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Engineering the Thermoelectric Transport in Half-Heusler Materials through a Bottom-Up Nanostructure Synthesis

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Half-Heusler (HH) alloys are among the best promising thermoelectric (TE) materials applicable for the middle-to-high temperature power generation. Despite of the large thermoelectric power factor and decent figure-of-merit ZT (\approx 1), their broad applications and enhancement on TE performance are limited by the high intrinsic lattice thermal conductivity ($\kappa_{\rm L}$) due to insufficiencies of phonon scattering mechanisms, and the fewer powerful strategies associated with the microstructural engineering for HH materials. This study reports a bottom-up nanostructure synthesis approach for these HH materials based on the displacement reaction between metal chlorides/bromides and magnesium (or lithium), followed by vacuum-assisted spark plasma sintering process. The samples are featured with dense dislocation arrays at the grain boundaries, leading to a minimum κ_1 of ≈ 1 W m⁻¹ K⁻¹ at 900 K and one of the highest ZT (\approx 1) and predicted η (\approx 11%) for n-type Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03}. Further manipulation on the dislocation defects at the grain boundaries of p-type Nb_{0.8}Ti_{0.2}FeSb leads to enhanced maximum power factor of 47×10^{-4} W m⁻¹ K⁻² and the predicted η of \approx 7.5%. Moreover, vanadium substitution in FeNb_{0.56}V_{0.24}Ti_{0.2}Sb significantly promotes the η to \approx 11%. This strategy can be extended to a broad range of advanced alloys and compounds for improved properties.

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A variety of structural defects from atomic to micrometer scales in especially nanostructured alloys or compounds, such as high-strength lightweight titanium alloy Ti185.^[1] aluminum- or magnesium-based alloys NH-7075 and NH-5083,^[2] and particularly thermoelectric materials,^[3] play vital roles in improving the performance. Thermoelectric (TE) materials can realize direct conversions between heat and electricity, and the maximum energy conversion efficiency (η_{max}) is primarily governed by the thermoelectric figure-of-merit $ZT (ZT = (S^2 \sigma / \kappa)T)$, where S, σ , κ , and T are the Seebeck coefficient, electrical conductivity (inverse of electrical resistivity $\sigma = 1/\rho$, thermal conductivity, and absolute temperature, respectively).

Recent studies have witnessed the fast growth of TE materials. Among the notable TE material systems, such as Bi_2Te_3 ,^[4,5] PbTe,^[6] AgSbTe₂,^[7] Zn₄Sb₃,^[8] Zintl phase,^[9] and SiGe,^[10,11] as well as

the recently emerged ionic conductor Cu₂Se,^[12] filled skutterudites,^[13] α -MgAgSb,^[14] SnSe,^[15] BiCuSeO,^[16] Mg₂Si_{1-x}Sn_x,^[17,18] etc., half-Heusler (HH) materials are the most promising ones in middle-to-high temperature (600–900 K) for power generation. Semiconducting HHs have the appropriate band gap size for applications from middle to high temperature^[19] (for instance, 0.51 eV for ZrNiSn,^[20] and 0.54 eV for NbFeSb).^[21] In the context of thermoelectric quality factor $\left(B = \frac{2k_B^2\hbar}{3\pi} \frac{N_v C_i T}{m_1^* E_{def}^2 \kappa_L}\right)$,^[22] HH materials exhibit superior electrical transport proper-

ties (for instance, the maximum power factors for n-type $Hf_{0.5}Zr_{0.5}NiSn_{0.99}Sb_{0.01}$ and p-type $FeNb_{0.95}Ti_{0.05}Sb$ reach 50 × 10^{-4} and 106×10^{-4} W m⁻¹ K⁻²,^[23,24] respectively, which outperforms the PbTe-based materials^[6] and Na-doped SnSe).^[25] Moreover, HH materials possess high thermal stability and superior mechanical strength over most other TE materials.^[26,27] Therefore, HH materials have become the focus of increasing interest in thermoelectric research.

HHs have a potential to reach higher *ZT*s due to the very high power factor if their intrinsic high thermal conductivity ($\approx 10 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K)^[28] dominated by phonons can be significantly reduced. Phonon scattering can be estimated by the Callaway model based on relaxation time approximation;^[29] the



existing phonon scattering mechanisms in the best HH materials is comprised of Umklapp process, grain boundary, point defect, and electron-phonon scatterings. However, despite of the reduction in $\kappa_{\rm L}$ obtained by all above mechanisms,^[30,31] there is still a large room for further κ_L reduction given the amorphous limit of κ_{\min} is $\approx 1 \text{ W m}^{-1} \text{ K}^{-1}$ for typical HH TE materials calculated by Cahill's formulation.^[32,33] To achieve this goal, it seems that new phonon scattering mechanism is needed for HH materials. It is important to note that the existing scattering mechanisms in HH materials target mostly at the high-frequency phonons through Umklapp and electronphonon scatterings, and the substantial portion of phonons in the low to middle frequency (≤30 THz) range have been overlooked. Therefore, a new mechanism, such as dislocation arrays at the grain boundaries,^[4] might be efficient in scattering low to middle frequency phonons.

