Intrinsic point defects in thermoelectric half-Heusler alloys

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Abstract

Single phase half-Heusler microstructure of ZrNiSn , $(\text{Zr}_{0.5}, \text{Hf}_{0.5})\text{NiSn}$, and $\text{Zr}(\text{Ni}, \text{Co}_{0.2})\text{Sn}$ alloys was found to contain high density of Heusler lattice bands with 2-7 nm widths. These nanoscale Heusler lattice bands were originated from clustering of Ni and/or Co antisites *via* occupation of structural vacancies by excess Ni or (Ni + Co) concentrations. The presence of these lattice point defects and their subsequent clustering could result in the reduction of thermal conductivity of the half-Heusler alloys.

The thermoelectric properties of half-Heusler (HH) semiconductor compounds are closely related to their electronic structure, which in turn is sensitive to deviation from stoichiometric composition. Current study is aimed at investigating microstructural changes, particularly generation of lattice point defects, which is often resulted from the deviation of HH stoichiometric composition. Point defects in HH alloys have been reported to reduce thermal conductivity (κ) and band gap (E_g), alter electrical transport, and possibly even induce half-metallicity [1-7]. Many have reported a variety of point defects in XYSn ($\text{X}=\text{Ti}, \text{Zr}, \text{Hf}$; $\text{Y}=\text{Ni}, \text{Co}$) HH alloys, including Ni antisites (where Ni occupies structural vacancies) [8], X-Sn swap disorders [1], and vacancies [6]; Ni antisites have been found the most energetically favorable [2,8,9]. In our previous studies [10,11], we showed in HH alloys that Ni antisites tend to cluster, forming Heusler (H) phase nanoprecipitates containing slight excesses of Ni. However, subsequent investigations suggested that the antisite clustering, prior to inducing the Heusler nanoprecipitation, might generate an intermediate nanoscale microstructure. Effect of the nanoscale microstructure will also be discussed mainly in conjunction with κ of the alloys that were determined previously by Kimura *et al.* [12,13].

HH (C1b -type) and H (L2_1 -type) crystal structures are formed by four interpenetrating face-centered cubic (fcc) sublattices located at I-(0, 0, 0), II-(1/4, 1/4, 1/4), III-(1/2, 1/2, 1/2), and IV-(3/4, 3/4, 3/4), see Fig. 1 in Ref. [11]. In both XYSn -HH and XY_2Sn H alloys, sublattices I and III are occupied by X and Sn atoms, respectively,

37 forming an energetically stable NaCl substructure. The HH structure becomes more
 38 stable when either the II or IV sublattice is occupied by Ni atoms while the other is
 39 vacant [1,8]. In the current letter we refer to the vacant site of the HH structure as a
 40 structural vacancy (SV) to avoid confusion with the vacancy point defect. In the H
 41 structure, both the II and IV sublattices are occupied by Ni atoms. The HH and H
 42 structures can be distinguished by their $\{111\}_{\text{HH}}$ lattice structure, as demonstrated in our
 43 previous study [10].

44 We chose three alloys for the current study: ZrNiSn, (Zr_{0.5}, Hf_{0.5})NiSn, and Zr(Ni,
 45 Co_{0.2})Sn. A previous study found that, in the Zr(Ni, Co_{0.2})Sn alloy, the additional Co
 46 atoms preferentially occupied the SVs of the HH structure [12]; we define these point
 47 defects as Co antisites. The alloys were prepared by arc melting, followed by directional
 48 solidification by using optical floating zone melting. Alloys prepared by this method
 49 have grain sizes well over 300 μm . Phase identity on microstructure of the alloys was
 50 determined by X-ray diffraction (XRD). In the current letter, the compositions of these
 51 alloys were analyzed by using a electron-probe microanalyzer (EPMA), and their
 52 microstructures were characterized by using transmission electron microscopy (TEM)
 53 and high-resolution TEM (HRTEM), operated at 200 kV. Our TEM specimen
 54 preparation has been described elsewhere [11].

