approximately equal for electrons and holes ($\sigma_n \approx \sigma_p$) and their mobilities are reasonably high, which can be achieved in intrinsic semiconductors. Whereas in the case of doped semiconductors, the electrons and holes cannot have high mobility simultaneously. Therefore, the bipolar contribution is ignorable below the excitation temperature [9]. In that case, only the carrier thermal conductivity and the lattice thermal conductivity are considered ($\kappa = \kappa_c + \kappa_L$).

The charge carriers in a semiconductor can transport heat and simultaneously scatter phonons. Thus, carriers have a significant influence on thermal conductivity. According to the Wiedemann-Franz law, the ratio of the carriers thermal conductivity to the electrical conductivity is proportional to the temperature, namely

$$\frac{\kappa_c}{\sigma} = LT . \tag{2.12}$$

Therefore, the carrier thermal conductivity is $\kappa_c = L\sigma T$, where the proportional constant *L* is the Lorenz number which is different for all materials. The studied compounds in my thesis follow the single parabolic band (SPB) model, making it possible to calculate the *L* by the SPB model [10].

2.2.4 The relationship between thermoelectric parameters

Obviously, from Equation (2.5), the thermoelectric performance is proportional to the electrical conductivity and Seebeck coefficient and inversely proportional to the thermal conductivity. In principle, a higher electrical conductivity, a larger Seebeck coefficient, and a lower thermal conductivity are simultaneously needed for good thermoelectric materials. However, these physical parameters are not independent with each other. Therefore, it is impossible to adjust one parameter without deteriorating the others. Specifically, with the increase of the electrical conductivity increases as a function of charge carrier concentration, as shown in Figure 2.5. In that case, the best TE performance will be found in semiconductors with carrier concentrations between 10^{19} - 10^{21} cm⁻³[11].



Figure 2.5 The relationship between thermoelectric parameters [11].

2.3 Strategies for improving the thermoelectric performance

2.3.1 Strategies to enhance electrical conductivity

According to Equation (2.10), the electrical conductivity is related to the carrier concentration and mobility. Therefore, optimizing carrier concentration or increasing carrier mobility is the most effective strategy to enhance electrical conductivity.

2.3.1.1 Carrier concentration optimization

Generally, the optimum carrier concentration for a good TE material is between the order of 10^{19} to 10^{21} cm⁻³. There are three methods to tune carrier concentration, e.g. substitution, introducing extrinsic point defects, and composite engineering.

(1) Substitution

Substitution introduces guest atoms from the same group or the neighboring groups in the periodic table to the parent atoms, which can adjust the carrier concentration by introducing the differences of electronegativity and the electron counts [12]. For instance, higher electrical conductivity was achieved in BaZn₂Sb₂ substituted by Sr on the Ba site because of the electronegativity difference between Ba and Sr [13,14]. Substituting Na at the Ba site in BaCu₂Se₂ enhanced the electrical conductivity by increasing the hole concentration [15]. However, the optimum carrier concentration cannot be achieved because of

the dopants solubility limit and doping efficiency, which is the reason that some theoretically calculated higher thermoelectric performance could not be realized in experiments [16].

(2) Introducing point defects

Introducing point defects (vacancies, interstitial atoms, or anti-sites) has been considered to be an effective way to tune carrier concentration, playing an important role in thermoelectric materials [17]. Since the intrinsic point defects are very sensitive to the composition, a smaller deviation in composition would decrease the defects formation energy and further influence the carrier concentration. For example, manipulating Ge vacancies in GeTe optimized the carrier concentration and achieved an extraordinary *ZT* peak of 2.3 [18]. In *n*-type Bi₂Te_{2.7+x}Se_{0.3}, the anti-site defects Te·_{Bi} were formed in Te-rich condition, resulting in the enhancement of carrier concentration and electrical conductivity [19].

(3) Modulation doping

Modulation doping is a strategy aimed to improve carrier concentration, and it was first developed in the field of two-dimensional electron gas film devices [20,21]. Zebarjadi et al. have introduced this approach into SiGe-based thermoelectric materials to enhance carrier concentration [22]. Subsequently, the thermoelectric performance of BiCuSeO and BiAgSeS was improved by this strategy [23,24]. In these works, modulation doping was realized by a physical process. Specifically, the pristine matrix was completely mixed with the heavily-doped counterpart at first, and then the mixed powder was condensed into a homogeneous composite (shown in Figure 2.6). Additionally, in 2017, T. Berry et al. [25] reported a chemical method to realize the modulation doping, where TiNiSn matrix and MnNiSb were fully mixed and formed a heavily doped $Ti_{1-x}Mn_xNiSn_{1-x}Sb_x$ phase. The dissolution of MnNiSb caused an inflow of electrons as charge carriers, increasing the carrier concentration.



Figure 2.6 Schematic drawing of a general process to realize modulation doping [25].

2.3.1.2 Increasing carrier mobility

In a semiconductor, the carrier mobility μ can be defined as

$$v_{\rm d} = \mu E, \tag{2.13}$$

where v_d is the drift velocity and *E* is the electric field applied to the carriers. Combining with Newton's second law, the carrier mobility can be further written as

$$\mu = \frac{e\,\overline{\tau}}{m^*}\,,\tag{2.14}$$

where *e* is the elementary charge, τ is the average electron relaxation time, and *m*^{*} is the effective mass. According to the definition, mobility is related to the drift velocity which is determined by relaxation time. While, at different temperatures, there are different dominated sources of scattering. For example, at low temperatures, the grain boundary-phonon and electron-phonon scatterings are dominated due to the low velocity of carriers. At medium temperature, the impurity-phonon scattering becomes the main scattering mechanism. With the increasing temperature, the average thermal speed of carriers is increased, generating more phonons. In that case, phonon-phonon scattering is dominated.

2.3.2 Strategies to enhance Seebeck coefficient

2.3.2.1 Band engineering

According to Equation (2.8), for a given carrier concentration, a higher DOS effective mass m_d^* is favorable for a high Seebeck coefficient. The m_d^* can be described as $m_d^* = N_v^{2/3} m_b^*$, where m_b^* is band effective mass and N_v is band degeneracy. Thus, a large m_d^* needs a high m_b^* or/and N_v .

The large band effective mass can be obtained by band flattening, thereby optimizing the Seebeck coefficient. Specifically, the band shape has an impact on the m_b^* . The m_b^* can be described via the energy dispersion relationship [26]:

$$m_b^* = \hbar^2 \left(\frac{\partial^2 E(k)}{\partial k^2}\right)^{-1},\tag{2.15}$$

where \hbar is the reduced Planck constant, E(k) is the energy dispersion function, and k is the wave vector in reciprocal space. This equation demonstrates that a flat band shape will lead to a high band effective mass. For instance, in *n*-type PbTe, alloying S or Mn obtained obvious band flattening and enlarged band effective mass, shown in Figure 2.7 (a). Therefore, the ZT_{max} values were improved to 1.4 at 923 K [27] and 1.6 at 723 K [28], respectively.



Figure 2.7 Schematic band flattening after S or Mn alloying in *n*-type PbTe (a) and Pisarenko lines showing the different effective masses with doping and alloying [26].

Increasing band degeneracy is another commonly adopted strategy to enhance DOS effective mass m_d^* , which can be realized by doping or alloying. For example, in *p*-type GeTe, doping Bi increased the energy of the L band in the valence band and also slightly decreased the energy of the Σ band (shown in Figure 2.8). The reduced energy difference between the L and Σ bands increased the band degeneracy, leading to an extraordinarily high *ZT* of ~ 2.0 at 650 K [29]. Moreover, it was proved experimentally that in PbTe compounds the energy difference between L band and Σ band can be adjusted by alloying or doping some specific elements such as Sr [30], Mg [31], Mn [32], and Cd [33], indicating that the band degeneracy can be manipulated to the desired value.



Figure 2.8 Schematic diagram representing the convergence of bands [29].

2.3.2.2 Energy filtering effect

The energy filtering effect is to introduce energy barrier layers ($1 \sim 10 k_B T$) in the bands of the host thermoelectric materials, which can impede the transmission of the lower-energy charge carriers (shown in Figure 2.9), increasing the Seebeck coefficient and thereby keeping a high PF. Normally, energy barriers can be formed by grain boundaries and interfaces. Therefore, introducing nanostructures or inclusions is an effective way to enhance electrical transport properties. Shakouri and Bowers [34] firstly implemented energy barriers into semiconductor superlattices for selectively scattering electrons to achieve the energy filtering effect. It was found that the superlattice could be a better strategy for electron filtering if the cost is not an issue. In addition, dislocations can also induce the energy filtering effect for Seebeck coefficient enhancement, which was demonstrated in Yb-filled CoSb₃ with excess Sb [35].



Figure 2.9 Schematic diagram of the electron energy filtering mechanism (electrons moving from materials 'A' to 'B') [36].

2.3.2.3 Resonant levels

Resonant levels (shown in Figure 2.10) originate from the doping of hetero-electrons. In general, impurity atoms in semiconductor lattices will generate an impurity level within the bandgap. When the impurity level is near to the bottom of the conduction band or the top of the valence band, it can be excited to the conduction band or the valence band, participating in electrons or holes conduction. While, sometimes this impurity atom can produce a resonant level that lies above the conduction band edge or

below the valence band edge, which will enhance the electronic density of state and further the Seebeck coefficient. The contribution of resonant level to electrical properties depends on the energy of the resonant level (E_D) and the width of the resonant state (Γ). A high E_D and a narrow Γ can obtain a large Seebeck coefficient. J. P. Heremans et al. first reported that doping 2 % Tl produced a resonant level in PbTe, and the Seebeck coefficient was increased remarkably [37].



Figure 2.10 Schematic electron density of states (DOS). ED is the resonance level, and Γ is the resonance width [36].

2.3.3 Strategies to reduce lattice thermal conductivity

The lattice thermal conductivity is the only independent property in TE parameters. Thus, reducing lattice thermal conductivity is the most popular and straightforward strategy to improve TE performance. In bulk materials, the lattice thermal conductivity κ_L is defined by

$$\kappa_L = \frac{1}{3} c_v v_g^2 \tau_p , \qquad (2.16)$$

where c_v is the specific heat, v_g is the group velocity, and τ_p is the phonon relaxation time. Therefore, a lower κ_L relies on low v_g , small c_v , and reduced τ_p (displayed in Figure 2.11).

In Figure 2.11 (a), the group velocity is related to the atomic distance *a* (chemical bonds strength) and atomic mass *m*. Obviously, materials with weak chemical bonds and large atomic mass possess low v_g and, thus, low κ_L . Additionally, complex crystal structures can effectively scatter acoustic phonons

which usually are the dominated heat transport in the lattice, leading to a small acoustic specific heat (Figure 2.11 (b)). Recently, it has been found that some novel materials such as Ag₈SnSe₆ [38], Ag₉GaTe₆[39], β -Zn₄Sb₃ [40], and Ba₈Ga₁₆Ge₃₀ [41] possessed weak chemical bonds, large atomic mass, and complex crystal structures simultaneously, resulting in an extremely low intrinsic κ_L and therefore becoming potential thermoelectric materials.



Figure 2.11 A schematic illustration to reduce the lattice thermal conductivity [42].

As for reducing τ , the most popular method is to suppress the propagation of phonons with different frequencies. As shown in Figure 2.11 (c), to reduce τ , it is possible to introduce multiscale phonon scattering centers into the host, including on electron scale, atomic scale, nanoscale, and sub-micro scale. Electron-phonon interaction plays an important role in phonon transport and contributes to a significant reduction in κ_L at room temperature. On the atomic scale, lattice distortions, rattling fillers, and point defects can scatter high-frequency phonons and reduce κ_L at room temperature. However, the disadvantage of this method is that the induced defects may also lead to carriers scattering, which deteriorates carrier concentration. On the nanoscale, the nano-precipitates and dislocations can achieve mid-frequency phonon scattering. Up to now, the most successful technologies to form nanoscale powders in the matrix are ball-milling and melting-spinning [43]. In addition, grain boundaries are

believed to be effective in scattering low-frequency phonons, which are usually dominated at low temperatures [44]. Generally, decreasing grain size or introducing nano-inclusions are adopted to increase grain boundaries. Therefore, introducing scattering centers on different scales can achieve the whole-frequency phonon scattering, which remarkably suppresses κ_L and thus enhances TE performance.

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Chapter 3 Experimental Methods

3.1 Material synthesis and preparation

The most common synthesis methods of half-Heusler compounds are based on the melting-andsolidification approach. In this thesis, arc melting followed by a direct annealing method was used to synthesize NbCoSn-based samples. While, ZrNiSn-based samples were obtained by arc melting, ball milling, and then spark plasma sintering (SPS) processes. Afterward, these annealed ingots or bulk samples were cut into bars and pellets for TE properties measurements. The detailed synthesis processes are stated in the corresponding chapters.

3.1.1 Arc melting

Figure 3.1 shows a schematic of an arc-melting furnace. The raw materials are placed in a water-cooled Cu crucible, which acts as an electrode. Another electrode is the tip made of W-based alloy, hanging above the Cu-crucible. To prevent oxidation, everything is enclosed in a sealed chamber. This chamber is evacuated and refilled with Ar several times before arc melting.



Figure 3.1 Scheme of an arc melting furnace [1].

The arc melting process is performed in an Ar atmosphere with pressure ranging from 0.4 bar to 0.6 bar. An ingot of Ti is placed beside the raw materials and is firstly melted to remove the remaining oxygen inside the chamber, purifying the atmosphere. A generator is applied to provide electrical current flowing through the sample and cause an arc between the sample and the tip. Then melting is occurred. After cooling down, the sample is turned over and remelted several times to ensure a complete reaction. Afterward, the sample is taken out and crushed for the next melting. The whole processes repeat several times to improve the homogeneity.

The as-prepared samples after arc melting are inhomogeneous and exist a lot of structural defects. Thus, additional post-treatments are highly needed to reduce inhomogeneities. The properties of half-Heusler compounds are extremely sensitive to the synthesis and post-processing procedures [2]. The post-treatments include long-term annealing, ball-milling, and SPS processes.

3.1.2 Annealing

Annealing is a heat treatment that can alter a material's physical or sometimes chemical properties. It involves heating a material above its recrystallization temperature, maintaining a certain temperature for an appropriate time, and then cooling slowly in air or quenching in water. The annealing process in this thesis was performed on the as-casted samples sealed in evacuated quartz tubes. Specifically, after placing the wrapped samples with carbon paper inside the quartz tubes, they were evacuated and re-filled with high purity Ar several times. Finally, the quartz tubes were sealed using a propane-oxygen burner after the last gas evacuation. Annealing was performed in an ordinary laboratory furnace at a certain temperature for one week. Then the sealed quartz tubes were directly quenched in ice water to keep some defects or some high-temperature secondary phases [3,4].