Fabricating dense dislocation arrays at the grain boundaries for HH materials as well as in other allovs is a great challenge due to the coexistence of multiple thermodynamic phases constituted by more than three elements during the nonequilibrium dynamic synthesis process, which is believed to be far more complicated than that in Bi_{0.5}Sb_{1.5}Te₃ system^[4] and in the $Pb_{1-x}Sb_{2x/3}$ Se solid solutions.^[34] In this paper, we proposed a bottom-up nanostructure synthesis approach for HH materials based on the displacement reaction between metal chlorides/bromides and magnesium (or lithium), followed by vacuum-assisted spark plasma sintering (SPS) process. The new HH samples are featured with dense dislocation arrays at the grain boundaries, and these dislocation defects can be manipulated to adjust the thermal and electrical transports through the sintering process during SPS, leading to significantly lowered κ_L and one of the highest ZT (≈ 1) for n-type Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03}, as well as enhanced thermoelectric performance for p-type Nb_{0.8}Ti_{0.2}FeSb and FeNb_{0.56}V_{0.24}Ti_{0.2}Sb. This strategy can be extended to other good TE materials for improved properties.

2. Results and Discussion

Schematic diagram of the synthesis of a series of bulk HH samples is illustrated in Figure 1. As shown in the figure, based on a simple displacement reaction between metal chlorides/ bromides and the metal magnesium (or lithium), stoichiometric ratios of metal chloride or bromide powder and Mg/Li metal granules are put into the stainless steel ball milling jar, followed by 2-5 h high-energy ball milling process. During the ball milling process, a mixture of multiple metal nanoparticles and MgX₂/LiX were formed, as can be identified by the X-ray diffraction (XRD) results shown in Figure S1a (Supporting Information). However, removing the MgX₂/LiX byproducts from the metal nanoparticles may be difficult, which is why this method was not heavily reported. Interestingly, we discovered that the MgX₂/LiX byproducts can be expelled by vacuum-assisted SPS process, which can be ascribed to the lower melting point and high vapor pressures of MgX₂/ LiX. Indeed, uniformly distributed MgX₂/LiX powder can be observed all around the surface of the graphite dies and the vacuum chambers after the spark plasma sintering process. The obtained HH bulk samples (as shown in the photo images in lower left of Figure 1) exhibit the same appearance and phase purities, and enhanced thermoelectric properties (particularly for p-type) as those made by the conventional metal alloying method, which will be discussed in the following context.

Seven typical HH thermoelectric materials were synthesized by the new approach, and for each composition, three samples have been made with the sintering time of 5 min, 20 min, and 4 h, respectively. The obtained bulk samples were first characterized by powder XRD, typically for the samples being sintered for 20 min, as shown in **Figure 2a**. The XRD for 5 min sintered samples were shown in Figure S1b (Supporting Information). All patterns corresponding to six compositions in Figure 2a and Figure S1b (Supporting Information) can be indexed to the MgAsAg prototype structure (space group, $F\overline{43m}$) with the



Figure 1. Schematic illustration of the synthesis process of half-Heusler materials based on displacement chemical reactions and spark plasma sintering process.





Figure 2. a) Room temperature powder X-ray diffraction patterns for seven half-Heusler samples. The inset shows the crystal structure model of half-Heusler and the corresponding space group (S.G.); b) SEM images and EDX mappings of the compositional element distribution for Nb_{0.8}Ti_{0.2}FeSb (NTFC-20min); and c) Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03} (HZNSS-20min).

representative formula of XYZ.^[35] The structures is composed of three interpenetrating *fcc* sublattices, each of which is occupied by the X, Y, and Z atoms, as shown in the inset of Figure 2a. With respect to ZrCoSb and Zr_{0.44}Hf_{0.44}Ti_{0.12}CoSb_{0.85}Sn_{0.15}, two minor peaks at $2\theta \approx 28.6^{\circ}$ and 31.5° can be observed, as can be seen from the enlarged XRD pattern between 25° and 35° in Figure S1c (Supporting Information), which is believed to originate from the Zr/Hf oxides during the preparation. In addition, the impurities in above two samples cannot be easily removed, which would induce poor electrical transport properties for these two compositions. Meanwhile, no visible peaks of the impure phases can be observed for other four compositions. Thus, in this work, we focused on p-type Nb_{0.8}Ti_{0.2}FeSb (NTFC-20min) and n-type Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03} (HZNSS-20min) samples being sintered for 20 min during SPS to elucidate the underneath relations between their rich varieties of structural defects and the TE properties, particularly on the phonon transport.

Meanwhile, in order to check the loss of materials due to liquid expelling in the SPS process, we use the inductively coupled plasma mass spectrometry (ICP-MS) to confirm the accurate elemental compositions. The results indicate that the actual compositions of the (NTFC-20min) and (HZNSS-20min) bulk samples are consistent with the stoichiometric ratio of the starting materials within the standard deviation of 1%-3% (Table S1, Supporting Information). Furthermore, energy dispersive X-ray spectroscopy (EDX) mapping analysis indicates that the compositional elements distributed uniformly, as shown in Figure 2b,c. In Figure 2b,c and Figure S2 (Supporting Information), from the scanning electron microscopy (SEM) images of the cross sections, we can see that the grains are relatively compact, while the grain size are around 150-400 nm for NTFC-20min, and 500 nm in average for HZNSS-20min. These grain sizes and morphologies are similar to those conventionally sintered samples reported in the literature,^[30] the details of the microstructure in the lattice and atomic level are investigated using transmission electron microscopy (TEM) technique.