55 Compositions analyses by EPMA have found that the alloys are HH phase with
 56 slight deviations from stoichiometric compositions, Zr_{0.95}Ni_{1.09}Sn, (Zr_{0.5},
 57 Hf_{0.5})_{0.91}Ni_{1.09}Sn and Zr_{0.95}(Ni, Co_{0.16})Sn, see Table 1. Note the trend in composition
 58 deviation: the Zr and (Zr + Hf) concentrations were often slightly lower than the
 59 stoichiometric value (i.e., molar ratio <1) and accordingly the Ni and (Ni + Co)
 60 concentrations were slightly higher (i.e., molar ratio >1). Because of the additional Co
 61 in the Zr(Ni, Co_{0.2})Sn alloy, we expected the (Ni + Co) molar ratio to be greater than 1.
 62 Similar trends in compositional deviations have been noted in HH alloys fabricated with
 63 other techniques (e.g., levitation melting) [14]. The XRD profiles in Fig. 1(a) have
 64 further confirmed the three alloys, ZrNiSn, (Zr_{0.5}, Hf_{0.5})NiSn and Zr(Ni, Co_{0.2})Sn alloys,
 65 are single HH phase. Nevertheless, detection of any microstructural changes in these
 66 alloys induced by the subtle deviation from HH stoichiometric composition was rather
 67 difficult using XRD and scanning electron microscopy. In contrast, using TEM we did
 68 observe microstructural changes, as shown in Fig. 1.

69 Bright-field TEM images in Figs. 1(b)-(d) show the HH microstructure of the
 70 ZrNiSn, (Zr_{0.5}, Hf_{0.5})NiSn and Zr(Ni, Co_{0.2})Sn alloys, respectively. Their microstructure
 71 was found to contain a high density of strain contrast that resembled a “modulated”-like
 72 structure with a very small spacing (<10 nm). Using HRTEM, it was found that the

modulated structure originated from lattice distortions throughout the HH matrix, as shown in Figs. 2(a)–(c). These lattice distortions also contributed to splitting of the diffraction spots in the corresponding $[110]_{\text{HH}}$ fast Fourier transform (FFT) patterns; these distortions are indicated by arrows in the insets of the enlarged diffraction spots in Figs. 2(a)–(c). This behavior implies that the lattice distortions must be caused by localized variation of lattice sizes within the HH matrix. To further analyze the distorted lattice structure, we performed inverse FFT (IFFT) image processing, as shown in Figs. 2(d)–(f). These IFFT images reveal that the lattice distortions are not randomly distributed; they are “grouped” together, forming networks of small distorted lattice bands, 2–7 nm wide, throughout the HH matrix. The nanoscale bands are coherent with the surrounding HH matrix, exhibit no preferred orientation, and have widths that do not vary appreciably across the three alloys. However, the spacing between the nanoscale distorted lattice bands appears to be larger in the ZrNiSn and $(\text{Zr}_{0.5}, \text{Hf}_{0.5})\text{NiSn}$ alloys (≈ 7 and 8 nm, respectively) than in the $\text{Zr}(\text{Ni}, \text{Co}_{0.2})\text{Sn}$ alloy (≈ 5 nm), indicating in the latter a larger volume fraction of bands.