3.1.3 Ball milling

Ball milling is a grinding method that is often applied as a homogenizing post-treatment, which can produce nano-sized powder samples as well [5,6]. During the ball milling process, the collision between balls and samples in a container will generate high localized pressure. Normally, ceramic, stainless steel, and Tungsten Carbide (WC) jars are used. Figure 3.2 shows the ball mill used in our experiments. Since the ball-milled half-Heusler powder is sensitive to air, which will significantly undermine the electrical conductivity. Thus, the processes of loading the samples into and taking them out from the jars were carried out in the glove box with Ar atmosphere.



Figure 3.2 Ball mill equipment used in the experiment.

3.1.4 Spark Plasma Sintering

The SPS equipment used in our experiments is presented in Figure 3.3. The process is performed in a sealed, vacuumed chamber. The ball-milled powder surrounded by graphite foil is loaded in a graphite die and pressed uniaxially by a certain pressure. Afterward, a pulsed electrical current is driven through the die, and then the sample itself is heated to a set temperature at a certain heating rate. The isothermal step takes several minutes, followed by an uncontrolled cooling step. SPS is a quick sintering technique, and thus the formation of impurity phases is prevented during the heating and cooling steps [7].



Figure 3.3 SPS equipment used in the experiment.

3.2 Sample Characterization

3.2.1 Crystal structure characterization

X-ray diffraction (XRD) is an analytical technique used to identify the structure of materials and can provide information to determine unit cell dimensions and grain sizes [8]. The measurement principle follows Bragg's Law.

Neutron diffraction (ND) is a technique to determine atomic properties or/and crystalline structures of materials using neutron scattering, which is similar to X-ray diffraction but has much more advantages [9]. Neutrons are scattered by the nucleus of the atoms, while X-rays are scattered by electrons of atoms. Thus neutrons depend on the properties of the nucleus, whereas X-rays are related to the atomic number of the atoms. The nucleus of every atom has completely different characteristics, even the isotopes from the same element, making it possible to distinguish atoms that have a similar atomic number. Besides, neutrons can be used to study the properties near the surfaces of materials due to the capability to penetrate a few centimeters into the materials.

3.2.2 Microstructure characterization

Scanning electron microscope (SEM) is an important electron microscopy technique that can achieve a detailed visual image with high resolution, which is widely employed to observe the surface microstructure of materials. The electron beam interacts with atoms at various depths in the sample, producing various signals including secondary electrons (SE), back-scattered electrons (BSE), X-rays, and Cathodoluminescence (CL). The signal from SE can be localized at the point of impact of the primary electron beam, making it possible to collect images from the sample's surface. BSE signal is strongly related to the atomic number of the elements, providing information about the elemental distribution, further the different phases of the samples. With energy-dispersive X-ray spectroscopy, the actual composition in the micro-zone of samples can be analyzed [10]. The SEM equipment used in this thesis is described in detail in every chapter.

High-resolution scanning transmission electron microscopy with high-angle annular dark-field (STEM-HAADF) is a STEM method that provides annular dark-field images by electrons scattered at an angle large than 5° (Rutherford scattered electrons). It is developed for precise and accurate observation of atom configurations since it is highly sensitive to the atomic number, becoming a powerful tool to study the atomic-scale properties of materials [11,12]. In this thesis, the STEM-HAADF technique was used to determine the atom occupations in the lattice.

3.2.3 Thermoelectric properties characterization

3.2.3.1 Electrical conductivity and Seebeck coefficient

The electrical conductivity and Seebeck coefficient were measured on the ZEM-3 instrument (Ulvac-Riko, Japan, shown in Figure 3.4) using the four-point probe method. During measurement, the sample should be a standard rectangular bar and retain a certain amount of Helium to avoid sample oxidation at high temperatures.



Figure 3.4 ZEM equipment used in the experiments.

For the Seebeck coefficient, the schematic principle is shown in Figure 3.5. At a certain temperature, a temperature difference constant ΔT is generated between the two probes (A and B). According to the Seebeck effect, a voltage ΔU of the sample is obtained. Thus, the Seebeck coefficient *S* of the sample at this temperature can be calculated:

$$S = \frac{\Delta U}{\Delta T} \,. \tag{3.1}$$



Figure 3.5 The schematic principle of Seebeck coefficient measurement.

The principle of electrical conductivity measurement is shown in Figure 3.6. At a certain temperature, the electrical current I flows through the sample and at the same time, the voltage of the sample is measured. Therefore, the electrical conductivity σ at this temperature can be described:

$$\sigma = \frac{I\Delta x}{\Delta US_c},\tag{3.2}$$

where Δx is the distance between the thermocouple and S_c is the cross-sectional area of the sample.



Figure 3.6 The schematic principle of electrical conductivity measurement.

3.2.3.2 Thermal conductivity

The thermal conductivity of materials is calculated by the following equation:

$$\kappa = DC_p d_s, \tag{3.3}$$

where D, C_p , d_s are the thermal diffusivity, specific heat capacity, and sample density, respectively. Thus, D, C_p , d_s should be measured to get the thermal conductivity.

There are two techniques to measure thermal diffusivity D, static methods and dynamic methods [9]. In static methods, measurements are carried out only after thermal equilibrium has been established. Such methods guarantee the achievement of high accuracies, but it is time-consuming, and the measured temperature range and thermal diffusivity range are limited, mainly applied for materials with lower thermal diffusivity at moderate temperature. On the other hand, in dynamic methods, thermal gradients are observed as a function of time, enabling measurements to be made quickly and over a wide temperature range.



Figure 3.7 Netzsch laser Flash system (LFA-457).

In this work, one of the dynamic methods, the laser pulse heating method, was used to measure the thermal diffusivity in LFA 457 (NETZSCH, Germany), shown in Figure 3.7. The measurement principle is shown in Figure 3.8. The bottom surface of the sample is irradiated with a short burst of radiant energy, the duration of which is short compared to the transit time of the pulse through the sample. As an assumption, there are no heat losses from the sample. Then, the temperature at the upper surface of the sample will rise to a maximum value and remain constant. Therefore, the thermal diffusivity can be calculated by

$$D = \frac{0.1388d_t^2}{t_{1/2}},$$
(3.4)

where d_t is the thickness of the sample and $t_{1/2}$ is the time that the temperature at the upper surface rises to half of the maximum value. The sample should be coated with graphite during the measurement for

better and more homogeneous heat absorption and emission at the surfaces. The uncertainty of the value measured from LFA is around 5 - 10 %.



Figure 3.8 The schematic principle of LFA.

The specific heat capacity C_p can be obtained by Differential Scanning Calorimetry (DSC) using DSC 204 (NETZSCH, Germany) apparatus. C_p is the amount of heat energy required to raise the temperature of a sample by per degree for per unit of mass. DSC records signals at different temperatures and compares them to a reference simultaneously (generally a sapphire sample with known specific heat capacity $C_{p,sapp}$, and mass m_{sapp}). The C_p of the sample is evaluated by the following method:

$$C_{p} = \frac{m_{sapp}}{m_{sample}} \frac{DSC_{sample} - DSC_{baseline}}{DSC_{sapp} - DSC_{baseline}} C_{p,sapp}, \qquad (3.5)$$

where m_{sample} , DSC_{sample} , $DSC_{baseline}$ and DSC_{sapp} are the mass of the sample, DSC signals of the sample, DSC signals from the baseline, and DSC signals of the sapphire, respectively. Besides, the specific heat can be calculated by Dulong-Petit law as well, which considers the atoms' vibration degrees of freedom. If one atom vibrates around its equilibrium position, it will possess the energy of k_BT in each degree of freedom. Since each atom vibrates in three dimensions, the energy of one atom will be 3 k_BT . As we know, the total inner energy U equals the average energy of each atom multiplies the number of atoms in one mole N_A ($U = 3 k_BTN_A$). Then the mole heat capacity can be described as:

$$C = \frac{\partial U}{\partial T} \approx 3N_A k_{\rm B} = 3R , \qquad (3.6)$$

where R is the gas constant. The specific heat capacity is the heat capacity related to the mass of the material. Thus, the specific heat Cp can be calculated by

$$C_p = \frac{3NR}{M}, \qquad (3.7)$$

where N is the number of atoms in one formula, and M is the molar mass of the compound.

Samples' density d_s is calculated based on the Archimedes principle. The weight of samples in the air m_{dry} and the water m_{wet} are obtained by a balance with a special device (shown in Figure 3.9). Then the density of samples can be calculated by

$$d_{s} = \frac{m_{dry}(\rho_{water(T)} - \rho_{air(T)})}{C(m_{dry} - m_{wet})} + \rho_{air(T)},$$
(3.8)

where $\rho_{water(T)}$ and $\rho_{air(T)}$ are the density of water and air at the measured temperature, *C* is the correction factor (*C* = 0.99983).



Figure 3.9 Archimede's kit for density measurement.

3.2.3.3 Hall measurement

The Hall measurement is an important approach to determine the dominant charge carrier concentration and mobility in the materials according to the Hall effect. All the information can be derived from the Hall constant R_H , which is proportional to the Hall resistivity ρ_H and the applied magnetic field B_z . The scheme of Hall measurement is shown in Figure 3.10. The magnetic field B_z is perpendicular to the top surface of a sample, and the electrical current *I* is flowing along its one axis. R_H is given by the equation

$$R_H = \rho_H / B_z, \tag{3.9}$$

where $\rho_{\rm H}$ is defined as

$$\rho_H = \frac{V_H}{I} \frac{A}{W},\tag{3.10}$$

where V_H is the Hall voltage, A is the sample's cross-section, and W is the perpendicular distance of two sides electrodes, which equals to the sample's width a.

The experimental procedures include setting temperature and measuring V_H at several different values of B_z . Afterward, R_H is obtained by Equation (3.9). Therefore, the Hall concentration n_H and Hall mobility μ_H can be calculated from R_H and σ :

$$n_{H} = \frac{1}{R_{H} |e|}, \qquad (3.11)$$

$$\mu_H = \sigma R_H \,. \tag{3.12}$$



Figure 3.10 Scheme of Hall effect measurement [13].

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Chapter 4 Thermoelectric properties of *n*-type NbCoSn with Ni introduction

This chapter is based on the publication:

"Effects of doping Ni on the microstructures and thermoelectric properties of Co-excessive NbCoSn half-Heusler compounds" by Ruijuan Yan, Ruiwen Xie, Wenjie Xie, Chen Shen, Wei Li, Benjamin Balk, Songhak Yoon, Hongbin Zhang, and Anke Weidenkaff. *ACS Applied Materials and Interfaces*, 13 (2021) 34533-34542.

Abstract

Doping/substitution and tailoring of microstructures are common experimental approaches to enhance the TE performance of HH compounds. However, detailed theoretical insights into the effects of doping on the microstructures and TE properties are still missing. In this work, due to the existence of intrinsic excessive Co/Ni, the microstructure of NbCoSn was tailored by precipitating the FH phase in the HH matrix by changing the nominal ratio of Co and Ni on the Co site. Further, first-principles calculations were employed to understand the relationship between the microstructure and the TE properties from the thermodynamic point of view. Detailed analysis of the electronic structure revealed that the excessive Co/Ni defects contributed to the increased carrier concentration. Through an increase in the electrical conductivity and a reduction in the thermal conductivity, the TE performance was enhanced. The present work offered a new pathway and insights to enhance the TE properties of HH compounds by engineering the intrinsic defects.

4.1 Introduction

Recently, several studies have been carried out to enhance the TE performance of the NbCoSn compound, mostly via modifying the chemical compositions and tailoring the microstructures [1-6]. For instance, recent experimental results showed that the figure of merit of *n*-type NbCoSn can be significantly improved by substituting Sb or Pt [3,4]. Besides, forming full-Heusler (FH) precipitates by adding extra Co can also enhance the figure of merit of NbCoSn via significantly reducing the thermal conductivity [5,6]. Among all the intriguing phenomena reported in NbCoSn so far, the existence of intrinsic excess Co in the directly melted (arc-melted or optical float zone melted) NbCoSn compounds is of great interest. The excess Co resembles the existing "interstitial" Ni atoms in the MNiSn (M = Tiand Zr) system [7-11], partially occupying the 4d Wyckoff position. This observation leads us to investigate how doping influences the phase structure, microstructure, and the corresponding transport properties of the intrinsic Co-excessive NbCoSn compound. Previous work usually focused on evaluating the TE properties by doping, while a detailed theoretical analysis of the doping effect on phase stability is still missing. In the presented work, the effect of Ni doping into the Co site of NbCoSn was investigated. Since Ni atoms have a comparable atomic radius with Co, it is natural to ask where the extraneous elements will occupy: (1) 4c position; (2) 4d position; (3) both are possible? With density functional theory (DFT) calculations [12], the phase structure, microstructure, and thermoelectric transport properties were studied and discussed to gain physical insights into the consequences of introducing Ni.

4.2 Experimental

The ingots with nominal compositions of NbCo_{1-x}Ni_xSn (x = 0, 0.02, 0.04, 0.06, 0.08, and 0.10) were prepared by arc melting the stoichiometric amounts of Nb (wire, 99.999 %), Co (bulk, 99.999 %), Ni (wire, 99.99 %), and Sn (shot, 99.99 %) under an argon atmosphere. To ensure homogeneity, the ingots were flipped and remelted several times. Afterward, all ingots were annealed in evacuated quartz tubes at 1173 K for 7 days and then directly quenched in ice water. Subsequently, the annealed ingots were cut into discs and bars for phase characterization, structural analysis, and TE property measurements. The powder XRD patterns of all samples were obtained on a diffractometer (STOE STAD) using Mo K α 1 radiation. The diffraction patterns were analyzed with the Rietveld refinement incorporated in the program *Fullprof*. Scanning electron microscopy (SEM, TESCAN, VEGA 3) with energy-dispersive X-ray spectroscopy (EDX, AMETEX) was carried out to determine the phase composition. The calculation of thermal conductivity κ and the measurement of the corresponding parameters were mentioned in Chapter 3. Here, the *C*_p was determined by the Dulong-Petit law. ZEM-3 (Ulvac-Riko, Japan) measurements were employed to get the electrical conductivity σ , and the Seebeck coefficient *S*. The charge carrier concentration $n_{\rm H}$ and mobility $\mu_{\rm H}$ at room temperature were measured by the commercial Hall measurement system (Fraunhofer IPM, HT-Hall, Germany) under a magnetic field from – 520 to 520 mT. The uncertainties are ± 10 % on κ , ± 5 % on *S*, and ± 3 % on σ .

