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Citation for published version:
Downie, RA, Barczak, S, Smith, R & Bos, J-WG 2015, 'Compositions and thermoelectric properties of XNiSn (X = Ti, Zr, Hf) half-Heusler alloys', Journal of Materials Chemistry C, vol. 3, no. 40, pp. 10534-10542. https://doi.org/10.1039/C5TC02025E

Digital Object Identifier (DOI):
10.1039/C5TC02025E

Link:
Link to publication record in Heriot-Watt Research Portal

Document Version:
Publisher's PDF, also known as Version of record

Published in:
Journal of Materials Chemistry C

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Compositions and thermoelectric properties of XNiSn (X = Ti, Zr, Hf) half-Heusler alloys

R. A. Downie, S. A. Barczak, R. I. Smith and J. W. G. Bos

Rietveld analysis of neutron powder diffraction data has been used to investigate the compositions of XNiSn (X = Ti, Zr, Hf) half-Heusler alloys prepared by solid state reactions. All samples containing Ti have 2–3% excess Ni, whereas the samples with X = Zr, Hf are almost stoichiometric. Samples with mixed X-metals are characterised by the presence of 3–4 distinct X_{1−y}X′_{y}Ni_{1+y}Sn half-Heusler phases. Variable temperature and time dependent neutron powder diffraction for X = Ti and X = Ti_{0.5}Hf_{0.5} demonstrates that both the amount of excess Ni and the phase distribution are stable up to at least 600 °C. Debye temperatures of 367(2) K and 317(2) K were obtained from the thermal displacement parameters. The samples containing Ti are characterised by a ~0.15 eV bandgap and a monotonously decreasing Seebeck coefficient. The compositions with Zr and Hf have similar bandgap values but show ambipolar transitions. Analysis of the thermoelectric transport data of degenerately doped Ti_{0.5}Zr_{0.5}Ni_{1+y}Sn_{1−y}Sb, samples using a single parabolic band model demonstrates that the transport is limited by alloy scattering and yields an effective carrier mass of 2.5(1) m_{e}.

Introduction

Half-Heuslers (HHs) show great promise in the field of thermoelectric waste heat recovery, in which they can be used to improve the energy efficiency of any heat-generating process.1 The performance of a thermoelectric material is determined by its electrical resistivity, \( \rho \), the Seebeck coefficient, \( S \), and the electronic thermal conductivity, \( \kappa_{el} \). The compositions with Zr and Hf have similar bandgap values but show ambipolar transitions.

The large power factors \( (S^2/\rho) \) possessed by HHs make them an obvious choice for thermoelectrics research, but high values mean that alterations to the structure must be made to reduce \( \kappa_{lat} \) and achieve high \( zT \) values.2–6

Recently, phases on the XNiSn–XNi_{2}Sn HH full-Heusler (FH) pseudo-binary have generated substantial interest (where X = TiNiSn series).8–13 However, not all samples containing excess Ni (\( y > 0 \)) show enhancements of \( S \) and \( \sigma \), and other reports observe only micro-inclusions of the FH phase.11,12 We recently reported an in-depth study of TiNiM_{x}Sn (M = Co, Ni, and Cu) nanocomposites prepared via solid state reactions and showed that the excess metal is relatively homogeneously distributed with an upper limit <2 nm for any segregated TiNi_{1+y}Sn FH inclusions.18 The absence of clear inclusions demonstrates that the degree of segregation is sensitively dependent on the sample processing, which is in keeping with the wide variety of nanostructures reported in the literature.3,6 Another topical issue in this field regards the low \( \kappa \) (<2–3 W m\(^{-1}\) K\(^{-1}\)) that is sometimes observed in XNiSn and XCoSb samples with mixtures of Ti, Zr, and Hf, and which is important to underpin \( zT > 1 \).19–23

Recent studies have linked the low \( \kappa \) to phase segregation into multiple HH phases with different ratios of X-metals.6,21,24 However, our results for the Ti_{1−x}Zr_{x}NiSn series indicate that this multiphase behaviour is kinetically controlled, and has a secondary impact on \( \kappa(T) \) after alloy scattering, suggesting that the presence of all three of Ti, Zr, and Hf is needed.25 Other approaches aimed at minimising \( \kappa_{lat} \) include off-stoichiometric X_{x}Ni_{1+y}Sn_{1−y} (X = Ti, Zr) compositions that form a HH matrix and a number of segregated phases,26,27 addition and \( \sigma \) are not expected in homogenous semiconductors, where they depend inversely on carrier concentration.1 The observation of this effect therefore suggests that potential barriers, due to FH nano-inclusions, filter out low energy carriers leading to an enhancement of \( S \).17

(\( T_{c} \))
of a Ti$_{70.5}$Fe$_{29.5}$ eutectic, InSb inclusions in TiCoSb, and phase segregation involving mixtures of HH phases.