Figures 3(a)–(c) show sections of the IFFT images, which consist of the distorted and HH lattices. The structures of the distorted lattice bands are *i*, *iii*, and *v*, while the corresponding HH lattice structures are *ii*, *iv*, and *vi*. By analyzing the *i*, *iii*, and *v* configurations, we found they most resembled the lattices of H-phase structures. This result suggests that the SVs in the supposed HH structure are occupied, most likely by excess Ni atoms in the ZrNiSn and $(\text{Zr}_{0.5}, \text{Hf}_{0.5})\text{NiSn}$ alloys, forming Ni antisites as shown schematically in Figs. 3(a) and 3(b), and excess Ni and Co atoms in the $\text{Zr}(\text{Ni}, \text{Co}_{0.2})\text{Sn}$ alloy, forming Ni and Co antisites as shown schematically in Fig. 3(c). We only considered Ni point defects and Co antisites here because their formations were more energetically favorable than other point defects [2,3,8,9]. Figures 1-3 further suggest clustering in the HH matrix of Ni and/or Co antisites, forming the larger H-lattice bands. The coexistence of nanoscale H-lattice bands and the HH matrix also suggests that the HH and H phases lack mutual solubility, agreeing with predictions by Kirievsky *et al.* [9]. Although these nanoscale bands were showing similar H-phase lattice structure to those of the $\{001\}_{\text{HH}}$ H-phase nanoscale precipitates [10,11,15], however, their morphologies and length scales are rather different. The former has rather irregular morphology with inter-band spacing often less than 10 nm. The H-phase nanoscale precipitates on the other hand, have tendency to orientate parallel to $\{001\}_{\text{HH}}$ and their inter-precipitate spacing was much larger, ranging between 5 - 250 nm, depending on size and morphology of the H-phase precipitates. The absent of H-phase precipitates indicates that the excess Ni and (Ni + Co) in the ZrNiSn, $(\text{Zr}_{0.5}, \text{Hf}_{0.5})\text{NiSn}$ and $\text{Zr}(\text{Ni},$

109 $\text{Co}_{0.2}\text{Sn}$ alloys must be below supersaturation limit for H-phase precipitation. Were the
 110 Ni or (Ni + Co) to exceed the supersaturation limit, the H-phase nanoscale bands could
 111 possibly act as precursors for the H-phase precipitation.

112 Because the H-lattice bands form by clustering of Ni and Co antisites, the band
 113 microstructure would be affected by deviations from HH stoichiometry by adding
 114 excess Ni or (Ni + Co). There was about twice as much excess (Ni + Co) present in
 115 $\text{Zr}(\text{Ni}, \text{Co}_{0.2})\text{Sn}$ as excess Ni in ZrNiSn and $(\text{Zr}_{0.5}, \text{Hf}_{0.5})\text{NiSn}$ (see Table 1), which may
 116 explain the larger volume fraction of H-lattice bands in $\text{Zr}(\text{Ni}, \text{Co}_{0.2})\text{Sn}$. In other words,
 117 the number of Ni and Co antisites in $\text{Zr}(\text{Ni}, \text{Co}_{0.2})\text{Sn}$ was about twice the number of Ni
 118 antisites in ZrNiSn and $(\text{Zr}_{0.5}, \text{Hf}_{0.5})\text{NiSn}$. However, our analysis of the lattice structure
 119 of the HH matrix (Fig. 3) suggests that the actual density of Ni and/or Co antisites in
 120 each alloy is likely much higher. The lattice configurations *ii*, *iv*, and *vi* of the HH
 121 matrix resemble the corresponding configurations of the HH lattice (see schematics in
 122 Figs. 3(a)–(c)), but this is not always the case. In some regions of the HH matrix, the
 123 lattice structure resembles the NaCl structure, indicating that the supposedly Ni- and/or
 124 Co-occupied lattice sites of the HH structure are vacant (we term vacant sites as
 125 vacancy defects). This observation is interesting because, in HH alloys slightly rich in
 126 Ni or (Ni + Co), the NaCl structure is energetically less favorable than the HH and H
 127 structures according to theory [8,9]. Such a discrepancy may be caused by thermal
 128 fluctuations in the alloys. Unlike theoretical calculations made at ground state and 0 K,
 129 we performed our experiments near room temperature, in which case atoms vibrate
 130 from added thermal energy. In this case we anticipate that pairs of Ni/Co antisites and
 131 vacancy defects, where Ni and/or Co atoms swap with SVs in the HH structure, will be
 132 more energetically favorable than other defects and thus will form more easily. We
 133 presume that these Ni and/or Co antisites cluster together, contributing to the formation
 134 of adjacent H-lattice bands. The remaining vacancy defects in the HH matrix, however,
 135 would appear as an NaCl lattice structure. The formation of NaCl, HH, and H lattice
 136 structures (from the generation and clustering of Ni and Co antisites as well as vacancy
 137 defects in the alloy) would cause local variations of lattice size (i.e., smallest size in
 138 NaCl and largest in H). These variations would generate coherency strain, seen as the
 139 modulated structure in the HH microstructure. We also believe that this local variation
 140 of lattice size caused the splitting of diffraction spots in the $[110]_{\text{HH}}$ FFT patterns, as
 141 shown in Figs. 2(a)–(c).