Total energy and band structure calculations were performed in the framework of DFT as implemented in the Exact Muffin-Tin Orbitals (EMTO) method [13,14]. The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation was used for the exchange-correlation functional [15]. A ferromagnetic order was assumed for all the systems, but for NbCoSn and Ni-excessive NbCoSn, their ground states converged to a nonmagnetic state [16]. The chemical disorder induced by Ni-substitution was simulated using the coherent potential approximation (CPA) [17-19]. The application of CPA enabled us to readily obtain the band structures of NbCoSn with interstitials using the primitive unit cell. The full charge density (FCD) technique was implemented for accurate total energies [20]. The s, p, d, f orbitals were included in the EMTO basis. The one-electron equations were solved within the scalar relativistic approximation and the soft-core scheme [21]. For total energy and band structure calculations, the total numbers of k-points in the irreducible Brillouin zone were 3009 and 6689, respectively.

4.3 Results and discussions

4.3.1 Phase composition and microstructure characterization

Figure 4.1 shows the XRD patterns of nominal NbCo_{1-x}Ni_xSn (x = 0, 0.02, 0.04, 0.06, 0.08, and 0.10; hereafter named as Ni-*x*, for simplicity) samples and the corresponding refinement results of Ni-*x* samples are shown in Figure 4.2. The lattice parameters obtained by refinement are in good agreement with the reported values [4,22], shown in Table 4.1. The weight fraction (%) of each phase analyzed by Rietveld refinement is summarized in Table 4.2. Besides the main HH phase, the Ni-0 and Ni-0.02 samples have a small percentage of elemental Sn, and all samples have minor Nb₃Sn impurities with a weight fraction less than 1.5 %. A similar result has been obtained in the arc-melted NbCo_{1.00}Sn compound [6], in which the secondary phases Nb₃Sn and Sn can be identified as well. Moreover, it is found that the amount of Nb₃Sn impurities roughly gradually decreases with increasing Ni content except for the Ni-0.06 sample. One possible explanation for such phenomenon is that there might be a competition between the reaction of Sn and Nb and the reaction of Sn and Ni in the Ni-*x* samples. According to the Ni-Sn and Nb-Sn binary phase (~ 1200 K) [24]. When Ni is added, it will first form the Ni-Sn phase rather than the Nb₃Sn phase. Then, the Ni-Sn binary phases react with Nb and Co, obtaining HH and/or FH phases. In this case, the more Ni we add, the less Nb₃Sn we observe. Besides,

the refinement results indicate that the samples with Ni introduction contain the FH phase as an extra secondary phase, which was confirmed by the SEM and EDX analysis as well (shown below).



Figure 4.1 XRD patterns of Ni-*x* samples.

Table 4.1. Lattice parameters of HH and FH phases. R_{wp} and χ^2 are the reliability factor and goodness-of-fit, respectively.

Sample name	Lattice parameter of HH phase (Å)[Nb(Co,Ni)Sn]	Lattice parameter of FH phase (Å) [Nb(Co,Ni) ₂ Sn]	R_{wp}	χ^2
Ni-0	5.949(4)	-	15.2	5.48
Ni-0.02	5.949(4)	6.151(7)	14.2	5.88
Ni-0.04	5.950(4)	6.153(0)	15.1	6.63
Ni-0.06	5.950(3)	6.153(0)	17.8	4.62
Ni-0.08	5.949(0)	6.153(0)	17.1	5.31
Ni-0.10	5.949(0)	6.153(0)	15.4	4.47



Figure 4.2 XRD refinement results of Ni-*x* samples.

Table 4.2 The weight fraction (%) of each phase analyzed by Rietveld refinement for Ni-*x* samples.

Sample name	HH phase [Nb(Co,Ni)Sn]	Nb ₃ Sn	FH phase [Nb(Co,Ni) ₂ Sn]	Sn
Ni-0	96.01 ± 0.46	1.36 ± 0.05		2.63 ± 0.07
Ni-0.02	97.16 ± 0.43	0.97 ± 0.04	0.84 ± 0.06	1.02 ± 0.05
Ni-0.04	96.98 ± 0.46	0.93 ± 0.08	2.10 ± 0.08	
Ni-0.06	96.41 ± 0.53	1.17 ± 0.09	2.43 ± 0.10	
Ni-0.08	96.95 ± 0.51	0.85 ± 0.08	2.20 ± 0.10	
Ni-0.10	98.08 ± 0.46	0.57 ± 0.07	1.35 ± 0.05	

Figure 4.3 shows the microstructure of Ni-x samples collected from the fresh cross-sections. The grain size of all samples is larger than 100 μ m. The back-scattered electron (BSE) images and the corresponding EDX mappings of Ni element were collected on the polished surfaces of Ni-x samples, shown in Figure 4.4. As indicated in the XRD patterns, the secondary phase Nb₃Sn can be confirmed by combining the BSE and EDX analysis and revealing bright areas in the BSE images (Figure 4.4). The formation of the Nb₃Sn phase is hardly possible to avoid during the direct melting method since Nb₃Sn is a very stable competing phase in the Nb-Co-Sn phase diagram [25,26]. The EDX analysis shows the composition of the HH phase in Ni-0 is Nb_{0.87}Co_{1.07}Sn_{0.94}, indicating that the HH phase of Ni-0 contains excessive Co. A similar result has been reported by Kimura and Tamura, and a careful inspection revealed that the main HH phase of the nominal stoichiometric NbCo_{1.00}Sn alloy obtained by the optical floating zone melting method was Nb_{31.4}Co_{35.4}Sn_{33.2} [5]. Further, we justified the thermodynamic stability of the Co-excessive HH phase by calculating its formation energy using EMTO. The computational results show negative formation energies in Co-excessive HH phases with excessive Co content ranging from 0 to 100 at. %, in which the configuration with 70 at. % excessive Co exhibited the highest formation energy of approximately -0.06 eV/site (Figure 4.5). Therefore, combining the experimental measurements and theoretical stability evaluation, the excessive Co is expected to exist in the HH phase.



Figure 4.3 The microstructure of Ni-*x* samples.



Figure 4.4 The BSE images of samples (a) Ni-0.04, (b) Ni-0.06, (c) Ni-0.08, (d) Ni-0.10, and the corresponding EDX mappings of Ni (e), (f), (g) and (h).



Figure 4.5 The formation energy of Co on 4d site.

Nominal composition	EDV regults	d (g/cm ³)	Relative	
Nominal composition	EDA lesuits		density (%)	
NbCoSn	Nb _{0.87} Co _{1.07} Sn _{0.94} (I)	8.33	98	
$NbCo_{0.98}Ni_{0.02}Sn$	$Nb_{0.88}Co_{1.06}Ni_{0.015}Sn_{0.94}$ (I)	8.38	98	
NbCoss-Niss-Sp	$Nb_{0.89}Co_{1.11}Ni_{0.03}Sn_{0.97}$ (I)	8 1 2	99	
10000.961010.04511	$Nb_{0.86}Co_{1.01}Ni_{0.41}Sn_{0.72}$ (II)	0.42		
NhCo. Nie Sn	$Nb_{0.89}Co_{1.11}Ni_{0.04}Sn_{0.96}$ (I)	8 16	99	
110000.941110.06511	$Nb_{0.85}Co_{1.00}Ni_{0.46}Sn_{0.70}\left(II\right)$	0.40		
NbCoo ooNio ooSn	$Nb_{0.89}Co_{1.09}Ni_{0.06}Sn_{0.96}$ (I)	8 11	99	
110000.92110.08511	Nb _{0.84} Co _{0.93} Ni _{0.39} Sn _{0.91} (II)	0.44		
NhCoNiSn	$Nb_{0.93}Co_{1.02}Ni_{0.07}Sn_{0.98}$ (I)	Q /1	00	
110000.901110.10511	Nb _{0.78} Co _{0.83} Ni _{0.63} Sn _{0.77} (II)	0.41		

Table 4.3 Nominal composition, EDX results, and samples' relative density of Ni-x.

As shown in Figure 4.4, for the samples Ni-0.04 and Ni-0.06, there are some areas of the Ni-rich dark gray phase (labeled phase II in the BSE images) distributed in the matrix, and those Ni-rich phases formed a sort of network. The EDX results (Table 4.3) reveal that the composition of phase II is close to the FH compound. This is also in good agreement with the XRD refinement analysis, in which the FH phase can be identified. However, when x > 0.06, the network-distributed dark gray Ni-rich areas disappear, and instead, the dot-shaped areas show up (Figure 4.4 (g) and 4.4 (h)). The formation of the FH phase can be understood from the thermodynamical point of view based on DFT calculations. Starting from HH NbCoSn, the introduced Ni atoms could occupy three possible sites in the lattice: (1) substituting on Co 4c positions; (2) occupying 4d positions to form the (Co,Ni)-excessive HH structure (inset of Figure 4.6 (a)); or (3) occupying the left empty 4d positions of the Co-excessive HH structure to form the FH structure (inset of Figure 4.6 (b)). The corresponding formation energies were then calculated using CPA embedded in EMTO. It is observed from Figure 4.6 (a) that Ni tended to thermodynamically occupy the vacant 4d site. Besides, the stability of the FH phase with Ni and Co together occupying the 4d site was evaluated (Figure 4.6 (b)). The configuration with Ni = 0 at. % and Ni = 100 at. % represents the FH NbCo₂Sn and NbCoNiSn phases, respectively. The reduction of the formation energy with Ni content indicates that the introduction of Ni on the 4d site is capable of stabilizing the FH phase as compared to NbCo₂Sn. According to the XRD refinements (Table 4.2) and EDX results (Table 4.3), the main phase in Ni-x samples is Co-excessive HH phase, and roughly one-third of added Ni atoms occupy the left empty 4d position to form the FH phase. From Table 4.3, it is noted that the Ni composition in the FH phase increases with the Ni content. Therefore, combined with the EMTO results, it can be concluded that the microstructure of NbCoSn can be tailored by doping Ni.



Figure 4.6 (a) The formation energy of Ni-excessed NbCoSn phase with Ni occupying the 4c/4d sites and (b) FH phase with Ni occupying the 4d sites in Co-excessed NbCoSn. The doping of Ni simulated by CPA is illustrated in the insets of (a) and (b). Here, Em denotes the empty sphere that is used to simulate vacancies in CPA.

4.3.2 Electrical transport properties

The electrical conductivity σ and the Hall measurement results (electron concentration $n_{\rm H}$ and mobility $\mu_{\rm H}$) of Ni-*x* are displayed in Figure 4.7. The electrical conductivity σ of all samples decreases with increasing temperature, indicating a metal-like behavior. With Ni introduction, σ increases gradually from 6.1 × 10⁴ to 20.5 × 10⁴ S/m at room temperature, which is comparable with that of NbCo_{0.85}Pt_{0.15}Sn (~ 24 × 10⁴ S/m) [4], and then drops when *x* is larger than 0.08. This trend can be explained by the variation of the electron concentration $n_{\rm H}$. For the pristine NbCoSn sample (Ni-0), the $n_{\rm H}$ value is around 4 × 10²⁰ cm⁻³, and this value increased to ~ 24 × 10²⁰ cm⁻³ and then decreased to ~ 12 × 10²⁰ cm⁻³ after Ni introduction, which is consistent with the trend of σ . However, the mobility $\mu_{\rm H}$ has the opposite trend with $n_{\rm H}$, which varied in the range of 5-12 cm²/Vs.



Figure 4.7 Temperature dependence of the electrical conductivity σ (a), and the electron concentration $n_{\rm H}$ and the mobility $\mu_{\rm H}$ at room temperature (b) for Ni-*x* samples.

The reason for the enhancement in $n_{\rm H}$ has multiple aspects. Firstly, substituting one Ni atom will generate one extra electron. Besides, it has been verified both theoretically and experimentally that excess Ni can contribute in-gap states and extra electrons in MNiSn (M = Ti, Zr, and Hf) compounds [27,28]. It is expected that excess Ni/Co can also donate charge carriers to NbCoSn compounds. Lastly, the formed half-metallic FH can donate extra charge carriers as well [29]. Theoretically, 1 % Ni-substitution on the 4c site of Co will introduce 1.88×10^{20} cm⁻³ electrons to the studied samples. However, in fact, the $n_{\rm H}$ of Ni-0 is 4 \times 10²⁰ cm⁻³, and with 6 % nominal Ni-substitution, the measured $n_{\rm H}$ of Ni-0.06 is 24 × 10²⁰ cm⁻³, which is much higher than 15.2 × 10²⁰ cm⁻³ (4 × 10²⁰ cm⁻³ + 6 × 1.88 × 10²⁰ cm⁻³). It should be mentioned that according to the EDX results shown in Table 4.2 the actual doping content of Ni in the sample Ni-0.06 is about 3.5 %. Obviously, Ni-substitution is not the major contributor to the enhancement of $n_{\rm H}$. To figure out which effect dominates, the nominal Ni content x dependence of $n_{\rm H}$, the atomic ratio of (Co, Ni):Nb in the HH phase, and the weight fraction of the FH phase are summarized in Figure 4.8. The atomic ratio of (Co, Ni):Nb in the HH phase can be treated as a measure of excess (Co and Ni) content in the HH phase. It shows a clear correlation between $n_{\rm H}$ and the atomic ratio of (Co, Ni):Nb in the HH phase as well as the weight fraction of the FH phase. Thus, it can be speculated that excess (Co, Ni) or/and FH phase is/are the major donor(s). To verify this speculation, the band structures and density of states (DOS) of Co/Ni-excessive NbCoSn were calculated, and the results are shown in Figure 4.9. The excessive Co/Ni concentration was settled to 30 at. % in the simulation cell to model the measured phase composition according to the EDX result in the nominal NbCo_{0.94}Ni_{0.06}Sn sample (see Table 4.3). Similar to the *M*NiSn (M = Ti, Zr, and Hf) compounds [8-11], the excess Ni in NbCoSn induces the in-gap states as seen from Figure 4.9 (a) and 4.9 (b), leading to the reduced bandgap and thus the increased carrier concentration. In addition, the
excess Co plays a similar role to the excess Ni in NbCoSn. The band structure and DOS corresponding to the majority spin channel in Co-excessive NbCoSn exhibit a similar pattern as compared to that of the Ni-excessive case. What differentiates the Co-excessive and Ni-excessive NbCoSn phases is the induced ferromagnetism in the Co-excessive NbCoSn, which might have a minor influence above room temperature as the systems become paramagnetic. In contrast to the majority spin channel, the minority spin channel showed increased DOS at the bottom of the conduction band and the top of the valence band. The changes of the DOS due to excessive Co obtained in the current work are consistent with those reported in ref [30]. Besides, it is noteworthy that the Co anti-site defects are not energetically favorable, of which the formation energy is about 2 eV higher than that of the Co interstitials [30].