The morphology of the grain boundary structures in NTFC-20min and HZNSS-20min is displayed in the TEM images as shown in Figure 3a-l. Generally, in comparison to the nanostructured HH TE materials synthesized by conventional process,^[23,28] two kinds of dislocations with significantly high densities were found at the grain boundaries of these two samples. Similar but not identical to the grain boundary structures as observed in Bi0.5 Sb1.5 Te3 synthesized by the liquidphase compacting process,^[4] TEM images in Figure 3b,h, and Figure 3c,e,j,k reveal the existence of twist-type grain boundaries and Mioré patterns (up to 15 nm wide), respectively, for both samples. Since these two structures are indication of highly crystalline with clean grain boundaries for both samples, the presence of dislocation arrays are required to lower the energy at the grain boundaries for these samples.^[36] These dislocation arrays are described in details individually in the following.

Figure 3a,b displays the low-magnification TEM image of NTFC-20min and the enlarged view of boxed region in (a), respectively. Dislocation arrays with the periodic misfit spacing of 2.5 nm were observed in high-resolution TEM (HRTEM) image (Figure 3c), which can be viewed as a result of the compensation effect for the misorientation between two adjacent grains on the (010) atomic planes along the dislocation arrays marked in red in Figure 3d (as the inverse fast Fourier-transformed (IFFT) image for Figure 3c). In addition, the Burgers vector of each dislocation in Figure 3d is identified as $B_{\rm D} = \langle 010 \rangle$. Another kind of dislocation array is shown in the transitional Mioré patterns in HRTEM image of Figure 3e, which has the periodic misfit spacing of 5 nm. The IFFT and fast Fourier-transformed (FFT) images of Figure 3e are shown in Figure 3f and the upper inset of Figure 3f, respectively. The dislocation arrays in Figure 3f are shown in red circles, and the boxed region shows the enlarged view of the dislocation. The zone axis is identified as [100] for both adjacent grains in Figure 3f and the atomic planes are (010). The dislocation arrays featured by transitional Mioré patterns are observed as the major dislocation at the grain boundaries for NTFC-20min, which may reflect the higher crystal symmetry of HH materials (F43*m*) than that of the $Bi_{0.5}Sb_{1.5}Te_3$ structure (R3*mH*). As expected, the dense dislocation arrays are also observed in the HZNSS-20min sample, as shown in Figure 3h,j,k, while Figure 3h,j shows the enlarged HRTEM images for the boxed



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Figure 3. TEM images showing dislocations along the grain boundaries. a) Low-magnification TEM image of NTFC-20min; b) enlarged view of the boxed region in (a); c) high-resolution TEM image of a grain boundary; d) inverse FFT image of (c), which shows the dislocation arrays as indicated by the red symbols, and inset is the enlarged view of a dislocation; e) high-resolution TEM image of another grain boundary; f) inverse FFT image of (e), which shows some dislocations encircled in red, and insets are the enlarged view of a dislocation (lower left) and FFT image (upper) of the right grain; g–l) TEM images featured with the dense dislocation arrays at the grain boundaries of HZNSS-20min.

areas of Figure 3g,i, respectively. Transitional Mioré patterns are observed in Figure 3j and the enlarged image in Figure 3k. The IFFT and the FFT images of Figure 3k are shown in Figure 3l and the left inset in Figure 3l, respectively, while the right inset in Figure 3l is the enlarged IFFT image for the boxed dislocation area in Figure 3l. The zone axes of atomic planes in Figure 3l is identified as [211], and the Burgers vector of each dislocation in Figure 3l is $\langle 0\overline{1}1 \rangle$. Overall, the dislocation arrays observed for NTFC-20min and HZNSS-20min samples have close spacing of 2.5–6 nm between the cores, which corresponds to a dislocation density of $\approx 1 \times 10^{11}$ cm⁻².

To the best of our knowledge, bulk HH TE materials exhibiting dense dislocation arrays at the grain boundaries have not been reported.^[23,30] The formation mechanism of the dislocations in NTFC-20min, HZNSS-20min, and others samples should be similar to those observed in materials possessing enhanced mechanical strength,^[37] magnetism properties,^[38] and TE performance.^[39] During the SPS process, the MgX₂/LiX

byproducts produced in the high-energy ball milling process can be liquefied and expelled at elevated temperatures above 873 K. The existence of liquid MgX_2/LiX phase facilitates diffusion at the grain boundaries of HHs, which upon heating and compacting leads to the appearance of dense dislocation arrays at grain boundaries, resulting in a semi-coherent interface structure for the HH material.

The temperature dependence of the total thermal conductivity κ_{tot} for six samples of Nb_{0.8}Ti_{0.2}FeSb and Hf_{0.25}Zr_{0.75}Ni_{1.05}Sn_{0.97}Sb_{0.03}, as shown in **Figure 4**a, are calculated from $\kappa_{tot} = DC_pd$, where *D* is the thermal diffusivity coefficient (Figure S3a, Supporting Information), C_p the specific heat capacity (Figure S3b, Supporting Information), and *d* the density. Figure 4b shows the temperature-dependent electrical thermal conductivity κ_e for all samples, which was determined via the Wiedemann–Franz relation $\kappa_e = L\sigma T$, where *L*, σ , and *T* are the Lorenz number (Figure S4, Supporting Information), temperature-dependent electrical conductivity, and the absolute







Figure 4. Thermal conductivity dependence of temperature. a) Total thermal conductivity κ_{tot} of all samples; b) electron thermal conductivity κ_e of all samples; c) lattice thermal conductivity and bipolar thermal conductivity ($\kappa_L + \kappa_{bip}$) of NTFC-5min, NTFC-20min, and NTFC-4h samples; d) ($\kappa_L + \kappa_{bip}$) of HZNSS-5min, HZNSS-20min, and HZNSS-4h samples; e) calculated phonon relaxation time τ versus frequency ω for NTFC-20min sample and for f) HZNSS-20min sample; g) comparison between experimental and the fitted κ_L for three Nb_{0.8}Ti_{0.2}FeSb samples, and for h) three Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03} samples.