Neutron powder diffraction is a powerful tool to characterise metal-rich HH alloys due to the excellent scattering contrast between the elements present. In addition, the bulk nature of the technique means a representative average picture is obtained. For the TiNi$_{M}$Sn ($M = \text{Co, Ni, and Cu}$) nanocomposites it was possible to account for all excess metal present in the sample. In case of the $M = \text{Ni}$ series, the excess Ni was divided over the matrix (nano-inclusions with diameter < 2 nm) and over a distinct FH phase with the sum of excess Ni equal to the nominal y value. This analysis also allowed us to determine that Co substitutes in the matrix, while Cu is part of a nanosegregated FH phase. This has enabled the accurate determination of the experimental compositions, and of the multiphase behaviour that occurs in these samples. In addition, we also present a detailed thermoelectric property analysis of degenerately and non-degenerately doped XNiSn and X$_{0.5}X'_{0.5}$NiSn compositions.

**Experimental**

The synthesis of the XNiSn and X$_{0.5}X'_{0.5}$NiSn ($X, X' = \text{Ti, Zr or Hf}$) samples has been reported in ref. 25. Neutron powder diffraction data for these samples were collected on the upgraded POLARIS instrument at the ISIS facility, Rutherford Appleton Laboratory, UK. Powders were loaded into cylindrical sample cans and diffraction data were collected at room temperature for 300 $\mu$A h proton beam current to the ISIS target, corresponding to ~2 hours neutron beam time. In addition, two samples were studied at elevated temperatures: TiNiSn (373 to 973 K in 100 K steps) and Ti$_{0.5}$Zr$_{0.5}$NiSn (293, 473, 673 and 873 K). The neutron scattering lengths are $b_{\text{Ti}} = 3.4 \text{ fm}$, $b_{\text{Zr}} = 7.2 \text{ fm}$, $b_{\text{Hf}} = 7.7 \text{ fm}$, $b_{\text{Ni}} = 10.3 \text{ fm}$ and $b_{\text{Sn}} = 6.2 \text{ fm}$. Crystal structure refinement was by the Rietveld method using the GSAS suite of programs and the EXPGUI graphical interface. Profile function three for time-of-flight data in GSAS was used to fit the peak shape. The thermoelectric characterisation for these samples was reported in ref. 25 but no data fitting was undertaken in that study.

**Results**

1. **Room temperature structures**

A convenient way to view the XNiSn half-Heusler structure is as a face-centred-cubic lattice of Sn, where all the octahedral holes are occupied by X and half the tetrahedral holes (herein Y1) are filled with Ni. This leaves half the tetrahedral holes empty (Y2). The Y2 sites are fully occupied in the Heusler structure, leading to an increase in space group symmetry (from $F\bar{4}3m$ to $Fm\bar{3}m$) and lattice parameter ($\Delta a \sim 0.2 \text{ Å}$). TiNiSn is semiconducting with strong hybridisation between Ni and Sn s- and p-orbitals, while the valence and conduction bands are formed by hybridisation of the Ti and Ni d-orbitals. TiNi$_2$Sn in contrast is metallic, and this difference in chemical bonding is responsible for the absence of solid solution formation.
reported values. Maintaining a stoichiometric TiNiSn model, with Ti, Ni and Sn on their expected sites (X, Y1, Z), results in $\chi^2 = 8.8$. Two models were subsequently identified that resulted in an improvement in $\chi^2$. The first of these involves 2% excess Ni on the vacant tetrahedral Y2 site. The second model has 3% inversion of Ti and Sn (i.e. Ti$_{0.97}$Sn$_{0.03}$Ni$_{0.97}$Sn$_{0.03}$-Ti$_{0.03}$). Both models produce $\chi^2 = 8.2$ ($\chi^2 = 7.9$ from a LeBail fit). Larger degrees of inversion are needed for the previously reported TiNi$_{1.04}$Sn (6% inversion) and TiNi$_{0.06}$Sn (10% inversion) samples. A minimal TiNi$_{0.93}$ sample was also prepared by standard solid state reaction and best-fit models were found for TiNi$_{1.056(2)}$Sn or 9% Ti-Sn inversion. Furthermore, HfNiSn requires 30% inversion of Hf and Sn, or < 1% excess Ni. ZrNiSn was found to be stoichiometric despite the presence of Zr$_2$Sn$_4$ and Ni$_3$Sn$_2$ secondary phases. The much smaller variation in Y2 site occupancies suggests that the presence of excess Ni is the most plausible interpretation of our data. This is in keeping with the covalent bonding in these structures and the large energetic cost for XSn inversion.29