Figure 4.8 The nominal Ni content *x* dependence of $n_{\rm H}$, the atomic ratio of (Co,Ni):Nb, and the weight fraction of the FH phase.



Figure 4.9 Band structures and density of states (DOS) of (a) NbCoSn, (b) 30 at. % Ni(4d)-excessed NbCoSn, 30 at. % Co(4d)-excessed NbCoSn for (c) majority spin and (d) minority spin channels.

The temperature dependence of the Seebeck coefficient *S* for Ni-*x* samples is shown in Figure 4.10 (a). The bipolar conduction is observed at 800 K in the pristine NbCoSn sample. The absolute *S* increased almost linearly with the rise of temperature after introducing Ni and there is no obvious contribution from the bipolar conduction. This indicates that the introduction of Ni can suppress the intrinsic excitation and thus raise the application temperature. Besides, since *S* follows the notion $S \propto n^{-2/3}$ for the degenerated semiconductor, the absolute *S* of Ni-*x* gradually decreases and then increases slightly with the increase of *x*. To further understand the transport properties, the experimental data were analyzed by the Boltzmann transport equation within the relaxation time approximation. Assuming that the electron transport agrees with the single parabolic band (SPB) model, the Seebeck coefficient *S* and the electron concentration *n* can be defined by the following equations:

$$S = -\frac{\kappa_B}{e} \left[\frac{(2 + \lambda F_{\lambda+1}(\eta))}{(1 + \lambda) F_{\lambda}(\eta)} - \eta \right]$$
(4.1)

$$n_{\rm H} = 4\pi \left(\frac{2m^* k_B T}{h^2}\right)^{3/2} F_{1/2} \tag{4.2}$$

$$F_{j}(\eta) = \int_{0}^{\infty} f\xi^{j} d\xi \int_{0}^{\infty} \frac{\xi^{j}}{1 + e^{(\xi - n)}} d\xi, \qquad (4.3)$$

where $k_{\rm B}$ is the Boltzmann constant, *e* is the elementary charge, λ is the scattering factor ($\lambda = 0$ for NbCoSn [2]), *h* is the Planck constant, and *m*^{*} is the DOS effective mass. Additionally, $F_j(\eta)$ is the Fermi integral, which is the function of the reduced chemical potential η ($\eta = (E_{\rm F} - E_{\rm c})/k_{\rm B}T$, $E_{\rm F}$ and $E_{\rm c}$ are the energy of the Fermi level and the bottom of the conduction band, respectively) [31]. Accordingly, the Pisarenko plot at 310 K for Ni-*x* samples was obtained, and the corresponding effective mass is $m^* = 5.4 m_e$ (shown in Figure 4.10 (b)). This m^* value is close to that of the NbCo(Sn,Sb) compound [3] but still lower than the reported value of Nb(Co,Pt)Sn (6.5 m_e) [4], which originates from the heavy-doped effect caused by the Pt element in the band structure of NbCoSn.



Figure 4.10 (a) Temperature dependence of Seebeck coefficient *S*, (b) Seebeck coefficient versus electron concentration at 310 K for Ni-*x* samples.

The calculated power factor (PF = $S^2\sigma$) by the measured σ and S is plotted in Figure 4.11. A maximum PF of ~ 2.4 mW/mK² is obtained at 700 K for Ni-0.10 sample, mainly originating from its relatively larger absolute *S* compared with other Ni-*x* ($x \neq 0$) samples. However, this value is still lower compared to the reported value in NbCo(Sn,Sb) and Nb(Co,Pt)Sn (~ 3.4 mW/mK²) compounds [3,4] due to the lower Seebeck coefficient, which might result from the existence of metallic impurities (Nb₃Sn and FH phases) in our samples. Thus, much more effort should be made to improve the phase purity.



Figure 4.11 Temperature dependence of the power factor PF for Ni-x samples.

4.3.3 Thermal transport properties

The thermal conductivity κ of Ni-*x* samples as a function of temperature is shown in Figure 4.12 (a). It roughly decreases with Ni concentration in the whole measured temperature range. To further understand this behavior, the electron component κ_e (= $L\sigma T$, L is the Lorenz number obtained by the single parabolic band model [32], and the values are shown in Figure 4.13) and the lattice component κ_L (= $\kappa - \kappa_e$) were calculated and shown in Figure 4.12 (b) and 4.12 (c). The κ_e value gradually increases with the increase of Ni content and then decreases when Ni > 0.06, following the same trend with σ , which is originated from the variation of electron concentration $n_{\rm H}$. By contrast, a remarkable decrease in κ_L is observed after Ni introduction, and the maximum decrease is around 31 % in the Ni-0.06 and Ni-0.08 samples over the whole temperature range. The reason for that is the strong point-defect and boundary phonon scattering induced via Ni introduction and the FH precipitates. Nevertheless, the thermal conductivity of all samples is still much higher than that reported in NbCoSn_{1-x}Sb_x [3] and NbCo_{1-x}Pt_xSn [4] compounds, which might be ascribed to the larger grain size of Ni-*x* samples (Figure 4.3) synthesized by arc melting and annealing method.



Figure 4.12 Temperature dependence of (a) thermal conductivity κ , (b) electrical thermal conductivity κ_{e} and (c) lattice thermal conductivity κ_{L} for Ni-*x* samples.



Figure 4.13 Temperature dependence of Lorenz number for Ni-x samples.

4.3.4 Figure of merit and reproducibility

Due to the simultaneous improvement of PF and reduction of κ , the TE performance ($ZT = S^2 \sigma T/\kappa$) of the Ni-*x* samples was improved by doping Ni (Figure 4.14). A maximum *ZT* value of ~ 0.4 was achieved at 1000 K for the Ni-0.10 sample, which is 73 % higher than that of the pristine NbCoSn sample. Notably, the almost linear enhancement of *ZT* as a function of temperature indicated that a higher *ZT* value can be obtained at a higher temperature, which makes NbCoSn a promising candidate for high-temperature application. Additionally, the reproducibility of electrical transport properties was evaluated for Ni-0.08 and Ni-0.10 samples as well, which is shown in Figure 4.15. It is noted that the heating and cooling curves of σ and *S* coincided with each other very well, indicating that these samples are thermally stable in the whole measured temperature range (300 - 1000 K).



Figure 4.14 Temperature dependence of ZT for Ni-x samples.



Figure 4.15 The heating and cooling curves of electrical conductivity σ (a) and Seebeck coefficient *S* (b) for Ni-0.08 and Ni-0.10 samples.

4.4 Conclusions

To summarize, the current work utilizes a combined experimental and DFT-based computational method to elucidate the influence of Ni on the microscopic phases and further the TE properties. The compounds with nominal compositions of NbCo_{1-x}Ni_xSn ($x = 0 \sim 0.10$) were synthesized using arc melting, followed by annealing treatments. With the assistance of DFT calculations, the microstructure and TE properties were systematically investigated. It was found that Ni atoms preferred to occupy the 4d position in these Co-excessive NbCoSn compounds. Additionally, the introduction of Ni on the 4d site in the

Co-excessive NbCoSn to form the FH phase is more energetically favorable than forming the FH NbCo₂Sn phase. This makes it possible to modify the microstructure by directly tailoring the Ni concentration. With the synergistic effects of Ni-substitution, Co/Ni excess, and FH phase, the carrier concentration and the electrical conductivity enhanced significantly. The physical picture regarding the enhanced carrier concentration can be deduced from the excess Co/Ni-induced in-gap states and thus the reduced bandgap. Furthermore, the thermal conductivity κ decreased dramatically due to Ni introduction and the existence of the FH phase in the HH matrix. At last, the peak *ZT* value reached ~ 0.4 at 1000 K for the sample with a nominal composition of NbCo_{0.90}Ni_{0.10}Sn. Further enhancement of *ZT* would be expected through depressing the lattice thermal conductivity by reducing grain size and/or doping Ta on Nb as well as optimizing the carrier concentration.

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Chapter 5 Thermoelectric properties of *p*-type NbCoSn with Sc substitution

This chapter is based on the publication:

"Realizing *p*-type NbCoSn half-Heusler compounds with enhanced thermoelectric performance via Sc substitution" by Ruijuan Yan, Wenjie Xie, Benjamin Balke, Guoxing Chen, and Anke Weidenkaff. *Science Technology Advanced Materials*, 21 (2020) 122-130.

Abstract

The intrinsic *n*-type half-Heusler NbCoSn was calculated as a promising *p*-type thermoelectric material, which is attractive for thermoelectric applications. While the desired *p*-type NbCoSn counterpart shows poor thermoelectric performance. In this work, *p*-type NbCoSn has been obtained using Sc substitution at the Nb site, and their thermoelectric properties were investigated. Of all samples, the Nb_{0.95}Sc_{0.05}CoSn compound shows a maximum power factor of 0.54 mW/mK², which is the highest among the previously reported values of *p*-type NbCoSn. With the suppression of thermal conductivity, the *p*-type Nb_{0.95}Sc_{0.05}CoSn compound shows the highest measured figure of merit ZT = 0.13 at 879 K.

5.1 Introduction

NbCoSn is one of HH thermoelectric compounds with a bandgap of 0.987 eV [1], and such a bandgap fulfills the '10 $k_{\rm B}T_0$ ' rule. In addition, the small difference in electronegativity between Co (1.88) and Sn (1.96) ensures larger carrier mobility. Therefore, NbCoSn is a promising mid/high temperature thermoelectric material. Unsubstituted NbCoSn is an intrinsic *n*-type semiconductor. In 2006 Ono et al. [2] investigated the Sb and Ti substituted *n*-type NbCoSn, and the highest ZT of 0.3 was achieved in the $Nb_{0.99}Ti_{0.01}CoSn_{0.9}Sb_{0.1}$ at 850 K. A decade later, R. He et al. [3] synthesized the *n*-type NbCoSn_{1-x}Sb_x samples by arc melting combined with ball milling and hot-pressing processes, and the highest ZT reached ~ 0.6 at 1000 K for NbCoSn_{0.9}Sb_{0.1}. Generally, a TE device needs not only high ZT in *n*-type and *p*-type materials, but the *n*-type and *p*-type materials should have similar compositions, obtaining comparable mechanical properties and thermal expansion coefficient. For instance, *n*-type *M*Ni(Sn,Sb) [4] and p-type MCo(Sb,Sn) [5,6] (M = Zr and Hf) compounds fulfill such criteria, in which the thermoelectric module made of them reaches a record-high conversion efficiency of 12.4 % with a temperature difference of 698 K [7]. For fabricating p-n NbCoSn couple, a p-type NbCoSn based compound is needed to match the developed *n*-type NbCoSn compounds. However, few efforts have been devoted to investigating p-type NbCoSn. To the best of our knowledge, D. A. Ferluccio et al. [8] first realized the *p*-type NbCoSn via substituting Ti and Zr at the Nb site, but the maximum ZT value for *p*-type Nb_{0.8}Zr_{0.2}CoSn is only 0.03 at ~ 790 K. Obviously, the ZT value of *p*-type Nb_{0.8}Zr_{0.2}CoSn compounds is much inferior to those of *n*-type counterparts. Therefore, it is crucial to identify new *p*-type dopants and further improve the thermoelectric performance of *p*-type NbCoSn.

In this work, the NbCoSn compound has been prepared through arc melting followed by annealing processes, and then Sc, chosen as a *p*-type dopant, is substituted at the Nb site to obtain Nb_{1-z}Sc_zCoSn ($z \le 0.1$) samples. The phase composition and TE properties were investigated. There are two main reasons for choosing Sc as a *p*-type dopant: (1) The substitution of Nb (III B) by Sc (V B) can create more holes in this compound and further achieve a *p*-type NbCoSn. (2) The larger mass fluctuation between Nb (92.91 g/mol) and Sc (44.96 g/mol) can strengthen defect and alloying phonon scattering, which can significantly suppress the lattice thermal conductivity.

5.2 Experimental

Nb_{1-z}Sc_zCoSn ($z \le 0.1$) compounds were prepared by arc-melting stoichiometric amounts of the elements Nb (wire, 99.999 %), Sc (piece, 99.99 %), Co (bulk, 99.999 %), Sn (shot, 99.999 %) in Ar atmosphere. The ingots were melted several times with flipping twice over each time to ensure homogeneity. The obtained ingots were sealed into evacuated quartz tubes and annealed at 1173 K for 7 days. Then, the bars and pellets for measurements were prepared by cutting these annealed ingots.

The crystal structures of samples were investigated by powder X-ray diffraction (PXRD) on a Rigaku diffractometer (Rigaku, Japan) using Cu K α radiation ($\lambda_0 = 1.5418$ Å). The microstructures of polished samples were characterized by scanning electron microscopy (SEM, Zeiss Gemini, Germany), and the phase compositions were analyzed by energy-dispersive X-ray spectroscopy (EDX, Bruker, Germany). Electrical transport properties (Seebeck coefficient and electrical conductivity) were simultaneously measured by a ZEM-3 instrument (Ulvac-Riko, Japan) under He atmosphere from 300 to 900 K. The measurement errors for all samples are around ± 3 % (electrical conductivity) and ± 5 % (Seebeck coefficient). The Hall carrier concentration $p_{\rm H}$ ($n_{\rm H}$) and mobility $\mu_{\rm H}$ were calculated via $p_{\rm H} = 1/eR_{\rm H}$ ($n_{\rm H} =$ $-1/eR_{\rm H}$) and $\mu_{\rm H} = \sigma R_{\rm H}$, where e is the unit charge and $R_{\rm H}$ is the Hall coefficient measured by commercial Physical Properties Measurement System (PPMS, Quantum Design, USA) under magnetic fields from - 5.2 T to 5.2 T. The thermal conductivity was calculated by the formula $\kappa = DC_p d_s$, where D is thermal diffusivity measured by laser flash instrument (NETZSCH, LFA457, Germany) by coating all samples with a thin layer of graphite to minimize emissivity errors (the actual measurement error is about 3 %), C_p is the specific heat derived by temperature-dependent heat data using the differential thermal analyzer (NETZSCH, DSC204F1, Germany), and d_s is the samples' density estimated by the Archimedes method. The relative densities of these samples are about 95 %.

5.3 Results and discussions

5.3.1 Phase and microstructure

The cubic NbCoSn crystal structure is shown in Figure 5.1. The element Nb (4a site) and Sn (4b site) form the NaCl sublattice with octahedral coordination, leaving all tetrahedral central sites (4c and 4d sites) to the element Co, but only half of the sites (4c site) is occupied by Co, forming this half-Heusler compound. Simply, by applying the Zintl chemistry concept [9], this crystal structure can be described into an anionic framework [CoSn]⁵⁻ formed by the tetrahedral coordination of Co and Sn, and an electropositive Nb⁵⁺ filled in the octahedral voids formed by these tetrahedral frameworks.



