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Publication Date

2013

DOI

10.1016/j.solidstatesciences.2013.09.005

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Influence of Ni nanoparticle addition and spark plasma sintering on the TiNiSn-Ni system:
Structure, microstructure, and thermoelectric properties

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Abstract. The electronic and thermal properties of thermoelectric materials are highly dependent on their microstructure and therefore on the preparation conditions including the initial synthesis and, if applicable, densification of the obtained powders. Introduction of secondary phases on the nano- and/or microscale is widely used to improve the thermoelectric figure of merit by reduction of the thermal conductivity. In order to understand the effect of the preparation technique on structure and properties, we have studied the thermoelectric properties of the well-known half-Heusler TiNiSn with addition of a small amount of nickel nanoparticles. The different parameters are the initial synthesis (levitation melting and microwave heating), the amount of nickel nanoparticles added and the exact pressing profile using spark plasma sintering. The resulting materials have been characterized by synchrotron X-ray diffraction and microprobe measurements and their thermoelectric properties are investigated. We found the lowest (lattice) thermal conductivity in samples with full-Heusler TiNi₂Sn and Ni₃Sn₄ as secondary phases.

Keywords: half-Heusler TiNiSn, thermoelectrics, microstructure, Ni nanoparticles, spark plasma sintering

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1. Introduction

One of society's biggest challenges is addressing the increasing energy demand worldwide. With much of this energy being lost through waste heat, thermoelectric materials offer a way to convert this thermal energy into useful electricity. The advantages of this solid-state conversion are mainly high reliability and low maintenance costs due to the absence of moving parts. The downside is the relatively low conversion efficiency, which is directly related to the thermoelectric figure of merit containing interdependent physical properties ($zT = \alpha^2 T / (\rho \kappa)$, where α is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity and T is the absolute temperature [1]). This means that by positively affecting one material property another one is negatively affected, e.g. decreasing the resistivity usually also decreases the absolute value of the Seebeck coefficient.

The half-Heusler compound TiNiSn is a promising thermoelectric material in the intermediate temperature range (750 K) with reported maximum figures of merit of around 0.5 [2-4]. In particular, its high Seebeck coefficient α and low electrical resistivity ρ are able to balance out the thermal conductivity κ , which can be four to five times higher than that of state-of-the-art telluride materials. In order to increase the figure of merit, different approaches have been reported that mainly focus on the reduction of the thermal conductivity. Substitution with heavier elements introduces a mass difference that leads to point scattering of heat-carrying phonons [5, 6]. Another strategy is the introduction of a secondary phase on the nano- or microscale, which results in scattering of the short- to mid-wavelength phonons [7, 8]. All approaches reduce the lattice thermal conductivity effectively since it has been shown that scattering events on all length scales are required for the highest figures of merit [9].

For large-scale applications of thermoelectric materials, low toxicity and high abundance of the reacted elements and a cost-effective preparation process are of utmost importance. Since typical doping elements, such as Hf and Zr, are scarce and expensive [10], we have previously shown that zT can be enhanced through inclusion of a secondary full-Heusler phase by adding a small amount of additional Ni to TiNiSn [8]. Phonons are scattered on micron-sized TiNi₂Sn reducing the lattice thermal conductivity by about 30% when an ideal amount of 5% full-Heusler is present in the half-Heusler matrix. Encouraged by an earlier study, the half-Heusler/full-Heusler compounds were prepared by microwave reaction followed by spark plasma sintering. In the initial study, we have reported on a time- and energy-efficient technique using a

commercial microwave oven to prepare TiNiSn with zT comparable to that of the conventionally prepared material involving arc melting and annealing [4]. The microwave preparation reduces the reaction time from several days to minutes and the subsequent densification step eliminates most of the additional metallic phases present after the short microwave reaction.

The microstructure after the densification process is very important since it strongly influences the resulting thermoelectric properties. Additional metallic phases contribute electrons, thereby decreasing the electrical resistivity. As a result, a higher power factor α^2 / ρ can be reached if the Seebeck coefficient does not suffer too significantly. However, the most important aspect is the lattice thermal conductivity, which can be lowered effectively through phonon scattering on a suitable secondary phase inside the half-Heusler matrix. Reduction of the lattice thermal conductivity by about 50% has been reported in bulk $\text{Zr}_{0.25}\text{Hf}_{0.75}\text{NiSn}$ nanocomposites containing full-Heusler inclusions [7].