Ti$_{0.5}$Zr$_{0.5}$NiSn. Our previous work demonstrated that the ingots with mixed X metals are not phase pure but contain multiple X$_{1-x}$X$'$NiSn half-Heusler phases.25 A total of 4 half-Heusler phases were used to fit the NPD data, as shown in the inset to Fig. 1d. The lattice and atomic parameters for the four phases are presented in Table 2. The Zr content of each phase was calculated from the lattice parameters using Vegard’s law ($x_V$) and by refining the X-site occupancy ($x_R$). It was not possible to determine $x_R$ for the most minor phase, present at 3 wt%, and the occupancies were kept fixed at the $x_V$ values. The $x_R$ values are plotted against $x_V$ in Fig. 2a. From this figure, it may be seen that, for $x_V \geq 0.5$, there is good agreement between $x_R$ and $x_V$. At lower values of $x_V$ however, the refined $x_R$ are somewhat larger than $x_V$. This indicates a departure from Vegard’s law with the $x_R$ indicating a lower Zr-fraction than that derived from the lattice parameter. This discrepancy does not lead to any significant difference in average composition of the multiphase samples. The highest resolution backscattering

Table 1

| X | Ti | Zr | Hf |
|---|---|---|---|
| a (Å) | 5.929(1) | 6.1089(1) | 6.0795(1) |
| Ni(1) | 0.0049(4) | 0.0057(2) | 0.0047(5) |
| Ni(2) | 0.0049(5) | 0.00461(6) | 0.0046(5) |
| Sn | 0.0040(7) | 0.00221(2) | 0.0036(5) |
| wt% | 100 | 95.00(8) | 99.17(3) |
| $\chi^2$ | 8.2 | 9.9 | 7.4 |
| wR$_p$/% | Bank 5 | 3.4 | 3.0 | 2.8 |
| Bank 4 | 2.0 | 2.4 | 2.2 |
| Bank 3 | 2.1 | 2.5 | 2.2 |
| R$_p$/% | Bank 5 | 4.2 | 4.2 | 5.1 |
| Bank 4 | 3.2 | 5.0 | 4.2 |
| Bank 3 | 3.6 | 3.0 | 3.0 |
| R$_f$/% | Bank 5 | 5.7 | 7.1 | 8.5 |
| Bank 4 | 6.2 | 6.0 | 7.3 |
| Bank 3 | 7.5 | 7.2 | 5.3 |

reported values. Maintaining a stoichiometric TiNiSn model, with Ti, Ni and Sn on their expected sites (X, Y1, Z), results in $\chi^2 = 8.8$. Two models were subsequently identified that resulted in an improvement in $\chi^2$. The first of these involves 2% excess Ni on the vacant tetrahedral Y2 site. The second model has 3% inversion of Ti and Sn (i.e. Ti$_{0.97}$Sn$_{0.03}$Ni$_{0.97}$Sn$_{0.03}$-Ti$_{0.03}$). Both models produce $\chi^2 = 8.2$ ($\chi^2 = 7.9$ from a LeBail fit). Larger degrees of inversion are needed for the previously reported TiNi$_{1.04}$Sn (6% inversion) and TiNi$_{0.06}$Sn (10% inversion) samples. A minimal TiNi$_{0.93}$ sample was also prepared by standard solid state reaction and best-fit models were found for TiNi$_{1.056(2)}$Sn or 9% Ti-Sn inversion. Furthermore, HfNiSn requires 30% inversion of Hf and Sn, or < 1% excess Ni. ZrNiSn was found to be stoichiometric despite the presence of Zr$_2$Sn$_4$ and Ni$_3$Sn$_2$ secondary phases. The much smaller variation in Y2 site occupancies suggests that the presence of excess Ni is the most plausible interpretation of our data. This is in keeping with the covalent bonding in these structures and the large energetic cost for XSn inversion.29