temperature, respectively.^[40] The temperature-dependent lattice thermal conductivity κ_{L} and bipolar thermal conductivity κ_{bip} for the six Nb_{0.8}Ti_{0.2}FeSb and Hf_{0.25}Zr_{0.75}Ni_{1.05}Sn_{0.97}Sb_{0.03} samples were calculated by subtraction κ_{e} from κ_{tot} . The contribution of κ_{bip} arises slightly at high temperature for Nb_{0.8}Ti_{0.2}FeSb. As shown in Figure 4c,d, the temperature dependence of κ_{L} for NTFC-5min, NTFC-20min, HZNSS-5min, and HZNSS-20min

are significantly reduced, particularly by 40% and 44% at 300 K for the 5 min sintered samples in comparison to the literature values,^[21,23] respectively. For the HZNSS-5min sample, the κ_L approaches ≈ 1 W m $^{-1}$ K $^{-1}$ at 900 K, which is the minimum lattice thermal for HH materials. Whereas, the κ_L of 4 h sintered samples increase substantially and become comparable to the literatures,^[21,23] which can be ascribed to the growth of

grain sizes and annihilation of dislocations, as shown in TEM images in Figure S5 (Supporting Information). We noticed that from 5 to 20 min and 4 h, the bipolar effect in HZNSS samples became slightly obvious, which is probably due to the slight increase of the concentrations of the minor carrier originated from the intrinsic antisite defects between Zr and Sn sites, and in turn the band narrowing effect in HZNSS materials.^[41] The reductions on κ_L reveal that the unique dislocation arrays at the grain boundaries might have profound impact on the phonon scattering mechanism for these samples. In order to understand the details of the phonon scattering mechanisms, the lattice thermal conductivity κ_L was analyzed using the expression based on Callaway model as the following^[29]

$$\kappa = \frac{k_{\rm B}}{2\pi^2 \upsilon} \left(\frac{k_{\rm B}T}{\hbar}\right)^3 \int_0^{\theta_{\rm D}/T} \frac{\tau_{\rm total}(x) x^4 e^x}{\left(e^x - 1\right)^2} \mathrm{d}x \tag{1}$$

where v, $\theta_{\rm D}$, and ω is the phonon velocity, the Debye temperature, and the phonon frequency, respectively, x is defined as $x = \hbar \omega / k_{\rm B} T$, $\tau_{\rm total}$ (x) is the total effective relaxation time, which can be determined from the individual relaxation time originated from different scattering mechanisms. Based on the Matthiessen's rule, the total phonon relaxation time ($\tau_{\rm tot}$) is a reciprocal sum of the relaxation times of the following pertinent scattering mechanisms, which traditionally comprise phonon–phonon Umklapp scattering ($\tau_{\rm U}$), electron–phonon scattering ($\tau_{\rm EP}$), point defect scattering ($\tau_{\rm PD}$), and boundary scattering ($\tau_{\rm B}$).^[39]

However, in this work, due to the dense dislocations at the grain boundaries in the Nb_{0.8}Ti_{0.2}FeSb and Hf_{0.25}Zr_{0.75}Ni_{1.05}Sn_{0.97}Sb_{0.03} bulk samples, additional considerations have to be put forth regarding the phonon scattering from the dislocation cores (τ_{DC}) and the dislocation strain (τ_{DS}). The details of the calculation on the total phonon relaxation time (τ_{tot}), as well as the individual τ_{U} , τ_{EP} , τ_{PD} , τ_{B} , τ_{DC} , and τ_{DS} can be found in the Supporting Information.

Based on the calculations, phonon relaxation times from different scattering mechanisms are calculated and shown in Figure 4e,f for NTFC-20min and HZNSS-20min samples, respectively. The results show that dislocation strain is the dominant mechanism for low and middle frequency phonon scattering, and meanwhile the point defect and electron-phonon scatterings are the dominant mechanisms for high-frequency phonons in both materials. The comparison between experimental K_L for six Nb_{0.8}Ti_{0.2}FeSb and Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03} samples and the fitted $\kappa_{\rm I}$ based on the parameters from NTFC-20min and HZNSS-20min are shown in Figure 4g,h, respectively. For NTFC-5min, NTFC-20min, HZNSS-5min, and HZNSS-20min, the dislocation strain scattering is believed to contribute significantly on the reduction of lattice thermal conductivity below 800 K, and among them the experimental and fitting data of the 20 min sintering samples match well with each other. For Nb_{0.8}Ti_{0.2}FeSb samples, it is noted that the experimental thermal conductivity start to arise slightly above 800 K, which indicates that the minority carriers could have been excited and bipolar thermal conduction emerges. For sample NTFC-4h and HZNSS-4h, significant grain growth accompanied by annihilation of dislocation defects at the grain boundaries can be observed, as shown in the TEM images in Figure S5 (Supporting Information), which would account for the overall higher κ_L with respect to the other short time sintered samples.