Spark plasma sintering (SPS) is widely used as an alternative to classic hot pressing to densify various powders including intermetallics and oxides. Its advantages are fast heating and cooling rates, resulting in limited grain growth, high densities and improved properties [11, 12]. Additionally, SPS allows for the control of a wide number of parameters for the densification process, including pressure, heating rate, holding temperature and time. In contrast to hot pressing where the sample is heated externally, in SPS a current is passed through the graphite die and the sample heating it up more efficiently. So far, little is known about the exact effects of the current on the phase and microstructure of the densified pellet since these effects are highly dependent on the nature of the material (e.g. conducting or insulating).

In this study, we investigate the effect of the addition of commercially available Ni nanoparticles together with the initial synthesis technique and two different SPS conditions on the microstructure and thermoelectric properties of TiNiSn. Two kinds of the parent compound are prepared by either levitation melting or microwave reaction, followed by mixing with Ni nanoparticles and densification by spark plasma sintering. The obtained pellets are carefully characterized by synchrotron X-ray diffraction, electron microprobe and measurement of the transport properties. This investigation allows insight into the effect of the initial preparation technique and the compaction process on the microstructure of the thermoelectric pieces.

2. Materials and Methods

Five different samples (TiNiSn-NP and two reference samples (Ref-LF, Ref-MW)) were prepared for this study. For the preparation by levitation melting, Ti rod (99.7%), Ni foil ($\geq 99.9\%$) and Sn shot (99.8%), all from Sigma-Aldrich, were melted in a Crystallox MCGS5 induction levitation furnace in an Ar atmosphere. The charge was held molten for 120 s and then rapidly cooled, solidifying in a water-cooled Cu crucible. This method has already been used to prepare Ni-rich TiNiSn samples with improved thermoelectric properties [13]. For the microwave procedure, we followed a method reported in previous studies, involving the reaction of metal powders sealed into a quartz tube in a commercial microwave oven [4]. After the initial synthesis the molten compounds were roughly broken using a percussion mortar to obtain pieces no bigger than 3 mm in any dimension. In a typical experiment, 4 g of the parent compound were mixed with 0.5 weight % (1 weight %) of nickel nanoparticles (approx. 50-200 nm, Sigma-Aldrich) and the mixture was ball-milled in acetone for 15 min using a WC container and balls to ensure homogeneous distribution of the nanoparticles. After drying in a crystallization dish, the fine TiNiSn/Ni nanoparticle powder was consolidated into dense pellets by means of spark plasma sintering (SPS).

Two different pressing profiles (see Figure 1) were used in order to study the influence of the SPS technique on both the microstructure and the thermoelectric properties of the obtained compounds. After a pressure of 50 MPa was applied (A) and the samples were heated to 673 K (B), the temperature was controlled by the pyrometer. For one set of samples, the temperature was raised to 1223 K with a heating rate of 100 K/min (C) and the temperature was held there for 5 min (D). For the other set of samples, the temperature was raised to 1273 K with a heating rate of 50 K/min (C) and held there for 10 min (D). In both cases, the materials were allowed to quickly cool down to room temperature (15 min) while the pressure was decreased simultaneously (E). The reference samples were obtained through levitation melting (Ref-LF) and microwave reaction (Ref-MW), respectively, then crushed and consolidated by spark plasma sintering using pressing profile (b).

Powder X-ray diffraction data were obtained on a Philips X'Pert with $\text{CuK}\alpha$ radiation. In addition, a small piece of the pellets was finely crushed for high resolution synchrotron powder diffraction data, collected at beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory using a wavelength of $\lambda = 0.440649 \text{ \AA}$. Le Bail fits and Rietveld

refinements were performed with TOPAS Academic V4.1 [14]. None of the Rietveld fits had small R -factors – a consequence of large grain sizes yielding profiles that were difficult to model. None of the reported results are affected by the quality of the fit.

Electron Microprobe analyses were conducted using a Cameca SX100 equipped with 5 wavelength dispersive spectrometers (WDS). Probe Image and Probe for EPMA (Probe software Inc.) were used for acquisition of X-ray intensity maps and quantitative data respectively. Ti $K\alpha$, Ni $K\alpha$, and Sn $L\alpha$ X-ray intensities were measured using LPET, LLIF and LPET analyzing crystals. X-ray intensity maps were collected using 15 keV accelerating voltage with 100 nA of beam current. An area of $125 \times 125 \mu\text{m}$ was traversed using continuous stage translation to create a 256×256 pixel map with a dwell time of 125 ms per pixel. Quantitative analysis was conducted at 15 keV accelerating voltage and 10 nA beam current. Ti $K\alpha$, Ni $K\alpha$, and Sn $L\alpha$ intensities were measured on-peak for 20 seconds and 10 seconds off-peak either side of the peak to create a linear background interpolation. In order to visualize chemical compositional differences within the X-ray map data, individual element X-ray intensity channels were combined into three channels of a color image to create a false color composite image of X-ray intensity for all elements.