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Table 2

| a (Å) | wt% | X'X' | Ni(1) | Ni(2) | Sn | $x_V$ | $x_R$ | $\Delta x$ | $\chi^2$ | Bank | wR$_p$ | $R_p$ | $R_f$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| X$_{0.5}$X'$_{0.5}$NiSn | X = Ti, Zr, Hf | X | Ti | Zr | Hf |
| 5.981(2) | 18.3(2) | occ | 0.847(3)/0.153(3) | 1 | 0.052(2) | 1 | 0.29(1) | 0.153(3) | 0.12(1) | 5.5 |
| 6.024(2) | 19.7(7) | occ | 0.53(1)/0.47(1) | 1 | 0.0038(5) | 1 | 0.00213(4) | 0.00213(4) | 5.5 |
| 6.040(1) | 59.2(7) | occ | 0.1426(6)/0.586(6) | 1 | 0.032(4) | 1 | 0.62(1) | 0.586(6) | 0.07(1) | 4 |
| 6.102(2) | 2.7(1) | occ | 0.04(0.96) | 1 | 0 | 0 | 0.91(4) | 0.96 | 0.06(1) |
| 5.9834(3) | 14(1) | occ | 0.805(5)/0.185(5) | 1 | 0.030(4) | 1 | 0.36(1) | 0.195(5) | 0.12(1) | 6.0 |
| 6.004(3) | 23(1) | occ | 0.46(2)/0.54(2) | 1 | 0.00(2) | 1 | 0.50(1) | 0.54(2) | 0.04(1) | 5 |
| 6.0157(1) | 60.1(9) | occ | 0.4199(5)/0.581(9) | 1 | 0.026(4) | 1 | 0.57(1) | 0.581(9) | 0.03(1) | 3 |
| 6.0604(3) | 3.0(8) | occ | 0.13(0.87) | 1 | 0 | 0 | 0.87(1) | 0.87 | 0.08(1) |
| 5.983(4) | 0.94(4)/0.06(4) | 1 | 0.020(2) | 1 | 0.00495(6) | 0.00495(6) | 0.0017(2) | 3.1 |
| 5.983(4) | 0.94(4)/0.06(4) | 1 | 0.020(2) | 1 | 0.00495(6) | 0.00495(6) | 0.0017(2) | 3.1 |

Ti$_{0.5}$Hf$_{0.5}$NiSn contains 0.93(7) wt% Zr$_5$Sn$_4$, 3.36(3) wt% Ni$_2$Sn$_2$ and 0.44(1) wt% Ni$_2.67$Sn$_2$. HfNiSn contains 0.83(3) wt% HfO. Bank 5, 4 and 3 are the backscattering, 90 degrees and low angle detector banks, respectively.
detector (bank 5) was used to get an estimate of any peak broadening caused by further compositional fluctuations (Δx). All profile function parameters, except γ1 which models microstrain, were kept fixed at the average value for the XNiSn end-members. For a cubic system, the microstrain can be easily related to a spread in x value, and the calculated values for Δx are tabulated in Table 2 and are shown in Fig. 3a. Refinement of the Y2 site occupancy revealed that Ni partially occupies the Y2 site in 2 of the 4 HH phases (Table 2). The largest excess of Ni (y = 0.052(2)) was found in the phase with xR = 0.153(3). The average composition of this sample was found to be Ti0.495(7)Zr0.505(7)Ni1.028(3)Sn, which is in good agreement with the nominal x value and indicates the presence of 3% excess Ni.