Figure 5.1 The crystal structure of NbCoSn (a) and the coordination environment of Nb and Sn (b).

PXRD patterns of Nb_{1-z}Sc_zCoSn (z = 0, 0.01, 0.03, 0.04, 0.05, 0.06, 0.07, 0.10) samples are shown in Figure 5.2 (a). The diffraction peaks of all the samples can be indexed to MgAgAs cubic crystal structure despite some minor Nb₃Sn impurity phases, indicating all samples possess the HH phase. As it is visible from Figure 5.2 (b), the unit cell parameter calculated via PowderCell [10] software increases with the increasing Sc content. Since the ionic radius of Sc³⁺ (0.87 Å) is larger than that of Nb⁵⁺ (0.74 Å) [11], the observed lattice expansion indicates that Nb⁵⁺ is substituted by Sc³⁺.



Figure 5.2 (a) PXRD patterns and (b) cell parameters of Nb_{1-z}Sc_zCoSn samples.

The microstructure of the Nb_{0.93}Sc_{0.07}CoSn sample was investigated and is shown in Figure 5.3. The phase purity and elemental distribution were further examined by SEM combined with EDX mapping. Figure 5.4 shows the secondary electron image and the EDX mapings of the polished Nb_{0.95}Sc_{0.05}CoSn

sample, which indicates no obvious phase segregation and uniform elemental distribution on this scale. Table 5.1 summarizes the actual chemical compositions of all prepared samples analyzed by EDX, and it shows that the EDX results are close to the nominal compositions.



Figure 5.3 Typical scanning electron microscopy image of Nb_{0.93}Sc_{0.07}CoSn sample.



Figure 5.4 The secondary electron image and the elemental distribution maps of $Nb_{0.95}Sc_{0.05}CoSn$.

Nominal	EDX results	Density (g/cm ³)
$Nb_{0.99}Sc_{0.01}CoSn$	$Nb_{0.98}Sc_{0.01}Co_{1.05}Sn_{0.96}$	8.49
$Nb_{0.97}Sc_{0.03}CoSn$	$Nb_{0.97}Sc_{0.03}Co_{1.06}Sn_{0.94}$	8.46
$Nb_{0.96}Sc_{0.04}CoSn$	$Nb_{0.98}Sc_{0.04}Co_{1.03}Sn_{0.95}$	8.03
$Nb_{0.95}Sc_{0.05}CoSn$	$Nb_{0.97}Sc_{0.045}Co_{1.03}Sn_{0.95}$	8.39
$Nb_{0.94}Sc_{0.06}CoSn$	$Nb_{0.94}Sc_{0.053}Co_{1.05}Sn_{0.95}$	8.00
Nb _{0.93} Sc _{0.07} CoSn	$Nb_{0.93}Sc_{0.067}Co_{1.05}Sn_{0.96}$	8.37
$Nb_{0.90}Sc_{0.10}CoSn$	$Nb_{0.95}Sc_{0.09}Co_{1.03}Sn_{0.94}$	8.27

Table 5.1 Nominal, EDX results, and measured densities of Nb_{1-z}Sc_zCoSn.

5.3.2 Electrical transport properties

Figure 5.5 shows the electrical transport properties of Nb_{1-z}Sc_zCoSn at different temperatures. For comparison, the literature data of Nb_{0.8}Zr_{0.2}CoSn [8] are also plotted (black line). As shown in Figure 5.4 (a), the electrical conductivity (σ) of unsubstituted NbCoSn compound decreases with the rise of the temperature, showing a metal-like conduction behavior. While, after substituting Sc at the Nb site, the σ gradually increases with increasing temperature, indicating a semiconduction behavior. Besides, with the Sc concentration up to 0.05, the σ significantly decreases from 5.0 × 10⁴ S/m (NbCoSn) to 0.07 × 10⁴ S/m (Nb_{0.95}Sc_{0.05}CoSn) at room temperature and then goes up to ~ 0.6 × 10⁴ S/m with further increasing Sc concentration to 0.1 (Nb_{0.9}Sc_{0.1}CoSn). In addition, the bandgap can be obtained from the slope of ln σ vs. 1000/T curve (shown in Figure 5.5 (b)) using the Arrhenius equation

$$\rho = \rho_0 \exp\left(E_{\rm g}/2k_{\rm B}T\right),\tag{5.1}$$

where ρ_0 is a constant. The calculated band gap values are 0.35 eV, 0.33 eV, 0.29 eV and 0.20 eV for *p*-type Nb_{0.95}Sc_{0.05}CoSn, Nb_{0.94}Sc_{0.06}CoSn, Nb_{0.93}Sc_{0.07}CoSn and Nb_{0.90}Sc_{0.10}CoSn respectively. For the Nb_{1-z}Sc_zCoSn compounds with *z* > 0.04, the slope of σ -*T* changes above 500 K, which can be explained by the impact of intrinsic conduction.



Figure 5.5 Temperature dependence of the electrical transport properties of Nb_{1-z}Sc_zCoSn (a) electrical conductivity (b) $\ln\sigma$ vs.1000/*T* plot.

To further understand the conduction mechanism, the Hall coefficient at room temperature was measured, and the calculated charge carrier concentration and mobility are presented in Figure 5.6 (a) and (b). The electron concentration $n_{\rm H}$ for NbCoSn is 17×10^{19} cm⁻³, which is on the same order of magnitude as compared to the value reported by R. He et al. (~ 24×10^{19} cm⁻³) [3]. Moreover, the $n_{\rm H}$ decreases remarkably with the Sc content reaching 0.04. For z = 0.05, holes become the dominant carriers, and the hole concentration $p_{\rm H}$ increases gradually from 0.8×10^{19} cm⁻³ to 3.7×10^{19} cm⁻³ with the Sc content increasing from 0.05 to 0.10. Therefore, Sc is obviously an effective hole (*p*-type) dopant since it generates an acceptor level near the top of the valence band, shifting the Fermi level toward the valence band and increasing the hole concentration. As for the carrier mobility $\mu_{\rm H}$, the trend is similar to that of carrier concentration. Therefore, the σ decreases obviously and then increases slightly with an increase of Sc content.



Figure 5.6 The carrier concentration and carrier mobility of $Nb_{1-z}Sc_zCoSn$ samples at room temperature for (a) *n*-type, (b) *p*-type.

The temperature dependence of the Seebeck coefficient (*S*) in Nb_{1-z}Sc_zCoSn is shown in Figure 5.7 (a). The value of *S* for unsubstituted NbCoSn is $-185 \,\mu$ V/K at room temperature, showing that NbCoSn is an *n*-type semiconductor. With Sc content increasing, the values of *S* for Nb_{1-z}Sc_zCoSn change gradually from negative to positive with the increase of Sc content, which matches very well with the Hall measurements. The peak value of *S* reaches ~ 306 μ V/K at 850 K for the Nb_{0.95}Sc_{0.05}CoSn sample, which is much higher than that of Nb_{0.8}Zr_{0.2}CoSn (150 μ V/K). The single parabolic band (SPB) model is usually used to analyze the transport properties of half-Heusler compounds [12]. Assuming electron conduction occurs within an SPB, the Seebeck coefficient of a non-degenerate semiconductor is related to the effective mass *m**, carrier concentration *p*_H, and scattering parameter λ via

$$S = \frac{k_B}{e} \left\{ 2 + \lambda + ln \left[\frac{2(2\pi m k_B T / h^2)^{3/2}}{\rho_H} \right] \right\},$$
 (5.2)

where *e* is the elementary charge and *h* is the Planck constant [13]. For the NbCoSn compound, we assume that acoustic phonon scattering is the predominant scattering mechanism, thus $\lambda = 0$. According to the measured *S* and *p*_H, the *m*^{*} = 0.11 *m*_e is obtained. With the *m*^{*} = 0.11 *m*_e and equation (5.2), we can plot *S* at 300 K as a function of *p*_H, a plot well-known as a 'Pisarenko relation'. As shown in Figure 5.7 (b), the red line is the calculated Pisarenko plot, and the blue dots represent the measured data of Nb_{1-z}Sc_zCoSn compounds. Most of the data lie on the calculated line, except for that of the Nb_{0.93}Sc_{0.07}CoSn compound. The reason for such an exception is not clear yet. It is suspected that the second phase or/and the deviation of the composition may be responsible for such an exception.

Accordingly, the power factor (PF) was calculated via $PF = S^2\sigma$ and is shown in Figure 5.8. The highest PF of 0.54 mW/mK² is achieved for the Nb_{0.95}Sc_{0.05}CoSn compound mainly due to its high *S*, which is three times higher than that of *p*-type Nb_{0.8}Zr_{0.2}CoSn (0.125 mW/mK²) [8]. However, the PF of Nb_{0.95}Sc_{0.05}CoSn is still much lower than the state-of-the-art *p*-type HH compounds, such as (Ti,Hf)Co(Sb,Sn) [5] and NbFeSb [14]. Therefore, much more effort must be devoted to optimizing the carrier concentration of *p*-type NbCoSn compounds.



Figure 5.7 Temperature dependence of the Seebeck coefficient (a) and the Seebeck coefficient versus the carrier concentration(p-type) (b) of Nb_{1-z}Sc_zCoSn samples.



Figure 5.8 Temperature dependence of the power factor of Nb_{1-z}Sc_zCoSn samples.

5.3.3 Thermal transport properties

The temperature dependence of total thermal conductivity (κ) and lattice thermal conductivity (κ_L) are displayed in Figure 5.9. The κ_c is calculated using the Wiedemann-Franz law: $\kappa_c = L\sigma T$, where *L* is Lorenz number estimated by Fermi integral and the values are presented in Figure 5.10. The κ_L is derived from the value subtracting the carrier component κ_c from the total thermal conductivity. Because of the low electrical conductivity, the calculated κ_c is much lower than κ_L . In other words, for Nb_{1-z}Sc_zCoSn compounds $\kappa_L \approx \kappa$. As shown in Figure 5.9 (b), the κ_L of unsubstituted NbCoSn is ~ 10.8 W/mK at room temperature, which is similar as compared to the result reported by D. A. Ferluccio et al. [8]. After

substituting Sc, the room temperature κ_L decreases dramatically to 4.2 W/mK for Nb_{0.9}Sc_{0.1}CoSn, where a reduction of 60 % is achieved after Sc substitution. Such a significant reduction mainly ascribes to the point defect scattering due to the substantial atomic mass difference (mass fluctuation) and interatomic coupling force differences (strain field fluctuation) between Nb and Sc, thereby giving rise to the reduction of κ_L , especially at room temperature.



Figure 5.9 The temperature dependence of total thermal conductivity κ (a) and lattice thermal conductivity κ_L (b) for Nb_{1-z}Sc_zCoSn samples.



Figure 5.10 The values of Lorenz number for Nb_{1-z}Sc_zCoSn samples.

To explain the reduction of κ_L in terms of the phonon scattering mechanisms, the lattice thermal conductivity of Nb_{1-z}Sc_zCoSn can be evaluated via the Debye-Callaway model [15]:

$$k_{L} = \frac{k_{B}}{2\pi^{2}v_{s}} \left(\frac{2\pi k_{B}T}{h}\right)^{3} \int_{0}^{\theta_{D}/T} \tau_{C} \frac{x^{4}e^{x}}{\left(e^{x}-1\right)^{2}} dx, \qquad (5.3)$$

where *x* is the reduced frequency ($x = h\omega/2\pi k_B T$, ω is the phonon angular frequency), v_s is the sound speed, *h* is the Planck constant, θ_D is the Debye temperature, and τ_C is the combined phonon relaxation time. The literature data [8] of $\theta_D = 361$ K and $v_s = 3141$ m/s for NbCoSn are used in Nb_{1-z}Sc_zCoSn compounds as a reliable approximation. We assume all phonon scattering processes, including point-defect scattering, boundary scattering, Umklapp scattering, and phonon-free-electron scattering can occur in parallel. Thus, according to Matthiessen's rule, the τ_C can be formulated by

$$\tau_C^{-1} = \tau_{PD}^{-1} + \tau_B^{-1} + \tau_U^{-1} + \tau_{pe}^{-1},$$
(5.4)

where τ_{PD} , τ_B , τ_U , and τ_{pe} are phonon-point-defect scattering, phonon-boundary scattering, phononphonon Umklapp scattering, and phonon-free electron scattering relaxation times, respectively. The τ_{PD} can be obtained through:

$$\tau_{PD}^{-1} = \tau_{S}^{-1} + \tau_{M}^{-1} = \frac{V\omega^{4}}{4\pi v_{s}^{3}} (\Gamma_{S} + \Gamma_{M}), \qquad (5.5)$$

where τ_s and τ_M are relaxation times of the phonon point-defect scattering processes due to strain and mass field fluctuations, V is the volume per atom, Γ_s and Γ_M are the disorder scattering parameters due to strain and mass field fluctuations [16]. The experimental disorder scattering parameters ($\Gamma_{expt.} = \Gamma_s + \Gamma_M$) can be obtained by

$$\Gamma_{exp} = \frac{hv_s^2 u^2}{\pi^2 \theta_D V} \times \frac{1}{k_{L0}^p}, \text{ and } \frac{k_{L0}}{k_{L0}^p} = \frac{\tan^{-1}(u)}{u},$$
(5.6)

where *u* is the disorder scattering parameter, k_{L0} is the lattice thermal conductivity of the crystal with the disorder, and k_{L0}^{P} is the lattice thermal conductivity of the crystal without disorder [17]. The disorder scattering parameters of Nb_{1-z}Sc_zCoSn compounds calculated according to Equation (5.6) are listed in Table 5.2.

Composition	$\kappa_{\rm L}({\rm W/mK})$	и	Γ_{expt}
NbCoSn	10.8		
$Nb_{0.99}Sc_{0.01}CoSn$	8.4	1.03	0.0025(4)
$Nb_{0.97}Sc_{0.03}CoSn$	7.2	1.44	0.0049(8)
$Nb_{0.96}Sc_{0.04}CoSn$	6.8	1.61	0.0062(7)
$Nb_{0.95}Sc_{0.05}CoSn$	6.1	1.93	0.0089(8)
$Nb_{0.94}Sc_{0.06}CoSn$	5.0	2.59	0.016(1)
$Nb_{0.93}Sc_{0.07}CoSn$	4.6	2.88	0.019(9)
$Nb_{0.90}Sc_{0.10}CoSn$	4.2	3.27	0.025(6)

Table 5.2 The lattice thermal conductivity κ_L , disorder scaling parameter u, disorder scattering parameters Γ_{expt} .