For measurement of the electronic properties, bar-shaped pieces with the approximate dimensions $10 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$ were cut using a low-speed saw (Allied Inc.) with a diamond wafering blade. Seebeck coefficient and electrical resistivity in the temperature region between 300 K and 875 K were measured simultaneously on those samples using a ZEM-3 Ulvac instrument. The electronic transport properties were measured in two consecutive heating and cooling cycles. The data lie nearly on top of each other but a slight decrease in power factor (lower resistivity and absolute Seebeck coefficient) could be observed for some of the samples.

For thermal diffusivity measurements, disks, approximately 7.5 mm in diameter and 2 mm in thickness, were cut using wire electrical discharge machining (EDM, BROTHER HS-350) and sprayed with a layer of carbon paint in order to minimize errors in the emissivity. Thermal diffusivity was measured using the thermal flash technique between room temperature and 873 K under argon on an Anter Flashline 5000 system. The thermal conductivity was calculated using $\kappa = D d C_p$ where D is the thermal diffusivity, d is the density, and C_p is the specific heat. The Cowan model for diffusivity and the Dulong-Petit molar heat capacity, $C_p =$

3R, were utilized. Densities were obtained on the same pieces using a pycnometer (Micromeritics AccuPyc 1330 Pycnometer) and were found to be $\geq 99\%$ of the theoretical density. For microstructural investigations the remaining pieces were polished further in order to obtain a smooth surface for additional characterizations. Samples were fixed into an epoxy (Buehler Epomet) by hot compression mounting and polished using the following procedure: The samples were ground using silicon carbide abrasive paper and then polished to $0.25\mu\text{m}$ using colloidal diamond on cloth.

3. Results and Discussion

3.1. Samples. The scope of this study was to explore the influence of the following parameters on the microstructure and thermoelectric properties of TiNiSn compounds: (i) preparation technique of the initial TiNiSn compound, (ii) temperature and pressure profile of consolidation by spark plasma sintering, and (iii) effect of Ni nanoparticles added to the system (TiNiSn-NP). Therefore, five different samples and two reference samples were prepared through different synthesis and processing techniques. The two different pressing profiles are shown in Figure 1.

Samples that were pressed at 1223 K using a faster heating rate (100 K/min) and a shorter holding time (5 min) will be referred to as "LF-1223" and "MW-1223" (Figure 1(a)). Samples that were pressed at 1273 K following a slower heating rate (50 K/min) and a longer holding time (10 min) will be referred to as "LF-1273" and "MW-1273" (Figure 1(b)). The piston position during the pressing process is also shown in Figure 1. In both cases the major part of the consolidation starts at about 1200 K during the heating segment (C) and continues throughout the holding segment (D). At 1273 K the consolidation is almost fully completed which can be identified by the flattening piston position curve. The samples pressed at 1223 K show a slightly lower density than those pressed at 1273 K since consolidation does not seem to have reached completion.

Figure 1. Pressing profiles of the spark plasma sintering used to densify the samples showing the different segments of the process: A Compression, B heating to 673 K, C pyrometer-controlled heating, D densification, and E decompression and cooling. **(a)** and **(b)** display two different pressing profiles with final temperatures of 1223 K and 1273 K, respectively.

Figure 2. (a) X-ray powder diffraction data (filled dots) and le Bail fits of different phases (solid lines) of as-prepared microwave (MW) and levitation furnace (LF) samples; in both cases half-Heusler TiNiSn is the main phase and larger amounts of additional phases can be identified in the LF samples in comparison to the MW samples. **(b)** Synchrotron X-ray powder diffraction data of the samples after SPS consolidation, * and # indicating Sn and full-Heusler impurity phase, respectively. $Q = 2\pi/d$ represents the momentum transfer function, $Q = 4 \pi \sin(\theta)/\lambda$.

3.2. Phase characterization. Powder X-ray diffraction data of the as-prepared TiNiSn and the consolidated TiNiSn-NP compounds are presented in Figure 2. Note that high-resolution synchrotron XRD data were obtained only for the materials after spark plasma sintering (Figure 2(b)) since all further characterization was performed on those samples.