**Tl0.5Hf0.5NiSn.** This sample shows similar multiphase behaviour to Tl0.5Zr0.5NiSn and was analysed analogously. The refined Hf occupancies were found to be xR = 0.195(5), 0.54(2), 0.581(9) and 0.87, where the last value was fixed to xV due to the low abundance of this phase. The xR values are in good agreement with xV for xR ≥ 0.5, with a small discrepancy for lower x, as seen for Tl0.5Zr0.5NiSn (Fig. 2a). The Δx values are comparable to those found in Tl0.5Zr0.5NiSn and are shown in Fig. 3b. Two of the HH phases were found to contain Ni on the Y2 site. The refined values are presented in Table 2 and the Ni content is plotted in Fig. 2b. The average composition was found to be Tl0.53(1)Hf0.47(1)Ni1.019(5)Sn.

**Zr0.5Hf0.5NiSn.** The narrow range of unit cell parameters observed for this composition (due to the similar radii of Zr and Hf) means only one phase could be identified, instead of the three that were observable in the X-ray data (Fig. 1f). The lattice and atomic parameters are presented in Table 2. Refinement of the Y2 site occupancy suggested this sample is stoichiometric, and does not contain any excess Ni. The final fitted composition of this sample was found to be Zr0.59(4)Hf0.41(4)Ni1.002(3)Sn, consistent with the X-ray data, and the nominal composition.

### 2. Temperature dependence studies

**TlNiSn.** The fitted lattice parameters, fractional site occupancies and fit statistics are presented in Table 3. The unit cell volume was found to increase linearly above 300 K, as illustrated in Fig. 4a.
The volume expansion could be fitted by \( V(T) = V_0 + A \coth(\theta_D/T) \), where \( A \) is a scale factor and \( \theta_D \) is the Debye temperature. From this fit, \( V_0 = 205.4(1) \AA^3 \), \( A = 2.6(2) \) and \( \theta_D = 347(22) \) K. This is consistent with literature values which put \( \theta_D \) in the range 360–420 K.\(^{43}\) The temperature dependence of the thermal displacement parameters \( (U_{iso}) \) of each atom are plotted in Fig. 4b. The similar gradients and magnitudes indicate that all three atom types vibrate at around the same frequency. The values for Sn are slightly reduced compared with Ti and Ni due to its larger mass. Using the average slope and mass of TiNiSn a Debye temperature of 367(2) K was obtained,\(^{44}\) in excellent agreement with the value from the fit to cell volume, and the literature.

The Ni occupancies on the Y1 and Y2 sites were also refined for each temperature step and remained constant within one estimated standard deviation (Table 3).

**Table 3** Temperature evolution of the lattice parameter \( (a) \), thermal displacement parameters \( (U_{iso}/\AA^2) \), Y2 site occupancy \( (occ) \) and fit statistics for TiNiSn between 293 and 973 K

|         | 293 K   | 373 K   | 473 K   | 573 K   | 673 K   | 773 K   | 873 K   | 973 K   |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| \( a (\AA) \) | 5.9297(1) | 5.9333(1) | 5.9329(1) | 5.9453(1) | 5.9514(1) | 5.9576(1) | 5.9641(1) | 5.9710(1) |
| Ti \( U_{iso} \) | 0.00495(7) | 0.0061(1) | 0.0078(1) | 0.0095(2) | 0.0107(2) | 0.0130(2) | 0.0142(3) | 0.0167(2) |
| Ni(1) \( U_{iso} \) | 0.00499(5) | 0.00609(6) | 0.0078(1) | 0.00946(7) | 0.01099(9) | 0.01276(9) | 0.0147(2) | 0.0164(1) |
| Ni(2) \( occ \) | 0.022(1) | 0.019(1) | 0.019(1) | 0.018(1) | 0.019(1) | 0.015(1) | 0.020(1) | 0.015(1) |
| Sn \( U_{iso} \) | 0.00499(5) | 0.00609(6) | 0.0078(1) | 0.00946(7) | 0.01099(9) | 0.01276(9) | 0.0147(2) | 0.0164(1) |

\( \chi^2 \) = 8.6, \( wR_p \) = 3.1, \( R_p \) = 3.6, \( R_f^2 \) = 5.4

The 293 K pattern was collected outside of the furnace.
identical $S(T)$ is expected, and the familiar expressions for $S$ and $n$ can be used:

$$S = \frac{k}{e} \left( \frac{2F_1}{F_0} - \eta \right)$$

(1)

$$n = 4\pi \left( \frac{m^* kT}{h^2} \right)^{3/2} F_{1/2}$$

(2)