142 Based on the HRTEM images in Figs. 2–3, we estimated the coherency strain
 143 generated between the HH (or NaCl) and H lattices to be $\approx 0.1\text{--}0.3\%$. This coherency
 144 strain might contribute to phonon scattering process and hence a reduction of thermal

conductivity (κ) of the alloys. This may explain the κ (at room temperature) of the ZrNiSn, (Zr_{0.5}Hf_{0.5})NiSn, and Zr(Ni,Co_{0.2})Sn alloys were comparatively low, *i.e.* 6.3, 3.1, and 4.2 Wm⁻¹K⁻¹, respectively [12,13]. Note that the κ of Zr(Ni,Co_{0.2})Sn is near that of (Zr_{0.5}, Hf_{0.5})NiSn, demonstrating that κ can be reduced in these HH alloys by introducing the nanoscale H-lattice bands. This behavior occurs despite the minimal phonon scattering by grain boundaries (*i.e.*, because the grain-size diameter is >300 μ m) and the lack of strain and mass scattering effects caused by addition of heavy elements such as Hf. The length scale of the H-lattice bands ($\approx$ 5–8 nm) are similar order to the phonon mean free path in these HH alloys (a few nm), suggesting that the H-lattice bands can reduce κ in these alloys.

In this letter, we have explained the formation of H-lattice bands within the HH microstructure to be caused by clustering Ni and/or Co antisites, with the extent of formation closely related to the deviation from stoichiometric composition. However, Table 1 also indicates that the Zr and (Zr + Hf) concentrations in the alloys were deficient. This observation suggests other types of point defects, particularly Zr–Sn and Hf–Sn atomic swap disorders (*i.e.*, swapped atomic positions between fcc sublattices I and III), as suggested by Ogut et al. [1] and Qiu et al. [5]. However, we cannot yet confirm this point defect. Nevertheless, note that many of the lattice sites occupied by Zr and Sn, particularly in Zr(Ni, Co_{0.2})Sn, were slightly displaced from their supposedly NaCl substructure sites. The lattice displacement could have been caused either by the coherency strain field exerted by adjacent H-lattice bands or by atomic disorder. High-resolution analytical microscopy such as high-angle annular dark-field scanning transmission electron microscopy would be necessary to further investigate this issue.

In summary, we have provided direct experimental evidences of lattice point defects, Ni and/or Co antisites, and described their generations were closely related to the slightly off-stoichiometric HH composition, *i.e.* excess Ni or (Ni + Co), in three HH alloys, ZrNiSn, (Zr_{0.5}, Hf_{0.5})NiSn, and Zr(Ni, Co_{0.2})Sn. The excess Ni and (Ni + Co) promoted the formation of nanoscale H-lattice bands within the HH matrix via clustering of Ni and/or Co antisites; the extent of this formation was also closely related to the deviation from stoichiometry of Ni and (Ni + Co) in the alloys. Thermal fluctuations could have also contributed to the formation of the nanoscale H-lattice bands. As a result of the generation and clustering of antisites and vacancy defects, we observed localized formation of NaCl, HH, and H lattice structures in the HH microstructure. Consequently, we found high densities of coherency strain in the HH microstructure, was seen as modulated structure. This coherency strain is capable of reducing κ in the alloys by enhancing phonon scattering. These antisites and vacancy

defects may have reduced the band gaps of these alloys below reported theoretical values.

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Table 1. Composition analyses of the HH alloys by EPMA.