LeBail fits of the XRD data of the two different as-prepared compounds (Figure 2(a)) reveal the presence of half-Heusler TiNiSn and additional phases, full-Heusler TiNi₂Sn and various binary intermetallics. While XRD data of the microwave-prepared sample only exhibit small amounts of full-Heusler and Ti₆Sn₅, the sample prepared using the levitation furnace

contains a higher concentration of those phases and additional Ni_3Sn_4 and elemental Sn. This can be explained by the slower cooling rate in the case of the microwave-prepared samples, which results in the samples being at higher temperatures for a longer time than the rapidly cooled levitation-melted samples. Another reason is that powders are used as starting materials in the case of the microwave preparation, so smaller diffusion paths are expected in contrast to longer ones when large metal pieces are used (LF). Typically, a long-term annealing step is added after the initial synthesis to eliminate impurity phases and enhance ordering of the half-Heusler crystal structure [15-17,6]. Here, the samples were directly ball milled without further annealing, mixed with the nickel nanoparticles, and consolidated into dense pellets. Synchrotron XRD data of the different samples reveal that half-Heusler TiNiSn is the main phase and most of the secondary compounds have disappeared during spark plasma sintering (Figure 2(b)). Rietveld refinements of the synchrotron XRD data were performed (not shown here) and the resulting half-Heusler lattice constants and various phase fractions are summarized in Table 1.

Table 1. Preparation, half-Heusler lattice parameters, different phase composition and density for the consolidated samples

Method	SPS T K	Ni NP wt%	a (hH) Å	hH %	fH %	Sn %	Ni_3Sn_4 %	Ti_6Sn_5 %	d g/cm ³
LF	1223	0.5	5.92708	88.0	7.0	2.7	2.3	--	7.34
LF	1273	0.5	5.92798	90.3	3.6	3.0	3.1	--	7.39
MW	1223	0.5	5.91693	90.8	2.2	6.3	--	0.7	7.12
MW	1273	0.5	5.92068	91.9	2.2	3.2	--	2.7	7.32
MW	1273	1.0	5.92091	93.2	2.0	2.8	--	2.0	7.31

Half-Heusler lattice parameters match those reported in the literature [18] and only small deviations between the different samples can be observed. Lattice parameters of the MW compounds are slightly smaller than those of the LF compounds (possibly due to lower fractions of full-Heusler in the MW samples), and lattice parameters of the samples consolidated at 1223 K are slightly smaller than those consolidated at 1273 K. The major phase in all compounds

(around 90%) is the half-Heusler phase. Different additional phases can be identified, which are full-Heusler TiNi_2Sn , Sn, Ni_3Sn_4 , and Ti_6Sn_5 . Note that Ni_3Sn_4 and Ti_6Sn_5 can only be found in the LF and MW samples, respectively. The initial preparation method influences the microstructure after consolidation since full-Heusler TiNi_2Sn is the largest part of the additional phases in the LF samples while Sn represents the most prominent additional phase in the MW samples.

3.3. Microstructural analysis. Microprobe data of the surfaces of all five TiNiSn -NP pellets are shown in Figure 3. The background in all images is half-Heusler TiNiSn and different additional phases can be detected (light green, purple, red and blue in Figure 3).

Figure 3. Microprobe analysis of the different samples showing the different phases and metal-rich areas. LF (levitation melting) and MW (microwave heating) describe the initial synthesis technique, 1223 and 1273 are the spark plasma sintering temperatures in K, and 0.5 and 0.1 are the weight % of nickel nanoparticles added. Images are $128\mu\text{m} \times 128\mu\text{m}$.

Additional phases are elemental Ti and Sn and a binary Ti-Sn compound and these findings are in accordance with the results from the refinement of the XRD data (see Table 1). Ti (very likely some reduced titanium oxide) cannot be detected in the XRD data possibly due to very weak peaks associated with that phase. This demonstrates the importance of a combined

XRD and microprobe study in order to evaluate the samples. The sample observed to have the largest amount of fH (7%) by XRD, LF-1223(0.5), also exhibits the highest fraction of TiNi_2Sn (light green areas) by microprobe investigation. Similarly, the highest amount of elemental Sn is found in sample MW-1223(0.5) corresponding to many blue areas in Figure 3. Samples initially prepared by means of levitation melting show the highest amounts of full-Heusler. Apart from that observation, no clear dependence of the present phases on the initial synthesis and the densification parameters can be detected. In comparison with earlier studies where we investigated TiNiSn and $\text{TiNi}_{1+x}\text{Sn}$ samples processed with similar methods [4, 8], we find a higher fraction of additional metallic phases, which we attribute to the addition of Ni nanoparticles.