Here, $k$ is Boltzmann's constant, $e$ the electron charge, $h$ is Planck's constant, $m^*$ is the effective carrier mass, $\eta$ is the reduced Fermi level measured from the conduction band minimum ($E_F/kT$), and $F_1$ and $F_2$ are the Fermi integrals, which were evaluated numerically ($\epsilon$ is the reduced energy):

$$F_1(\eta) = \int_0^\infty \frac{e^\epsilon d\epsilon}{1 + e^{\epsilon - \eta}}$$

(3)

The magnitude of $S$ is therefore only a function of $\eta$ (eqn (1)), while $m^*$ can be evaluated using the $\eta$ value gained from the experimental $S$, and the chemical carrier concentration (eqn (2)). The calculated carrier concentrations were $(z = 0.005, 9.15 \times 10^{25} \text{ m}^{-3})$, $(z = 0.01, 1.83 \times 10^{26} \text{ m}^{-3})$ and $(z = 0.02, 3.66 \times 10^{26} \text{ m}^{-3})$ and the obtained $m^*$ values are $2.33 m_e (z = 0.005), 2.51 m_e (z = 0.01)$ and $2.64 m_e (z = 0.02)$ where $m_e$ is the electron mass. These values are in good agreement with published data for ZrNi$_2$Sn HH alloys. As a further test of the validity of the SPB model we calculated the predicted temperature dependence of $S$ using the constant carrier approximation, and these curves are plotted in Fig. 5b. There is a good agreement below 400 K, while $S$ is overestimated above this temperature, which typically signals the presence of minority charge carriers. The $\rho(T)$ and $S(T)$ for the non-Sb doped (non-degenerate) samples containing Ti are shown in Fig. 5c and d. The $\rho(T)$ follows a thermally activated temperature dependence over the entire measured temperature interval (300–730 K). The fitted bandgap values are $E_g = 0.12–0.15$ eV (see Table 5) which is much smaller than the 0.45 eV gap predicted from first principles calculations. The observation of reduced bandgaps is common for HHS, and points towards the presence of in-gap states due to structural disorder and/or excess Ni. Similar bandgap values are observed for SPS processed Ti$_{0.25}$Zr$_{0.75}$Ni$_3$Sn samples, demonstrating that these values are not affected strongly by porosity. The $S(T)$ for these compositions shows a gradual monotonous decrease (Fig. 5d). By contrast, the $S(T)$ for samples containing Zr and Hf are characterised by a maximum near 350 K ($X =$ Zr) and 550 K ($X =$ Zr$_{0.98}$Hf$_{0.02}$, Hf), followed by a rapid decrease (Fig. 5f). This rapid decrease is caused by the onset of minority carrier (p-type) conduction, which is also evident in the $\rho(T)$ data (Fig. 5e). The maximum for $X =$ Zr is lower than reported in the literature (550 K), and this may be linked to the presence of impurity phases in this sample (Table 1). The In $\rho(T) – 1/T$ data for the samples without Ti are shown in Fig. 5e, and reveals the presence of similar bandgap values below the onset of minority carrier conduction (0.07–0.16 eV, Table 5). In addition, the Goldsmid–Sharp formula was used to extract a value for the bandgap from the $S(T)$ data. These are larger and fall between 0.3–0.4 eV (Table 5). The discrepancy between the bandgap values from $\rho(T)$ and $S(T)$ data has recently been discussed and results from the mobility difference between electrons and holes, and leads to overestimates when using the classical Goldsmid–Sharp equation. The bandgap values observed here are consistent with recently reported values of 0.13 eV for ZrNiSn from room temperature optical measurements.