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Fig. 1. (a) XRD profiles indicate the ZrNiSn, (Zr_{0.5}, Hf_{0.5})NiSn and Zr(Ni, Co_{0.2})Sn

217 alloys, are nearly single HH phase. Bright-field TEM images reveals the modulated-like
 218 HH microstructure in the (b) ZrNiSn, (c) (Zr_{0.5}, Hf_{0.5})NiSn, and (d) Zr(Ni, Co_{0.2})Sn
 219 alloys. The enlarged images in the insets reveal the modulated structures.

220

221 Fig. 2. HRTEM images that reveal the HH lattice structure of (a) ZrNiSn, (b) (Zr_{0.5},
 222 Hf_{0.5})NiSn, and (c) Zr(Ni, Co_{0.2})Sn. The insets show the corresponding [110]_{HH} FFT
 223 patterns. The arrows indicate splitting of the diffraction spots. The inverse FFT images
 224 corresponding to (a), (b), and (c) are shown in (d), (e), and (f), respectively. The
 225 distorted lattice bands in the HH matrix are enclosed by dashed lines and highlighted by
 226 arrows.

227

228 Fig. 3. Enlarged inverse FFT images, revealing the lattice configurations of the distorted
 229 lattice bands (*i*, *iii*, and *v*) and the HH matrix (*ii*, *iv*, and *vi*) in (a) ZrNiSn, (b) (Zr_{0.5},
 230 Hf_{0.5})NiSn, and (c) Zr(Ni, Co_{0.2})Sn. The schematics show our analyses of the lattice
 231 configurations. The symbol *SV* represents structural vacancy of the HH crystal structure.

232

Fig. 1. (a) XRD profiles indicate the ZrNiSn, $(\text{Zr}_{0.5}, \text{Hf}_{0.5})\text{NiSn}$ and $\text{Zr}(\text{Ni}, \text{Co}_{0.2})\text{Sn}$ alloys, are nearly single HH phase. Bright-field TEM images reveals the modulated-like HH microstructure in the (b) ZrNiSn, (c) $(\text{Zr}_{0.5}, \text{Hf}_{0.5})\text{NiSn}$, and (d) $\text{Zr}(\text{Ni}, \text{Co}_{0.2})\text{Sn}$ alloys. The enlarged images in the insets reveal the modulated structures.

Fig. 2. HRTEM images that reveal the HH lattice structure of (a) ZrNiSn, (b) (Zr_{0.5}, Hf_{0.5})NiSn, and (c) Zr(Ni, Co_{0.2})Sn. The insets show the corresponding $[110]_{\text{HH}}$ FFT patterns. The arrows indicate splitting of the diffraction spots. The inverse FFT images corresponding to (a), (b), and (c) are shown in (d), (e), and (f), respectively. The distorted lattice bands in the HH matrix are enclosed by dashed lines and highlighted by arrows.

Fig. 3. Enlarged inverse FFT images, revealing the lattice configurations of the distorted lattice bands (i , iii , and v) and the HH matrix (ii , iv , and vi) in (a) ZrNiSn, (b) $(Zr_{0.5}, Hf_{0.5})NiSn$, and (c) $Zr(Ni, Co_{0.2})Sn$. The schematics show our analyses of the lattice configurations. The symbol SV represents structural vacancy of the HH crystal structure.

Table 1. Composition analyses of the HH alloys by EPMA.

Nominal composition	Chemical composition (at%)					Molar ratio
	Zr	Hf	Ni	Co	Sn	
ZrNiSn	31.2	-	35.9	-	32.9	Zr:Ni:Sn = 0.95:1.09:1
(Zr _{0.5} ,Hf _{0.5})NiSn	15.4	15.0	36.3	-	33.3	(Zr+Hf):Ni:Sn = 0.91:1.09:1
Zr(Ni,Co _{0.2})Sn	30.5	-	32.2	5.2	32.1	Zr:(Ni+Co):Sn = 0.95:1.17:1