Figure 5a,b displays the temperature dependence of electrical resistivity ρ and Seebeck coefficient S for all the Nb_{0.8}Ti_{0.2}FeSb and Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03} samples, respectively. For both compositions, the ρ and *S* increase with temperature and saturate at around 700 K for Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03}, which is consistent with the literature results for the similar compositions and also indicates the typical electrical transport behavior for degenerated HH semiconductors.^[21,23] It is noted here that with respect to the reported data for Hf_xZr_{1-x}NiSn_{0.99}Sb_{0.01}^[23] and Hf_xZr_{1-x}NiSn_{0.985}Sb_{0.015}^[41] compositions, the relatively higher ρ and lower S of HZNSS-5min and HZNSS-20min lead to lower power factors in the whole temperature range with a maximum value of 32×10^{-4} W m⁻¹ K⁻² at 673 K, while the power factors were increased by sintering process with a maximum of 38×10^{-4} W m⁻¹ K⁻² for HZNSS-4h, as shown in Figure 5g. The temperature-dependent electron carrier concentration, obtained from Hall measurement as shown in Figure 5c, reaches to 3.1×10^{20} cm⁻³ for HZNSS-20min. The nearly temperature-independent carrier concentration might be slightly higher in comparison to the optimized literature values,^[31] and it probably is the result of over doping based on the calculation for $n_{\rm H}$ dependence of power factor (*PF*) using the single parabolic band (SPB) model (supporting information) as shown in Figure 5h. Lowering the carrier concentration would favor higher Hall mobility and Seebeck coefficient. For instance, reducing the Sb content from 0.03 to 0.01 leads to S improvement from -130 to $-160 \mu V K^{-1}$, but no net gains on the PF. The temperature dependence of Hall mobility for HZNSS-20 min, as shown in Figure 5d, is around $\mu_{\rm H} \approx 29 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at near room temperature, which is comparable to the results for Hf_xZr_{1-x}NiSn_{0.985}Sb_{0.015} compositions,^[41] whereas the carrier concentration is as high as 4×10^{20} cm⁻³ for the later. Thus, the nominal doping level of Sb \approx 0.03 in HZNSS-20min is most probably higher than the actual level in the sample, which should be close to Sb \approx 0.015 based on the relation between carrier concentration and the Sb content in literature.^[41] This argument can also be supported by the fittings of $\mu_{\rm H}$ as a function of $n_{\rm H}$ for HZNSS-20min under the assumption of homogeneous alloying, as shown in Figure 5f. It is observed that the experimental $\mu_{\rm H} \approx 29 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is higher than the fitting value of 19 cm² V⁻¹ s⁻¹ in the curve under the same carrier concentration of 3.1×10^{20} cm⁻³, which obviously means the Sb content is less than 0.03. This is because the difference between the experimental and fitting values was supposed to be induced by the Sb content difference between actual and nominal values. Homogeneous doping or alloying is particularly important for an alloying scattering dominated carrier transport system, such as in ZrNiSn-based materials since the relatively low deformation potential and alloy scattering potential favor high carrier mobility.^[42] The relationship of $\mu_{\rm H} \approx T^{-0.5}$ for HZNSS-20min shown in Figure 5d indicates alloying scattering mechanism for the system and this is further confirmed by the modeling in Figure 5f. The details of the modeling can be found in the Supporting Information.

Here the question still arises why the *PF* in HZNSS-5min and HZNSS-20min is lower than those samples with similar

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Figure 5. Temperature-dependent thermoelectric properties. a) Electrical resistivity $\rho(T)$ of all samples; b) Seebeck coefficient S(T) of all samples; c) carrier concentration $n_{\rm H}$, and d) Hall mobility $\mu_{\rm H}$ for NTFC-20min and HZNSS-20min; e,f) the room temperature Hall mobility as the function of carrier concentration for NTFC-20min and HZNSS-20min, respectively. The curves were calculated by using $m^* = 6.9 m_{\rm e}$ for NTFC-20min and 3.05 $m_{\rm e}$ for HZNSS-20min; g) power factor *PF* for all samples of Nb_{0.8}Ti_{0.2}FeSb and Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03}; h) modulated *PF* as the function of carrier concentration for NTFC-20min and HZNSS-20min at 300 K with experimental data points for NTFC-20min, NTFC-4h, HZNSS-20min, and HZNSS-4h samples for comparison.

carrier concentration in the literature? Despite of the scattering induced by the minor inhomogeneity of Sb doping atoms in the sample, more contributions may come from the crystal defects at the nanoscale level in the bulk sample, which would scatter phonon and electron at the same time, given that the mean free paths for electron and phonon are both revealed to be around 5 nm above 200 K for the ZrNiSn-based materials.^[41]

The aforementioned dense dislocation strains and dislocation cores in the HZNSS-5min and HZNSS-20min bulk samples might be the key reason. As can be seen from HZNSS-4h, with the grain growth and annihilation of strain defects at the grain boundaries compared to two short time sintered samples, which is detected by the TEM techniques (Figure S5, Supporting Information), the electrical transport performance was enhanced as proved by the carrier concentration and increased carrier mobility in HZNSS-4h in Figure S6a,b (Supporting Information), leading to comparable power factors to the literature value.^[23]