**Discussion**

There is now substantial evidence confirming that there is no solubility of excess Ni in the HH structure, and that segregation into a HH matrix and FH inclusions occurs. We have previously reported extensive electron microscopy characterisation of a TiNi$_{1.05}$Sn sample which was prepared in an identical manner to the samples discussed here (e.g. by solid state reactions without post synthesis processing). This revealed that the excess Ni is finely dispersed within the matrix with a limit < 2 nm on the size of the nano-inclusions. We also demonstrated that ~2% additional Ni was present in all TiNi$_r$Sn samples investigated. This was attributed to the stability of competing Ti–Sn binary phases. The observation
of 2–3% excess Ni for the samples containing Ti, and the absence of excess Ni for samples with X = Zr, Hf (Tables 1 and 2), is in keeping with this earlier observation and emphasises the need for a tight control of the synthesis conditions. One of the most striking features of the transport data is the gradual decrease of $S(T)$ for samples containing Ti, and the absence of an ambipolar transition (the onset of minority carrier conduction). This occurs for both TiNiSn and the multiphase samples, suggesting that the phase segregation has limited impact. Density functional theory calculations reveal similar bandstructures for X = Ti, Zr and Hf with an indirect gap of $0.45 \, \text{eV}$ between the G and X points, and it is therefore not immediately apparent why $S(T)$ behaves differently. As the experimental bandgaps are also rather similar, it is tempting to link the absence of minority carrier conduction to the presence of electron doping from the 2–3% excess Ni in these samples. However, literature data reveals that the ambipolar transition survives in ZrNi$_{1+y}$Sn samples with 6% excess Ni, suggesting that there may not be a link to the amount of excess Ni, or that it may depend on the exact nature of the phase segregation. The ZrNi$_{1+y}$Sn samples were prepared from the melt.
and it is likely that this will cause a difference in the degree of segregation of the FH phases. This can have a significant impact on the properties: for example the changes in $S(T)$ and $\rho(T)$ in the TiNi$_{1-x}$Sn series with finely dispersed excess Ni are consistent with conventional doping, whereas enhancements in $S$ due to carrier filtering were observed in hot-pressed compositions containing well-defined FH inclusions. Further work is needed to fully elucidate the difference in behaviour between the samples that contain Ti and those that do not. Another plausible explanation is that the difference in behaviour is linked to a microstructural effect that only occurs in the presence of Ti, and is not directly linked to either the multiphase behaviour or the presence of excess Ni. The $S(T)$ for degenerately doped Ti$_{0.5}$Zr$_{0.5}$NiSn$_{1-x}$Sb$_x$ samples can be modelled adequately using a single parabolic band model with the mobility limited by alloy scattering. The observation of carrier transport limited by alloy scattering is reasonable as the compositional changes due to phase segregation of the X-site metals occur over relatively large length-scales (> 5 μm). These distances are greater than typical electron mean free paths, and are therefore not expected to impact strongly on the carrier transport.

Neutrons probe a larger sample volume than X-rays, and the phase distributions in the multiphase samples (Fig. 3) are significantly narrower than determined from X-ray data. The present data are more representative of the bulk, suggesting that 3–4 discrete phases are indeed present with the broadening of the individual HH X-ray and neutron profiles (quantified as $\Delta x$) at least partially due to microstructural effects and not solely linked to compositional variations. Some of the refined compositions fall outside of the thermodynamic limits for mixing of the X-metals, suggesting that the final observed phase distribution is kinetically controlled. The temperature-dependent neutron diffraction study into TiNiSn and Ti$_{0.5}$Hf$_{0.5}$NiSn showed no significant change in phase-distribution as the temperature was increased (Fig. 4, Tables 3 and 4). In addition to the temperature steps reported in Table 4, this sample was held at 600 °C for 6 hours and re-measured at regular intervals. The reflections remained the same shape throughout, indicating no change in the distribution. In terms of application this highlights that these materials show stability to prolonged exposure to high temperatures, which is of vital importance for thermoelectric materials. The variable temperature data also afforded the extraction of a reliable estimate of the Debye temperatures for TiNiSn ($\theta_D = 367(2)$ K) and Ti$_{0.5}$Hf$_{0.5}$NiSn ($\theta_D = 317(2)$ K).

The main conclusion is that XNiSn half-Heuslers samples are susceptible to phase segregation as exemplified by the presence of distinct half-Heusler compositions for samples with mixtures of X metals, and full-Heusler domains in samples containing Ti. The onset of minority carrier conduction observed for XNiSn samples with Zr and Hf is suppressed in the samples containing Ti.

Acknowledgements

The authors thank the EPSRC (grant EP/J000884/1 and EP/K036408/1), and the STFC for the provision of neutron beam time at ISIS. D. A. MacLaren is acknowledged for scientific discussions and preliminary TEM data.

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