3.4. Electronic transport properties. Electronic transport properties of all five samples are compared to two reference samples (Figure 4).

Figure 4. Electronic properties (resistivity, Seebeck coefficient and power factor) of the different samples. Filled symbols and solid lines represent data and fits, respectively.

Both reference samples show semiconducting behavior, with a decreasing resistivity with increasing temperature. In contrast to the reference prepared by levitation melting (Ref-LF), the reference sample that was prepared through microwave reaction and consolidated by spark

plasma sintering (Ref-MW) exhibits a smaller resistivity and smaller absolute values of Seebeck coefficient which overall results in a slightly higher power factor. This is most likely a result of the microstructure of the sample, which involves segregation of metallic phases, a phenomenon that has been observed in materials prepared by this method [4]. The three samples with the lowest room-temperature resistivities (LF-1223, LF-1273 and MW-1223) are those with the highest fraction of metallic segregations (Sn and fH, see Table 1 and Figure 3). Consequently, those samples also exhibit the lowest absolute value of Seebeck coefficient.

The resulting power factor reveals the big influence of the pressing profile on the electronic properties of the samples. While samples consolidated at 1223 K only show power factors of around $1\text{-}1.5 \times 10^{-3} \text{ Wm}^{-1} \text{ K}^{-2}$, compounds pressed at 1273 K have power factors comparable to that of the reference sample ($2.5 \times 10^{-3} \text{ Wm}^{-1} \text{ K}^{-2}$). It can also be observed that doubling the amount of Ni nanoparticles does not have a significant effect on the resulting power factor. The sample with a higher amount of Ni nanoparticles seems slightly more metallic (with a lower resistivity and absolute value of Seebeck coefficient) but the power factors of MW-1273 (0.5) and MW-1273 (1) are essentially the same.

3.5. Thermal transport properties. A full investigation of the thermal transport properties is presented in Figure 5.

Figure 5. Total thermal conductivity (a), electronic thermal conductivity (b), Lorenz number (c), and lattice thermal conductivity (d) of the five TiNiSn-NP and two reference samples.

Room-temperature thermal conductivities range from 4 to 6 $\text{Wm}^{-1} \text{K}^{-1}$, slightly lower than those reported in the literature [6, 19]. Thermal conductivities of the microwave-prepared samples (circles in Figure 5) are generally higher than those of the samples prepared by levitation melting (squares in Figure 5). This is true at temperatures below 600 K whereas high-temperature thermal conductivities are similar for all samples.

To learn more about the heat transport in the studied compounds, Lorenz numbers were calculated based on experimental Seebeck coefficients using an SPB model [20, 21], which allows for extraction of the electronic and the lattice contribution to the total thermal conductivity. In accordance with the electrical resistivity data, samples with the highest Lorenz numbers are those with the largest amount of metallic inclusions and therefore exhibit the highest electronic thermal conductivities. One of the microwave-prepared compounds (MW-1223 (0.5)) has a Lorenz number close to that of metals and the highest total thermal conductivity at room temperature among all samples. This can be explained by its high fraction of metallic tin detected by XRD and microprobe investigations (see Table 1 and Figure 3).

The electronic thermal conductivities, however, are rather low compared to the lattice thermal conductivities, which are the most significant contribution to the thermal conductivity. Here, more significant differences between the various samples can be observed. All microwave prepared samples show similar lattice thermal conductivities and the values of the studied materials compare well with the reference sample (circles in Figure 5). In general, all compounds prepared by levitation melting exhibit lower lattice contributions (squares in Figure 5) but we find a larger difference between the TiNiSn-NP samples and their reference sample. A reduction of about 1 $\text{Wm}^{-1} \text{K}^{-1}$ at room temperature is achieved as a result of the microstructure in both nanoparticle-infused compounds.

Doubling the amount of Ni nanoparticles again does not have a significant effect on the properties. Lorenz number and electronic thermal conductivity are slightly higher in the case of the higher nanoparticle content but the lattice thermal conductivity is almost identical. There is only a very marginal difference between the total thermal conductivity of MW-1273 (0.5) and MW-1273 (1).