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On the contrary to ZrNiSn-based materials, the p-type Nb_{0.8}Ti_{0.2}FeSb system is characterized by acoustic scattering dominated carrier transport properties, which is consistent with our analysis in the following context. In comparison with the literature data for the same composition,^[21] the Nb_{0.8}Ti_{0.2}FeSb bulk samples in our synthesis exhibit some interesting features in terms of its electrical transport properties. First of all, among three samples the temperature-dependent electrical resistivity ρ (Figure 5a) decreases with the increasing of sintering time from 5 min to 4 h, and their differences become significant at high temperatures, eventually NTFC-4h exhibits the lowest ρ and it reaches to 9.23 $\mu\Omega$ m at 925 K, which is higher than the literature's value of 7.15 $\mu\Omega$ m.^[21] Second, as for the S, there is not as much difference as that in the ρ for three samples except in high-temperature range, where the S of NTFC-4h reaches 187 $\mu V~K^{-1}$ at 925 K, nearly 14% higher than those of NTFC-5min and NTFC-20min. Moreover, in comparison to the literatures, the S of three samples are higher at 300 K (80 vs. 70 μ V K⁻¹), and gradually coalesce with the literature values until 925 K (184 μ V K⁻¹ from ref. [18]). This leads to 56% increase on the PF at 300 K for NTFC-4h sample with respect to literature,^[21] and reaches 39×10^{-4} W m⁻² K⁻¹ in our case, as shown in Figure 4g. Meanwhile, the PF of our sample gradually increase with temperature until reaches 47×10^{-4} W m⁻² K⁻¹ at 535 K, than decreases slowly to 37×10^{-4} W m⁻² K⁻¹ at 925 K, in comparison to 45×10^{-4} W m⁻² K⁻¹ at 925 K from literature.^[21] The temperature dependence of carrier concentration and Hall mobility of NTFC-20min are shown in Figure 5c,d, in which the carrier concentration of 20×10^{20} cm⁻³ is lower than the literature by 20%,^[21] probably reflecting inhomogenous Ti doping in this sample. On the other hand, the mobility starts from 17 cm² V⁻¹ s⁻¹ at 300 K, then degrades in a faster way to 5 cm² V⁻¹ s⁻¹ at 800 K compared to literature.^[21] The relatively lower Hall mobility in NTFC-20min at high temperatures is believed to be responsible for the low PF in the same high-temperature range. However, the carrier transport performance of NTFC-20min can be improved, as shown in Figure S6a,b (Supporting Information), and higher carrier mobility was found in the NTFC-4h samples. To better understand the charge carrier transport mechanism, we found the $\mu_{\rm H}$ exhibits a $\mu_{\rm H} \approx T^{-1}$ relationship for NTFC-20min, as shown in Figure 5d, which is the feature of acoustic scattering mechanism. Further analysis in Figure 5e indicates that the acoustic scattering play dominating role in the charge transport for NTFC-20min, which is well consistent with the literature.^[21] Here the details of modeling and calculation of the carrier transport mechanism can be found in Supporting Information. In connection with the new phonon scattering centers induced by the dislocation cores and strains at the boundaries of crystal grains in NTFC-20min bulk sample, it shows no significant influence on the charge transport, at least in the low-temperature range. However, as shown in Figure 3b, bipolar effect arises at high temperatures for NTFC-5min and NTFC-20min, which would be responsible for their relatively lower S. In addition, this is consistent with the slight inhomogeneity of Ti doping in both samples. Furthermore, the

theoretical *PF* independence of carrier concentration calculated based on the SPB model is shown in Figure 5h, which clearly shows that the improvement in the experimental *PF* through increasing the sintering time, as observed in NTFC-4h.

The temperature dependence of *ZT*s for the six Nb_{0.8}Ti_{0.2}FeSb and Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03} bulk samples are calculated based on the measured ρ , *S*, and κ values, and plotted in **Figure 6**a,b. The TE properties of $Hf_{0.44}Zr_{0.44}Ti_{0.12}CoSb_{0.85}Sn_{0.15}$ are also put in Figure S6 (Supporting Information). Overall, among the Nb_{0.8}Ti_{0.2}FeSb samples, the ZTs increase with the sintering time, particularly at high temperatures, where the maximum ZT of NTFC-4h reaches 0.73 at 925 K. The ZTs between room temperature and 700 K for all Nb_{0.8}Ti_{0.2}FeSb samples are about 30% higher than the literature value.^[21] Meanwhile, above 750 K the literature's ZT gradually outperforms our samples.^[21] These results are fully consistent with the characters of the interplays between temperature dependence of thermal conductivity and the power factors for the Nb_{0.8}Ti_{0.2}FeSb samples. Namely, the enhanced PF and reduced thermal conductivity at lower temperatures increase the ZTs over the references,^[21] while the lower PF at higher temperatures overturns the reduction in thermal conductivity, leading to lower ZTs, particularly in NTFC-5min, compared to the literature values.^[21] Inset in Figure 6b shows the carrier concentration dependence of calculated ZT based on the two-band model (conduction band and valence band) for NTFC-20min at 300, 600, 800 K. The measured ZTs of NTFC-20min and NTFC-4h at three different temperatures locate closely to the maximum positions in the curves, meaning that the carrier concentration and ZTs could have been optimized. On the other hand, for three $Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03}$ materials, their temperature-dependent ZTs increase continuously and show no significant differences until 820 K, at which HZNSS-5min continues to be comparable to the literature values for the Hf_{0.25}Zr_{0.75}NiSn_{0.99}Sb_{0.01} composition until 925 K due to its lowest thermal conductivity among three samples.^[23] Unlike the p-type Nb_{0.8}Ti_{0.2}FeSb materials, the interplays between suppressed lattice thermal conductivity and reduced electrical transport properties in HZNSS-5min and HZNSS-20min samples in comparison to the HZNSS-4h are more likely dominated by the lattice thermal conductivity part in the high-temperature range, which favors higher ZT peaks. Inset in Figure 6a shows the carrier concentration dependence of the calculated ZT based on the two-band model for HZNSS-20min at 300, 600, 800 K. The measured ZTs of HZNSS-20min and HZNSS-4h at three corresponding temperatures were compared with the modeling, which indicate that the carrier concentration and ZTs have been optimized. The details of modeling and calculation of the ZT can be found in Supporting Information.