For the phonon-boundary scattering, τ_B is independent of temperature and phonon frequency, and it can be described as $\tau_B^{-1} = v_s / d_g$, where d_g is the grain size of the bulk sample. For the Umklapp scattering, τ_U is dependent on temperature and phonon frequency and can be described as [18]

$$\tau_U^{-1} \approx \frac{h\gamma^2}{2\pi M v_s^2 \theta_D} \omega^2 \Gamma \exp(-\theta_D / 3T), \qquad (5.7)$$

where γ is the Grüneisen constant and *M* is the average atomic mass of the crystal. For the phonon-free electron scattering process [19], in the case of high carrier concentration τ_{pe} can be described as

$$\tau_{pe}^{-1} = \frac{4\pi^2 E_{def}^2 m^{*2} \omega}{h^3 d_s v_l} , \qquad (5.8)$$

where E_{def} is the deformation potential, d_s is the sample's density, and v_l is the longitudinal sound velocity. With the reference values of physics parameters (Table 5.3), the lattice thermal conductivity of Nb_{1-z}Sc_zCoSn can be calculated by Equation (5.3), and the results are presented in Figure 5.11. In the calculation, we assume that Sc substitution does not significantly affect the basic physical parameters, such as θ_D , γ , E_{def} and v_s , so the major variable parameter is Γ_{expt} . In such a case, Sc substitution mainly alters the τ_{PD} . Generally, the calculated κ_L matches with the experimental values, implying that calculations based on the Callaway-Debye model can give a rough prediction to the κ_L of the NbCoSn system. In short, at room temperature, the reduction of κ_L in Nb_{1-z}Sc_zCoSn compounds is mainly because of the Sc substitution inducing strong point defect phonon scattering.

Parameters	Value	References
$ heta_{ m D}$	361 K	[1]
\mathcal{V}_{S}	3141 m/s	[1]
γ	1.2	*
E_{def}	4.47	[2]
$m_{\rm d}^{*}$	3.4	**
\mathcal{V}_l	4956 m/s	*
d_{g}	$100-500 \mu\mathrm{m}$	Figure 5.3

Table 5.3 Physics parameters values: Debye temperature θ_D , sound velocity v_s , Grüneisen parameter γ , deformation potential E_{def} , density of state effective mass m_d^* , longitudinal sound velocity v_l and grain size d_g for transport properties calculation.



Figure 5.11 Comparison of experimental and calculated lattice thermal conductivities at 300 K for Nb_{1-z}Sc_zCoSn compounds.

5.3.4 Figure of merit

Figure 5.12 shows the dimensionless figure of merit *ZT* of *p*-type samples. Due to the dramatic enhancement of power factor, and the significant suppression of thermal conductivity, the highest *ZT* of *p*-type Nb_{0.95}Sc_{0.05}CoSn reached 0.13 at 879 K. It is much higher than that of Nb_{0.8}Zr_{0.2}CoSn [8], indicating Sc is an efficient *p*-type dopant for NbCoSn as compared to Zr.



Figure 5.12 The figure of merit ZT for p-type NbCoSn and Nb_{0.8}Zr_{0.2}CoSn.

5.4 Conclusions

In this work, homogenous Nb_{1-z}Sc_zCoSn compounds were prepared by an arc melting process followed by an annealing treatment. The *p*-type NbCoSn compounds were obtained by substituting iso-electronic Sc at the Nb site, and the effects on the electrical and thermal properties were investigated. Generally, the substitution of Sc at the Nb site can change the *n*-type NbCoSn to a *p*-type semiconductor by adjusting the Fermi level, indicating Sc is an appropriate *p*-type dopant. With the reduction in thermal conductivity, the *ZT* value is improved to 0.13 at 879 K in the *p*-type Nb_{0.95}Sc_{0.05}CoSn sample, which is roughly 5 times higher than that of *p*-type Nb_{0.8}Zr_{0.2}CoSn.

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Chapter 6 Thermoelectric properties investigation in ZrNiSn with Cu introduction

This work presented here is in preparation for publication.

Abstract

The interstitial defects intrinsically exist in many half-Heusler compounds synthesized by arc melting, such as ZrNiSn and TiNiSn, TaCoSn, etc, leading to slight deviations from the stoichiometric compositions. Interestingly, this interstitial defect can synergistically optimize the electrical and thermal transport properties, which has attracted growing attention nowadays. In this chapter, Cu is introduced into the ZrNiSn compound, aiming to increase the interstitial defects since Cu has similar elemental properties to Ni. We systematically investigated and analyzed the correlations between the crystal structure, microstructure, and thermoelectric properties by combining experiments and DFT-based computations. The results reveal that some Ni/Cu atoms occupied the interstitial 4d position in the arcmelted samples, reducing the bandgap and thus increasing the carrier concentration. In the samples with high Cu content, the full-Heusler phase is precipitated in the half-Heusler matrix. Due to the interfaces induced by the precipitations, the thermal conductivity is suppressed. As a result, a higher *ZT* value is achieved (~ 1.1 at 950 K) in the ZrNiCu_{0.05}Sn sample. This work analyses the possibility of interstitial defects from the energy point of view and highlights the importance of these defects to tune the thermoelectric properties in HH compounds positively.

6.1 Introduction

As studied in Chapter 4, the excessive Co intrinsically exists in the arc-melted NbCoSn-based compounds, behaving as the Y-off-stoichiometry in actual composition XYZ, which has important impacts on the crystal structure and the microstructure and provide a new point of view to understand the TE properties in HH compounds [1]. Notably, the Y-off-stoichiometry emerges not only in NbCoSn-based HH compounds but also in many other HH compounds, such as ZrNiSn [2], TiNiSn [3], and TaCoSn [4], etc. However, this phenomenon has not been noticed for a long time. Until recent years, due to the simultaneous investigation from experiments (neutron, TEM, XPS) to the band structure calculations, this Y-off-stoichiometry phenomenon is gradually emphasized and clearly explained, known as interstitial defects [5-7]. At the beginning, it was proposed that Zr/Sn and Ni/vacancy antisite defects lead to the reduction of the bandgap and the enhancement of electrical conductivity in synthesized ZrNiSn compounds [8-11]. Then, the high-resolution synchrotron radiation powder X-ray diffraction (SR-PXRD) was employed to investigate the atomic disorders in the ZrNiSn compound [12]. It was found that Zr/Sn antisite defects were not likely to present in the crystal structure, instead, some interstitial Ni atoms presented in the lattice, partly occupying 4d (3/4, 3/4, 3/4) positions which are empty in ordered ZrNiSn (crystal structure shown in Figure 6.1). As a result, the actual composition becomes $ZrNi_{1+x}Sn$. These interstitial Ni atoms form in-gap states between the conduction band and the valence band, leading to a shrinkage in the observable bandgap [13]. At the same time, H. Hazama et al. observed the in-gap states in the density of state (DOS) of TiNiSn compound by XPS, obtaining a bandgap of 0.12 eV which is much smaller than the calculated value of 0.4 eV [14]. Afterward, the interstitial defects attract more attention and are investigated further in ZrNiSn and TiNiSn systems. X. Li et al. studied how much interstitial Ni exists in the ZrNiSn system through different annealing treatments according to the phase diagram [15]. The more accurate amounts of interstitial defects were determined in $TiNiM_{y}Sn$ (M = Co, Ni, Cu) compounds by refinements of neutron powder diffraction data, and the microstructure and the TE properties of $TiNiM_vSn$ were investigated as well [16]. Furthermore, the TE performance of TiNiSn and ZrNiSn was improved by introducing excess Cu or Ni [17,14], where it is believed that the improvement in ZT is mainly ascribed to the reduction of thermal conductivity due to the interstitial disorders. However, they did not specifically explain how the interstitial defects influence the band structure and electrical transport properties. Therefore, it is meaningful to systematically investigate the impact of interstitial defects on the crystal structure, band structure, the TE transport properties.



Figure 6.1 The crystal structure of (a) ZrNiSn and (b) ZrNiSn with interstitial Ni.

In this chapter, the ZrNiSn HH compound is chosen as our starting compound, and extra Cu is introduced to form the Zr(NiCu_x)Sn compounds. With XRD refinements and DFT calculations, the phase composition, microstructure, and thermoelectric properties of Zr(NiCu_x)Sn are investigated. It is noted that the amounts of the interstitial Ni/Cu defects play an important role to the transport properties. This work highlights a profound impact of interstitial defects on the transport properties in half-Heusler ZrNiSn compounds, providing a basis for further understanding the functions of interstitial defects in HH compounds.

6.2 Experimental

Stoichiometric amounts of Zr (granules, 99.8 %), Ni (wire, 99.99 %), Cu (turnings, 99.9 %), Sn (shot, 99.99 %) with nominal compositions of ZrNiCu_xSn (x = 0, 0.01, 0.03, 0.05, 0.07, 0.09, 0.125, 0.15, 0.20) were weighted and loaded in a water-cooled arc-melter with Cu crucible to prepare each sample (around 8.5 g). Each ingot was flipped and melted several times under argon atmosphere to guarantee homogenization. Subsequently, the ingots were crushed and ground using a planetary ball mill (Retsch PM100) for 30 min, after which the obtained powders were loaded in a graphite die and sintered using spark plasma sintering (SPS) equipment at 1173 K for 3 min under a pressure of 50 MPa to obtain densified disc-shaped samples. The sintered samples were sealed into evacuated quartz tubes and annealed at 973 K for seven days to remove the residual impurities. Then, the obtained samples were used to characterize structure and transport properties.

The powder X-ray diffraction (PXRD) patterns of all samples were collected using a diffractometer (STOE STADI MP) with Mo- $K\alpha_1$ radiation. The room temperature neutron powder diffraction (NPD) data were performed on the D2B beamline of the Institut Laue-Langevin (ILL) in Grenoble, France (transmission geometry with a wavelength of 1.594 Å). Fine powder samples around 5 g were loaded in

Indium-sealed 7.5 mm Vanadium cans, which were proceeded in a glove box with Ar atmosphere. The Rietveld refinement analysis for the diffraction patterns (PXRD and NPD) was undertaken using the Fullprof program. Microstructural analysis was performed using high-resolution scanning electron microscopy (HR-SEM) system (Philips, Eindhoven, Netherlands). The phase compositional analysis was carried out on another scanning electron microscopy (SEM, TESCAN, VEGA 3) with energy-dispersive X-ray spectroscopy (EDX, AMETEX). Atomic Probe Tomography (APT) was employed to carry out further microstructural analysis in our samples. The needle-sharped specimens were prepared by dual-beam SEM/FIB instrument (Helios Nanolab 600i). LEAP 5000XR instrument was operated in voltage/laser pulse mode at 50 K with a frequency of 200 kHz. Afterward, the data were reconstructed using Cameca IVAS 3.8.4 software tool. The thermal conductivity κ was calculated by the equation, $\kappa = DC_p d_s$, where D is the thermal diffusivity measured by laser flash apparatus (LFA 457, NETZSCH, Germany), C_p is specific heat calculated by the Dulong-Petit law, and d_s is the sample's density measured by an Archimedes' kit. High-temperature electrical conductivity σ and Seebeck coefficient S were performed on ZEM-3 equipment (Ulvac-Riko, Japan). The temperature dependence of charge carrier concentration $n_{\rm H}$ and mobility $\mu_{\rm H}$ were measured using the commercial Hall measurement system (Fraunhofer IPM, HT-Hall, Germany) under a magnetic field from - 520 to 520 mT. The uncertainties in the transport measurements are 10 % on κ , 5 % on S, and 3 % on σ .

Total energy and band structure calculations were performed in the framework of DFT as implemented in the Exact Muffin-Tin Orbitals (EMTO) method [18,19]. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional in the generalized gradient approximation (GGA) was adopted. [20]. The chemical disorder structure induced by Cu introduction was simulated using the Coherent Potential Approximation (CPA) [21-23]. The application of CPA enables us to readily obtain the band structures of ZrNiSn with interstitials using the primitive unit cell. The full charge density (FCD) technique is implemented for accurate total energy calculations [24]. The *s*, *p*, *d*, *f* orbitals are included in the EMTO basis. The one-electron equations were solved within the scalar relativistic approximation and the soft-core scheme [25]. For total energy and band structure calculations, the total numbers of k-points in the irreducible Brillouin zone were 3009 and 6689, respectively.

6.3 Results and discussions

6.3.1 Phase and microstructure characterization

The XRD patterns of synthesized ZrNiCu_xSn (x = 0, 0.01, 0.03, 0.05, 0.07, 0.09, 0.125, 0.15, and 0.20) samples (hereafter named Cu-*x* for simplicity) are shown in Figure 6.2 (a). The reflections in all the samples are well indexed with cubic MgAgAs-type half-Heusler structure (space group: 216, $F\overline{4}3m$) as the majority phase. When $x \ge 0.125$, the FH phase is observed as the secondary phase. The refinements were carried out by *Fullprof* software and the results are summarized in Table 6.1. The lattice parameters and the fractional occupancy on 4d position with Cu content were plotted, shown in Figure 6.2 (b). The calculated lattice constant for the ZrNiSn pristine sample is 6.1060(2) Å. With increasing Cu content, the lattice constant of HH increases (Cu < 0.09) and then decreases slightly (Cu > 0.09). Interestingly, the variation in lattice parameter is similar to that of the occupancy fractions on 4d position in our samples. Therefore, it is reasonable to consider that the variation in lattice parameters might be related to the amounts of the interstitial atoms. Specifically, with the lower concentration of Cu, most of the Cu atoms occupy the vacant interstitial 4d position, expanding the lattice; with the increasing of Cu, the FH phase is gradually formed, leading to the decrease of the occupation content on 4d position in the HH matrix, thereby shrinking the lattice. This trend of lattice constant in Cu-*x* samples is similar to that reported in TiNiSn compounds with Cu introduction [26]. It has to be mentioned here that since the refinements are based on the lab XRD data, the errors of the results are relatively large (large χ^2 , shown in Table 6.1), but the lattice parameters, 4d position occupation, and the σ at room temperature (Figure 6.11 (b)) show the similar trend, which can explain the correlations between them.



Figure 6.2 (a) XRD patterns and (b) lattice constant and fractional occupancy on 4d of Cu-x samples.

sample	a (Å)	<i>n</i> (4d)	$B_{\rm iso, overall}$ (Å ²)	χ^2
0	6.1060(2)	0*	0.13(4)	62.9
0.01	6.10631(3)	0.01*	0.40(3)	60.0
0.03	6.10857(3)	0.03*	0.40(3)	61.9
0.05	6.11026(3)	0.043(5)	0.31(3)	87.7
0.07	6.11317(3)	0.046(5)	0.25(3)	70.3
0.09	6.12055(3)	0.053(5)	0.46(4)	70.0
0.125	6.11782(4)	0.055(5)	0.44(4)	37.0
0.15	6.11318(3)	0.053(5)	0.29(3)	56.6
0.20	6.11055(3)	0.041(5)	0.59(4)	47.5

Table 6.1 Lattice parameters *a*, isotropic overall thermal displacement factors $B_{iso, overall}$, fractional occupancy on 4*d* position, and goodness-of-fit χ^2 for Cu-*x* samples (refinements based on lab XRD data).