These results demonstrate the striking importance of the exact microstructure of the different samples examined here. Due to different preparation methods and pressing conditions, different amounts of additional metallic phases can be found in the various samples. Although

they are all of similar size (microns), they do not show the same scattering effect on heat-carrying phonons. While elemental inclusions, such as Ti and Sn, seem to be rather ineffective scatterers, full-Heusler TiNi_2Sn interrupts the phonon path thereby reducing the lattice thermal conductivity. This is in accordance with findings in a similar study where we introduced TiNi_2Sn as a secondary phase in TiNiSn , which resulted in reduced lattice thermal conductivities [8]. The samples with the lowest lattice thermal conductivities are also those with the largest fractions of binary Ni_3Sn_4 . The reason for the different scattering behavior of the aforementioned phases could be the higher densities of full-Heusler TiNi_2Sn and Ni_3Sn_4 when compared to those of half-Heusler TiNiSn , elemental Sn, and Ti_6Sn_5 .

3.6. Thermoelectric figure of merit. The TiNiSn -NP samples can be divided into two groups with different figures of merit (see Figure 6). All samples pressed at higher temperature (Figure 1(b)) show figures of merit that are twice as high (around 0.4) as samples pressed at slightly lower temperature (around 0.2) (Figure 1(a)). The highest figure of merit (around 0.5) can be found in one of the reference samples (Ref-LF), which exhibits the best compromise between high power factor and low thermal conductivity. Owing to its higher thermal conductivity and lower power factor, the other reference sample (Ref-MW) shows a lower figure of merit (0.35).

Figure 6. Thermoelectric figure of merit of the five TiNiSn -NP and two reference samples.

4. Conclusions

In this contribution, we investigate the influence of the initial preparation method, pressing conditions, and addition of small amounts of Ni nanoparticles on the microstructure and thermoelectric properties of half-Heusler TiNiSn. Different binary and elemental phases along with TiNiSn can be identified in the materials after levitation melting and microwave heating, respectively. A larger fraction of secondary phases, especially full-Heusler TiNi₂Sn, is found in the compounds prepared by levitation melting. Spark plasma sintering that is used to densify the powders eliminates most of the additional phases resulting in mostly single-phase pellets. However, refinement of the synchrotron XRD data exhibits the presence of different minor phases, mostly full-Heusler in the case of the levitation-melted samples and Sn in the case of the microwave-treated samples. Microprobe images of the surface of the pellets show a variety of phases, confirming the XRD data. Their presence has already been suggested in earlier studies but seems to be amplified by the addition of small amounts of nickel nanoparticles. Power factors of the samples prepared in this study are lower than those of reference samples as a result of lower Seebeck effects arising from their more metallic nature. The reduction in power factor coupled with the thermal properties of the present compounds does not allow for enhanced thermoelectric figures of merit.

The thermal conductivities of all microwave-prepared pellets are higher than those of the reference samples because of the larger electronic contribution. Interestingly, samples with the highest amounts of full-Heusler (around 4-7%) and Ni₃Sn₄ as additional phases -- initially prepared by levitation melting -- exhibit reduced lattice thermal conductivity and therefore a lower thermal conductivity in comparison to the reference samples. This finding itself is valuable since it suggests that inclusions with higher densities, here full-Heusler and Ni₃Sn₄, scatter phonons more effectively than other phases. Controlling the microstructure of intermetallic compounds is not at all trivial and here we could show that one segregated phase is more beneficial for the thermoelectric performance than others. This adds to our understanding of the transport properties in heterostructured compounds and will hopefully lead to a better control of the overall thermoelectric properties in these systems.

5. Acknowledgment

This work was supported by NSF DMR 1121053. The authors thank Prof. Carlos Levi for useful discussions. C.S.B. is a recipient of the Feodor Lynen Research Fellowship supported by the Alexander von Humboldt foundation. J.E.D is supported by a fellowship from the ConvEne IGERT Program (NSF-DGE 0801627). B.R.L. is supported by an internship from the RISE program (NSF DMR 1121053). T.M.P. and R.S. are supported by the MRSEC Program (NSF DMR 1121053). G.D.S. acknowledges support from the Center for Energy Efficient Materials (CEEM), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Basic Energy Sciences under Award Number DESC0001009. Use of shared experimental facilities of the Materials Research Laboratory: an NSF MRSEC, supported by NSF DMR 1121053 is gratefully acknowledged. The MRL is a member of the NSF-supported Materials Research Facilities Network (www.mrfn.org). Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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