Furthermore, it was confirmed that the engineering $(ZT)_{eng}$ and $(PF)_{eng}$ of materials can predicted more accurately the practical performance of TE materials at any given temperature difference than the average $(ZT)_{avg}$ based on the constant property model.^[43,44] In terms of TE power generations, the output power and power density are equally important as that of η_{max} and $(ZT)_{eng}$ under the assumption of unlimited or free heat sources. Thus, the $(ZT)_{eng}$, $(PF)_{eng}$, P_d , and η are calculated for both Nb_{0.8}Ti_{0.2}FeSb and Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03} materials and compared with the closest composition in the literatures.^[21,23]



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Figure 6. Temperature-dependent thermoelectrical properties. Figure-of-merit *ZT* for a) Nb_{0.8}Ti_{0.2}FeSb and b) Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03} samples, the calculated respective *ZTs* as the function of carrier concentration are shown in the insets. The solid lines were calculated based on the two-band model. The calculated cumulative temperature (ΔT) dependent TE properties for all Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03} and Nb_{0.8}Ti_{0.2}FeSb samples are plotted and compared with the literatures values for the same compositions,^[21,23] the cold side temperature is fixed as *T_c* = 323 K for all analysis. c) ΔT dependence of (*ZT*)_{eng}, d) ΔT dependence of η , e) ΔT dependence of (*PF*)_{eng}, and f) ΔT dependence of power density *P_d*.

The $(ZT)_{eng}$, η , $(PF)_{eng}$, and P_d were calculated based on the experimental results and compared with the data calculated from the literatures' values.^[21,23] It is shown in Figure 6c,d that the temperature difference dependence of $(ZT)_{\mathrm{eng}}$ and η of three Nb_{0.8}Ti_{0.2}FeSb samples are substantially higher than that of the reference data, with a maximum η of 7.8% for NTFC-4h at $\Delta T \approx 600$ K. Regarding the temperature difference dependence of (PF)eng and Pd of the Nb_{0.8}Ti_{0.2}FeSb samples as shown in Figure 6e,f, the NTFC-4h outperforms NTFC-5min, NTFC-20min, and the reference data in the whole range, owing to its much enhanced PF at low temperatures. Meanwhile, for all Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03} samples, the temperature difference dependence of (ZT)_{eng} and η as shown in Figure 6c,d are competitive to reference data with a maximum η of 10.5% at $\Delta T \approx 600$ K. However, the temperature difference dependence of $(PF)_{eng}$ and P_d were outperformed by reference data as shown in Figure 6e,f, which also exhibits the trend of improvement with the increase of sintering time for the samples.

In order to increase the (ZT)_{eng} and η for the p-type Nb_{0.8}Ti_{0.2}FeSb and make them comparable to the Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03} materials for better devices, the vanadium-doped samples were prepared by the similar procedures, which was enlightened by outstanding performance of vanadium-doped materials in Zhu's report.^[45] The temperature dependence of thermoelectric performance for FeNb_{0.56}V_{0.24}Ti_{0.2}Sb sample is shown in **Figure 7**. The details of the temperature dependence of κ_{tot} , ρ , and S for this sample can be found in Figure S7 (Supporting Information). Figure 7a shows temperature dependence of ZT and PF, represented by red filled circle and blue filled square, respectively. It is noticed that although the PF were lower than that of Nb_{0.8}Ti_{0.2}FeSb owing to the decreased hole mobility and electrical conductivity, the ZT curve in convex upward shape reaches a peak of 0.92 at 925 K, favoring overall enhanced η as shown in Figure 7b. As a result, the maximum ΔT dependence of η reaches to 10.5% at $\Delta T \approx 600$ K accompanied by $P_{\rm d}$ of 15 W cm⁻², which is just slightly lowered than the $Nb_{0.8}Ti_{0.2}FeSb$.



(a) 1.00 (b)12 20 0.7 Wcm⁻ 8 5 0.50 15 0 0.2 FeNb_{0.56}V_{0.24}Ti_{0.2}Sb Sh FeNh ζ_{α 2}, Ti_o 0 0.00 ____0 1000 600 800 400 200 400 600 T (K) **∆T (K)**

Figure 7. Thermoelectric performance for FeNb_{0.56}V_{0.24}Ti_{0.2}Sb: a) temperature dependence of *ZT* represented by red filled circle, and power factor represented by blue filled squire; b) ΔT dependence of efficiency η and power density P_d , represented by the red filled hexagon and blue filled diamond, respectively.

3. Conclusion

In conclusion, a series of representative HH thermoelectric materials were prepared by a bottom-up nanostructure synthesis approach based on the displacement reaction between metal chlorides and metal magnesium or lithium, followed by vacuum-assisted SPS process. The samples are featured with dense dislocation arrays at the grain boundaries, leading to a minimum $\kappa_{\rm I}$ of ≈ 1 W m⁻¹ K⁻¹ at 900 K and comparable *ZT* (≈ 1) and $\eta \approx 11\%$ for n-type Hf_{0.25}Zr_{0.75}NiSn_{0.97}Sb_{0.03}. The phonon and electrical transports of p-type Nb_{0.8}Ti_{0.2}FeSb can also be manipulated by mainly adjusting the dislocation defects at the grain boundaries, leading to enhanced maximum power factor of 47×10^{-4} W m⁻¹ K⁻² and the predicted η of \approx 7.5%. Further vanadium substitution as shown in $FeNb_{0.56}V_{0.24}Ti_{0.2}Sb$ significantly promotes the η to \approx 11%. This strategy can be extended to some other notable TE materials and a broad range of advanced alloys and compounds for improved properties.