* parameter was fixed during refinements.

To further confirm that the interstitial Ni exists in our pristine ZrNiSn sample, the powder neutron diffraction (ND) data were collected. The refined patterns and the corresponding refinement results are shown in Figure 6.3 and Table 6.2, respectively. For comparison, two models are used to apply the refinements: one is to use the ideal HH structure (Figure 6.3 (a)), another one is to allow the partial occupation of Ni on the 4d site (Figure 6.3 (b)). Apparently, the differences between the experimental and the calculated data are narrowed in Figure 6.3 (b) compared to that in Figure 6.3 (a), especially for the reflections around 25°, 42°, and 78°. Moreover, it is noted from Table 6.2 that the R factors (R_p , R_{wp} , and R_{Bragg}) and the goodness-of-fit (χ^2) obtained from free refinements are smaller than that using the ideal HH structure. These observations indicate that the model with the partial occupation of Ni on the 4d site is close to the situation in our ZrNiSn sample. According to the refinement results, the actual composition of ZrNiSn is ZrNi1.036(5)Sn, around 3.8 % Ni occupying the 4d position, which is consistent with the previous studies [12,16,27,28]. The microstructures of all Cu-x samples were investigated by SEM, presented in Figure 6.4. The grain sizes for all samples are not homogeneous (roughly $< 20 \ \mu m$). In the Cu-0 sample, there are a lot of congregated small particles, but with increasing Cu content the amount of these particles gradually decreases. The possible explanation for such phenomenon is that Cu might be a metallic additive, which is helpful for bulk sintering [29].



Figure 6.3 The neutron diffraction pattern of ZrNiSn sample refined (a) using ideal HH structure and (b) allowing partial occupation of 4d positions by Ni.

Table 6.2 Structural data from Rietveld refinements for the ZrNiSn sample. In ZrNiSn, zirconium is located at Wyckoff site 4a, tin at 4b, and nickel on 4c (and 4d). Parameters fixed during the refinements are marked by *.

parameter	Ideal ZrNiSn	Free refinements of ZrNiSn
Space group		F43m
<i>a</i> (Å)	6.11479(5)	6.11480(4)
$B_{\rm iso,overall}$ (Å ²)	0.266(9)	0.308(8)
$P(\mathrm{Zr})$	1*	1*
P(Sn)	1*	1*
P(Ni-4c)	1*	0.998(1)
P(Ni-4d)	0*	0.038(4)
$R_p(\%)$	3.99	3.38
$R_{wp}(\%)$	5.01	4.22
$R_{Bragg}(\%)$	5.17	3.30
χ^2	22.2	15.7



Figure 6.4 Microstructure of Cu-*x* samples after SPS.

Figure 6.5 shows BSE images and the corresponding EDX mappings of Cu-0.05, Cu-0.09, and Cu-0.20 samples. As we can see, there are some Ni-Sn and Cu-Sn secondary phases in the Cu-0.05 sample, which cannot be observed in XRD patterns due to the detection limit. But these phases disappeared in samples with a high amount of Cu. Besides, Zr-rich impurities exist in all samples. The actual compositions of all samples are analyzed by EDX, shown in Table 6.3. It is noted that when $Cu \le 0.09$, the main phase is still HH phase, while when Cu > 0.09, phase II is precipitated in the main HH phase, and the actual compositions are close to the FH phase which has been observed from the XRD patterns. According to the XRD and ND refinement results, it is expected that some 4d positions are also occupied by Ni/Cu atoms in our samples, leading to the interstitial Ni/Cu defects. To verify this interpretation, a high-resolution STEM-HAADF measurement is employed to observe the atomic-scale microstructure for the Cu-0.05 sample, and the results are shown in Figure 6.6. It is not clear that some 4d sites are occupied and some are not occupied from this TEM image due to the unideal direction. But the image should be similar to what was reported in $Zr_{0.43}Hf_{0.57}NiSn$ by K. Gałązka et al. [30] if it is viewed from the (110) direction. Due to the similar elemental number of Ni (Z = 28) and Cu (Z = 29), they cannot be distinguished by the XRD refinements and even STEM-HAADF measurements. To figure out where is Cu and how much Cu is on the 4d position from experiments, it would be helpful to carry out the neutron diffraction and the APT measurements for samples with Cu introduction [16,30].

However, due to the time limitation, we have not yet obtained enough neutron diffraction data for Cu-x samples to do further analysis.



Figure 6.5 BSE images and the corresponding EDX mappings of (a) Cu-0.05, (b) Cu-0.09, and (c) Cu-0.20 samples.

samples	actual phase composition	d_s (g/cm ³)
Cu-0	$Zr_{0.90}Ni_{1.10}Sn_{0.99}$ (I)	7.67
Cu-0.01	$Zr_{0.90}Ni_{1.12}Cu_{0.01}Sn_{0.98}$ (I)	7.82
Cu-0.03	$Zr_{0.91}Ni_{1.13}Cu_{0.03}Sn_{0.99}$ (I)	7.82
Cu-0.05	$Zr_{0.94}Ni_{1.12}Cu_{0.04}Sn_{0.99}$ (I)	7.83
Cu-0.07	$Zr_{0.93}Ni_{1.13}Cu_{0.05}Sn_{0.99}$ (I)	7.83
Cu-0.09	$Zr_{0.93}Ni_{1.14}Cu_{0.08}Sn_{1.00}(I)$	7.9
Cu-0.125	$\begin{array}{l} Zr_{0.92}Ni_{1.14}Cu_{0.08}Sn_{1.01} \ (I) \\ Zr_{0.84}Ni_{0.99}Cu_{0.36}Sn_{0.92} \ (II) \end{array}$	7.71
Cu-0.15	$\frac{Zr_{0.93}Ni_{1.12}Cu_{0.12}Sn_{1.00}}{Zr_{0.85}Ni_{1.08}Cu_{0.29}Sn_{0.94}}$ (II)	7.86
Cu-0.20	$\frac{Zr_{0.94}Ni_{1.11}Cu_{0.11}Sn_{1.02}(I)}{Zr_{0.83}Ni_{1.40}Cu_{0.14}Sn_{0.85}(II)}$	7.79

Table 6.3 Actual phase compositions and samples' density d_s of Cu-x samples.


Figure 6.6 High-resolution STEM-HAADF image of Cu-0.05 sample.

APT measurements were carried out on the Cu-0.05 sample. Since the grain boundaries are not clear from the SEM, five small specimens were randomly cut (named SP13-1, SP13-2, SP13-3, SP13-4, and SP13-5) from the Cu-0.05 sample by FIB and the detected images are shown in Figure 6.7. It seems that the SP13-1 and SP13-3 belong to different grains, but the SP13-2, SP13-4, and SP13-5 are similar and might be from the same grain, which means that these five specimens include at least three different grains. The specimens SP13-1 and SP13-3 were analyzed in voltage-pulsed mode, and the specimens SP13-2, SP13-4, and SP13-5 were analyzed in laser-pulsed mode. The actual composition analyzed by APT is summarized in Table 6.4, and the corresponding histograms are plotted (Figure 6.8). Clearly, in SP13-1 and SP13-3 specimens, the composition of Zr and Sn is slightly less than the nominal composition, while the composition of Ni is more than the nominal composition. Whereas, in SP13-2, SP13-4, and SP13-5 specimens, the composition of Zr and Sn is more than the nominal composition, but the composition of Ni is less than the nominal composition. This difference might result from the different running modes. While, the compositions of Cu in all these specimens are much lower than the nominal composition except for the SP13-3 specimen, indicating the inhomogeneous distribution of Cu in our samples on nanoscale. Figure 6.9 shows the reconstructed atom maps of the SP13-5 specimen. It seems that all the elements are distributed homogeneously. Combining the results of SEM and APT, it reveals that our sample is ordered in the long-range (microscale) but disordered in the short-range (nanoscale).



Figure 6.7 The detected images of the five specimens from APT for the Cu-0.05 sample.

ZrNiCu _{0.05} Sn	Cu	Zr	Ni	Sn	Note
Nom.	1.64%	32.79%	32.79%	32.79%	-
SP13-1	0.29%	31.67%	35.52%	32.46%	Voltage
SP13-2	0.43%	33.28%	29.99%	36.20%	Laser
SP13-3	1.77%	31.86%	33.65%	32.67%	Voltage
SP13-4	0.85%	33.48%	28.00%	37.53%	Laser
SP13-5	1.07%	32.62%	31.56%	34.69%	Laser

Table 6.4 Analyzed composition (atomic ratio) of Cu-0.05 sample by the APT.



Figure 6.8 Compositions of (a) Zr, (b) Ni, (c) Sn, and (d) Cu for different areas of Cu-0.05 sample compared to the nominal compositions.



Figure 6.9 The atom maps of SP13-5 specimen run in voltage.

To gain insights into the interstitial Cu occupation and the phase stability, the formation energy of $ZrNiCu_xSn$ ($0 \le x \le 1$, Cu is fixed on 4d position) is further investigated by the DFT method using CPA embedded in EMTO, and the results are shown in Figure 6.10. It displays that the formation energy increases gradually with increasing Cu content, but all the values are still negative, indicating the interstitial Cu in the ZrNiSn-based systems are thermodynamically stable. This is the reason that the FH phase can be formed in the HH matrix, which is observed in XRD patterns and EDX mappings of ZrNiSn samples with high Cu content. Combined with the EMTO results, it is concluded that the microstructure of ZrNiSn can be tailored by interstitial Cu defects.



Figure 6.10 The formation energy of ZrNiCu_xSn (Cu atoms occupy the 4d position). Here, Em denotes empty positions.

6.3.2 Electrical transport properties

The electrical conductivity σ , Hall electron concentration $n_{\rm H}$ and Hall mobility $\mu_{\rm H}$ are presented in Figure 6.11. The σ of the pristine sample increases with temperature, indicating a semiconductor behavior, and it is consistent with the reported trend of σ for undoped ZrNiSn [12,31]. And with the excess Cu introduction, this trend gradually changes to decrease with temperature, resulting in a transition from a non-degenerate semiconductor to a degenerate semiconductor. Notably, at 310 K σ increases significantly from 0.96×10^4 S/m (Cu-0 sample) to 31.06×10^4 S/m (Cu-0.07 sample) and then decreases slightly with increasing Cu content. For comparison, the σ of ZrNi_{0.96}Cu_{0.04}Sn reported by S. Katsuyama et al. [32] is plotted as well. It shows that the σ for ZrNi_{0.96}Cu_{0.04}Sn is even lower than our ZrNiCu_{0.03}Sn sample, indicating that excessive Cu is more effective for σ than substituted Cu. The measured carrier concentration of Cu-x samples at room temperature is shown in Figure 6.11 (b). The electron concentration $n_{\rm H}$ of the pristine sample is ~ 4 × 10¹⁹ cm⁻³, which is comparable to the reported value $(5 \times 10^{19} \text{ cm}^{-3})$ by H. Xie et al. [33]. And $n_{\rm H}$ dramatically increases to $9.1 \times 10^{20} \text{ cm}^{-3}$ in the Cu-0.07 sample without degradation of $\mu_{\rm H}$ (Figure 6.11 (d)) and then decreases slightly to 6.03×10^{19} cm⁻³ with Cu content. Interestingly, this trend roughly follows the variation of the fractional occupancy on the 4d position, which might be related to the fractional occupancy of the 4d position (verified below with band structure calculations). It is noted as well that the $n_{\rm H}$ of Cu-x samples is higher than that of Ni-excessive ZrNiSn materials [31] due to the two effects of excessive Cu introduction in ZrNiSn: (1) Cu substitutes on the 4c Ni position, generating one more electron to the lattice; (2) Cu partially occupies the 4d position, forming the in-gap states and improving $n_{\rm H}$. However, once the FH phase is formed in the HH matrix, the interstitial Cu concentration decreases, which is the reason that $n_{\rm H}$ decreases after 9 % Cu. The temperature dependence of $n_{\rm H}$ and $\mu_{\rm H}$ were measured as well and are presented in Figure 6.11 (c) and (d). The $n_{\rm H}$ of all samples increases with temperature, which might originate from the gradually increased amounts of interstitials with temperature. With increasing Cu, the increase in $n_{\rm H}$ with temperature is gradually expanded, resulting from the increasing number of the impurity states after Cu introduction. The $\mu_{\rm H}$ of all samples exhibits an alloy scattering dominated charge transport mechanism, roughly following $T^{0.5}$ at the temperature below 650 K. At higher temperature, the $\mu_{\rm H}$ of all samples follows a temperature dependence of $\mu_{\rm H} \sim T^{1.5}$, revealing an acoustic phonon scattering dominated carrier scattering mechanism.



Figure 6.11 Temperature dependence of (a) electrical conductivity σ , (c) carrier concentration $n_{\rm H}$, (d) Hall mobility $\mu_{\rm H}$ and (b) room temperature charge carrier concentration and Hall mobility for Cu-*x* samples.

As it is known that some 4d positions are partially occupied by Ni/Cu atoms in the synthesized samples as well as the carrier concentration and the fractional occupancy on 4d position have a similar variation trend, it is reasonable to consider that the interstitial atoms could be the reason for the large improvement in $n_{\rm H}$ and further the σ . Since previous studies have demonstrated that the excess Ni can generate in-gap states, making the observable bandgap much smaller than the real one and providing more electrons [34], we wonder if Cu would have the same effect on the band structures. To further verify the speculation, the band structures of ZrNiSn and that with 25 %, 50 %, and 75 % excessive Cu on the 4d position were calculated and are displayed in Figure 6.12. Obviously, ZrNiSn shows a semiconducting behavior with an indirect bandgap of ~ 0.5 eV from the X point of conduction band minima (CBM) to the G point of valence band maxima (VBM), which matches the previously calculated values [35-37]. With Cu introduction on 4d position, the VBM gradually moves close to the CBM, indicating the reduction of the bandgap and the increased electron concentration. Clearly, there is no formed in-gap states with excessive Cu in the ZrNiSn compound, which is different to the excessive Ni. The reason for that could be the different electron configurations of Cu and Ni atoms.



Figure 6.12 Band structures of (a) ZrNiSn, (b) ZrNiCu_{0.25}Sn, (c) ZrNiCu_{0.50}Sn and (d) ZrNiCu_{0.75}Sn.

The variation of Seebeck coefficient *S* with temperature is shown in Figure 6.13 (a). The negative values of *S* indicate *n*-type semiconductors. For the pristine sample, the absolute *S* shows a maximum value at around 600 K. This maximum value gradually shifted to high temperatures with increasing Cu concentration (for example, T = 750 K for Cu-0.01 sample). Finally, the *S* becomes monotonous increase with temperature at higher Cu concentration. Generally, due to the contribution of minority carriers (bipolar conduction) at high temperatures, the absolute value of the Seebeck coefficient reaches a maximum at a certain temperature [38]. Thus, in Cu-*x* samples, a shifted peak position of *S* to high temperatures reveals that the contribution of minority carriers is suppressed after Cu introduction, thereby increasing the application temperature of ZrNiSn-based compounds. Additionally, with increasing Cu content an obvious decrease is observed in the absolute *S* at room temperature and then a slight increase, which can be understood in terms of the opposite correlation of *S* with $n_{\rm H}$ ($S \propto n_{\rm H}^{-2/3}$) [39]. It is important to analyze the experimental transport data using the Boltzmann equation within relaxation time approximation. With an assumption of a single parabolic band (SPB), the electron effective mass m^* can be estimated from the measured values of Seebeck coefficient and carrier concentration $n_{\rm H}$ using the following formulas:

$$S = \frac{k_B}{e} \left[\eta_F - \frac{(r+5/2)F_{r+3/2}(\eta_F)}{(r+3/2)F_{r+1/2}(\eta_F)} \right]$$
(6.1)

$$n = \frac{4}{\sqrt{\pi}} \left(\frac{2\pi m^* k_B T}{h^2} \right)^{3/2} F_{1/2}(\eta_F)$$
(6.2)

$$F_{i}(\eta_{F}) = \int_{0}^{\infty} \frac{x^{i}}{1 + e^{(x - \eta_{F})}} dx$$
(6.3)

$$\eta_F = \frac{E_F}{k_B T},\tag{6.4}$$

where $\eta_{\rm F}$, $F_i(\eta_{\rm F})$, $k_{\rm B}$, e, h, and r are the reduced Fermi level, the Fermi-Dirac integral, the Boltzmann constant, the electron charge, the Planck constant, and the scattering factor, respectively [40,41]. According to Figure 6.11 (d), alloy scattering is dominant at room temperature for all samples (scattering factor r = 0) [42]. The Pisarenko curves at room temperature for Cu-x samples are plotted and shown in Figure 6.13 (b). An effective mass $m^* = 2.9 m_{\rm e}$ is obtained for the pristine sample, which agrees well with the previously reported values [32,42,43]. And this value increases to 5.1 m_e for the samples with Cu introduction, suggesting an important effect of Cu on the band structure of ZrNiSn.



Figure 6.13 (a) Temperature dependence of Seebeck coefficient *S* and (b) Seebeck coefficient as a function of Hall charge carrier concentration for Cu-*x* samples. The solid curves are calculated Pisarenko curves for Cu-*x* samples.



Figure 6.14 The temperature dependence of power factor for Cu-x samples compared with values in Ref [32].

Figure 6.14 shows the calculated temperature dependence of the power factor for Cu-*x* samples. The power factor of Cu-*x* samples is enhanced up to x = 0.05, above which it decreases due to the decreased σ and unremarkable changed *S*. The maximum value of power factor is 6.2 mW/mK² at around 950 K for Cu-0.05 sample, which is about 68 % higher than that of reported value in ZrNi_{1.03}Sn compound [16]. Such a large improvement in power factor can be ascribed to the significant influence of Cu on the band structures of ZrNiSn.

6.3.3 Thermal transport properties

The temperature dependence of thermal conductivity κ is displayed in Figure 6.15 (a). The κ of Cu-0 sample shows an obvious increase above ~ 700 K because of the minority carrier contribution, but this trend is gradually suppressed with increasing Cu content. At room temperature, the value of κ is 8.5 W/mK for the Cu-0 sample, and it declines to 7.3 W/mK for the Cu-0.03 sample followed by an increase to 8.7 W/mK in the Cu-0.20 sample. The reason for the increase (Cu > 0.03) can be explained by the metallic nature of the samples (conducting behavior shown in Figure 6.11 (a)) and the quick increase in electrical thermal conductivity κ_e (shown in Figure 6.15 (b)). The electrical thermal conductivity κ_e is calculated by Wiedemann-Franz law $\kappa_e = L\sigma T$, where *L* is the Lorenz number obtained by the single parabolic band model [44] and the values are shown in Figure 6.15 (d). The κ_e increases gradually with increasing Cu content and then decreases slightly, following the trend of the σ . Besides, the lattice thermal conductivity κ_L is calculated by subtracting κ_e from κ , shown in Figure 6.15 (c). It is noted that all the values of κ_L for the samples with Cu introduction are lower than that of the Cu-0 sample

in the whole measured temperature range. At room temperature, the lowest value of κ_L is 5.9 W/mK for the Cu-0.05 sample, roughly 30 % reduction compared to that of the Cu-0 sample (~ 8.3 W/mK), which mainly results from the interstitial disorders in this system. In contrast, the reduction is more remarkable at high temperature from 4.7 W/mK for Cu-0 sample to 2.0 W/mK for Cu-0.05 sample (around 57 % decline), since the Umklapp scattering becomes more prominent at high temperature. However, the thermal conductivity is still much higher compared to the reported values [31,32], which might originate from the annealing treatment used in our samples. Compared to the unannealed samples, the concentration of Ni/vacancy defects can be strongly decreased after annealing [45,46].



Figure 6.15 Temperature dependence of (a) thermal conductivity κ , (b) electrical thermal conductivity κ_e , (c) lattice thermal conductivity κ_L , and (d) Lorenz number for Cu-*x* samples.

6.3.4 Figure of merit

The temperature dependence of the figure of merit ZT of Cu-x samples is presented in Figure 6.16 (a). The ZT of the pristine sample is comparable to the reported values by Zhao et al. [47], but it is slightly lower than the values reported by H. Xie et al. [33] due to the higher thermal conductivity caused by annealing treatment in our samples. An obvious improvement in *ZT* is observed for all samples with Cu introduction. And the highest value is ~ 1.1 at 950 K for the Cu-0.05 sample, which is 113 % higher than that of the pristine sample because of the enhancement in PF and the reduction in κ at the same time. For comparison, some reported maximum *ZT* values of ZrNiSn-based compounds are shown as well in Figure 6.16 (b) [15,31,33,47,48,49], where the *ZT* value in our work is comparable to that of Zr_{0.7}Hf_{0.3}NiSn (~ 1.2), but the composition of our sample does not contain Hf element (an expensive element), which is more favorable for practical applications.



Figure 6.16 Temperature dependence of *ZT* of Cu-*x* samples (a) and comparison with previously reported values (b).

6.4 Conclusions

In summary, the ZrNiSn samples with excess Cu were successfully synthesized by arc-melting, ball milling, SPS, and annealing treatments. With crystal structure, microstructure characterizations, and formation energy calculations, it is found that some Ni/Cu atoms occupied the interstitial 4d position and when Cu > 0.09 the FH phase was formed in the HH matrix, which benefits the electrical and thermal transport properties at the same time. The investigation of thermoelectric properties by combining experiments with the DFT computations demonstrates that the increase in σ is attributed to the occupancy of Ni/Cu on 4d position, leading to the movement of the valence band maximum to the conduction band minimum, thereby reducing the actual bandgap and increasing the $n_{\rm H}$. Due to the significant increase in σ , the power factor was enhanced more than twice compared to the pristine sample. Additionally, the existence of interstitial Cu defects and the FH secondary phase effectively scatters phonons, reducing the κ at the whole temperature range. With the simultaneous enhancement in PF and

the reduction in κ , the *ZT* is improved to ~ 1.1 for the ZrNiCu_{0.05}Sn sample at 950 K. It is believed that a further higher *ZT* could be achieved in this system if more efforts can be done on suppressing κ .

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Chapter 7 Summary and outlook

7.1 Summary

Half-Heusler compounds are an important family of new type mid/high-temperature thermoelectric materials due to their moderate electrical transport properties, thermodynamic stability, and lower toxicity, making them become highly practicable alternatives to other thermoelectric materials. In this dissertation, NbCoSn and ZrNiSn half-Heusler compounds were systematically studied, including phase structure, microstructure and compositions, band structures, and thermoelectric properties, to deeply understand the correlations between them.

N-type NbCo_{1-x}Ni_xSn samples were synthesized using arc melting followed by the annealing method. It was found that arc-melted NbCoSn always contained excessive Co occupied on 4d position. Then, in NbCo_{1-x}Ni_xSn samples, some Ni atoms substituted Co on 4c position and some Ni atoms occupied 4d position, leading to the formation of the FH phase in the HH matrix. Moreover, DFT calculations verified that Ni tended to occupy the vacant 4d position due to the negative formation energy, and also the occupancy of Ni on 4d position could stabilize the FH phase as compared to NbCo₂Sn. This kind of phase structure and microstructure influenced the electrical and thermal transport properties. The band structure calculations indicated that the electrical conductivity significantly increased mainly because of the Co/Ni atoms on 4d position, forming in-gap states between the conduction band and the valence band and hence reducing the bandgap. However, metallic impurities like Nb₃Sn and FH phases led to a lower Seebeck coefficient. The highest PF was ~ 2.4 mW/mK² at 700 K in the sample with 0.10 Ni. Additionally, the thermal conductivity decreased dramatically because of the point defects from Ni introduction and interface scattering from FH phases. Eventually, with the enhancement in PF and reduction in thermal conductivity, the maximum value of ZT was ~ 0.4 at 1000 K for the sample with 0.10 Ni. As demonstrated, the intrinsic interstitial defect can be utilized to adjust the thermoelectric properties in NbCoSn compounds.

Sc was substituted at the Nb site of NbCoSn as an acceptor to realize a *p*-type semiconductor. The samples were prepared by arc melting followed by annealing treatments. Since the radius of Sc⁵⁺ is larger than that of Nb⁴⁺, unit cell expansion was generated in the crystal structure but it was still a cubic MgAgAs structure. Because Sc provided one less electron than Nb, the electrons concentration gradually decreased while holes concentration gradually increased after Sc substitution. Thus, the electrical conductivity firstly decreased, and when holes became the dominant carriers (Sc \geq 0.05, positive Seebeck coefficient), electrical conductivity increased gradually with Sc content. At the same time, the positive values of the Seebeck coefficient indicated the achievement of *p*-type NbCoSn (Sc \geq 0.05). The maximum PF was 0.54 mW/mK² for the sample with 0.05 Sc, which was the highest reported value for *p*-type NbCoSn until now. In addition, mass and strain field fluctuations originating from mass, radius, and interatomic coupling force differences led to point defects and lattice distortions after Sc substitution, which strongly scattered phonons and reduced the thermal conductivity significantly. As a result, the maximum *ZT* for *p*-type NbCoSn was 0.13 in the Nb_{0.95}Sc_{0.05}CoSn sample at 879 K.

Following the work of NbCoSn with Ni introduction, ZrNiSn with Cu introduction was examined. Since ZrNiSn usually contains excessive Ni as well and it has original better thermoelectric performance than NbCoSn, a higher ZT could be achieved if applying the same effect in ZrNiSn. Therefore, $ZrNiCu_xSn$ (x = 0, 0.01, 0.03, 0.05, 0.07, 0.09, 0.125, 0.15, 0.20) samples were synthesized by arc melting and ball milling. Afterward, the powders were densified by SPS, and then the annealing treatment was applied to obtain phase-stable samples. The XRD and EDX results revealed that there were a lot of Ni/Cu-rich secondary phases, and with increasing Cu content to 0.09 these secondary phases became the FH phase, emerging in the HH matrix. TEM measurements showed that some 4d positions were occupied as well in the ZrNiCu_{0.05}Sn sample, which could be Ni or Cu atoms. However, Ni and Cu atoms cannot be distinguished by TEM. Therefore, Neutron diffraction data should be collected to analyze how much Ni or Cu is on the 4d position. Due to the time limit, we have not obtained enough neutron data to do further analysis. Formation energy calculations showed negative values, indicating that Cu can occupy the 4d position. The high-temperature electrical transport properties showed that the electrical conductivity increased significantly ($Cu \le 0.07$), resulting from reduction of the bandgap induced by Ni/Cu interstitial defects, which is different with the Ni excessed ZrNiSn and what we studied before in NbCoSn. However, when $Cu \ge 0.09$, the electrical conductivity decreased slightly, which might be ascribed to the decrease of the amount of interstitial Ni/Cu due to the formation of the FH phase. At the same time, the thermal conductivity was reduced for several samples. As a result, ZT was enhanced by 113 % (~ 1.1 at 950 K) compared to the pristine sample.

7.2 Outlook

Based on the results obtained in this dissertation, both NbCoSn and ZrNiSn are promising thermoelectric materials and deserve further studies in the future.

For the NbCoSn compound, the synthesized samples always contain some impurities (Nb₃Sn and Sn), which restricts the improvement in electrical properties and the figure of merit. Therefore, much more effort should be employed to improve the phase purity such as using ball milling and SPS methods [1], suppressing the impact of impurities on the electrical properties. Simultaneously, the ball milling could also reduce grain size and increase grain boundaries, enhancing phonon scattering and decreasing thermal conductivity [2]. In addition, considerable excessive Co always exists in the arc-melted polycrystalline NbCoSn compounds due to the rapid cooling rate, which is favorable for the electrical conductivity of the *n*-type NbCoSn. It is interesting as well how the electrical and thermal properties of NbCoSn behave without excessive Co and how to control these interstitial defects. Regarding this, some other synthesize methods (e.g. low-temperature techniques with slow cooling rate [3]) should be explored in the future. Moreover, this exploration is also meaningful for the achievement of a high-performance *p*-type NbCoSn since excessive Co provides more electrons, making the *p*-type dopants less effective. If NbCoSn compound with less interstitial Co can be obtained, the *p*-type NbCoSn will be extensively developed.

For the ZrNiSn compound, the most important highlight is that there are no expensive elements (like Hf), and a comparable value of *ZT* has been achieved, which is promising for commercial applications. However, the thermal conductivity did not reduce significantly after Cu introduction. To the best of our knowledge, extending ball-milling time and/or adjusting SPS time would be helpful to reduce grain size and enhance boundary phonon scattering [4]. Additionally, substituting other elements (Ti or rare-earth elements such as Yb) could be another method to strengthen point-defect scattering [5-7]. Therefore, it is promising to combine these two methods and investigate the thermoelectric performance in $ZrNiCu_xSn$ -based compounds.

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