4. Experimental Section

Synthesis: Six typical half-Heusler materials were synthesized through the combination of mechanochemical reaction and SPS process. All treatment and processing of the material were carried out in an argonfilled glove box to avoid oxidation. High purity metal chloride powders NbCl₅ (99.9%), TiBr₄ (98%), HfCl₄ (99.9%), ZrCl₄ (98%), FeCl₂ (99.5%), VCl₅ (99.5%), CoCl₂ (97%), NiCl₂ (98%), SbCl₃ (99%), SnCl₂ (98%), and metal Mg/Li (99.9%) granules from Alfa Aesar were used for the synthesis. Raw materials with a total weight of 5 g and appropriate ratios corresponding to the stoichiometric ratio of HH materials were transferred into the stainless ball milling jar. High-energy ball milling process was then performed for 2-5 h by using a SPEX Sample Prep 8000 Mixer/Mill. The finally produced fine powder that is composed by the mixture of transitional metal nanoparticles and MgCl₂/LiCl were carefully loaded into the graphite die in the glove box, and then treated by SPS process at 850-950 °C in the vacuumed chamber under 50 MPa for 5 min, 20 min, and 4 h, respectively. The final bulk pellet has the dimension of 12.7 mm (diameter) \times 2 mm (thickness). The measured density of all the pellets was up to 94%-98% of the theoretical density. The obtained samples were further characterized by XRD, SEM, and TEM techniques.

Powder XRD: Powder XRD patterns were collected on a diffractometer (PANalytical X'Pert Pro) in Bragg–Brentano reflection geometry with Cu K α radiation ($\lambda = 1.5418$ Å) and operated at 40 kV and 40 mA. The patterns were carried out in the 2θ range of 10° – 90° with a step size of 0.02° at room temperature in air.

Microstructure Analysis: The morphologies and element distribution of bulk samples were characterized by a SEM and EDX on the S-5200 field emission SEM (Hitachi). The chemical compositions were further checked by ICP-MS (X Series 2, Thermo Fisher Scientific). The microstructure and crystal defects at the atomic and lattice levels in the bulk samples were investigated by a TEM (F20, FEI).

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Thermoelectric Transport Properties: The temperature dependence of electrical resistivity and Seebeck coefficient were measured by using a commercial system (LSR-3, Linseis). The temperature dependence of thermal conductivity was calculated from the equation, $\kappa = DC_pd$, where D, C_p , and d are the thermal diffusivity, specific heat capacity, and density, respectively. The thermal diffusivity was measured by the laser flash method with a commercial system (LFA-1000, Linseis). The specific heat capacity was measured by differential scanning calorimeter (TA Q200). The density was determined by the Archimedes method.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

dislocation synthesis, enhanced TE performance, half-Heusler thermoelectrics, lattice thermal conductivity, transport properties manipulation

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- [1] S. Challipalli, F. H. Froes, Adv. Mater. 1993, 5, 96.
- [2] P. V. Liddicoat, X. Z. Liao, Y. Zhao, Y. Zhu, M. Y. Murashkin, E. J. Lavernia, R. Z. Valiev, S. P. Ringer, *Nat. Commun.* 2010, 1, 63.
- [3] J. R. Sootsman, D. Y. Chung, M. G. Kanatzidis, Angew. Chem., Int. Ed. 2009, 48, 8616.
- [4] I. S. Kim, K. H. Lee, H. A. Mun, H. S. Kim, S. W. Hwang, J. W. Roh, D. J. Yang, W. H. Shin, X. S. Li, Y. H. Lee, G. J. Snyder, S. W. Kim, *Science* **2015**, *348*, 109.
- [5] B. Poudel, Q. Hao, Y. Ma, Y. C. Lan, A. Minnich, B. Yu, X. Yan, D. Wang, A. Muto, D. Vashaee, X. Chen, J. M. Liu, M. S. Dresselhaus, G. Chen, Z. F. Ren, *Science* **2008**, *320*, 634.
- [6] K. Biswas, J. Q. He, I. D. Blum, C. I. Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid, M. G. Kanatzidis, *Nature* **2012**, 489, 414.
- [7] K. F. Hsu, S. Loo, F. Guo, W. Chen, J. S. Dyck, C. Uher, T. Hogan, E. K. Polychroniadis, M. G. Kanatzidis, *Science* 2004, 303, 818.
- [8] T. Caillat, J.-P. Fleurial, A. Borshchevsky, J. Phys. Chem. Solids 1997, 58, 1119.
- [9] S. R. Brown, S. M. Kauzlarich, F. Gascoin, G. J. Snyder, Chem. Mater. 2006, 18, 1873.
- [10] G. Joshi, H. Lee, Y. C. Lan, X. Wang, G. H. Zhu, D. Wang, R. W. Gould, D. C. Cuff, M. Y. Tang, M. S. Dresselhaus, G. Chen, Z. F. Ren, *Nano Lett.* 2008, *8*, 4670.
- X. W. Wang, H. Lee, Y. C. Lan, G. H. Zhu, G. Joshi, D. Wang, J. Yang,
 A. J. Muto, M. Y. Tang, J. Klatsky, S. Song, M. S. Dresselhaus,
 G. Chen, Z. F. Ren, *Appl. Phys. Lett.* **2008**, *93*, 193121.
- [12] H. L. Liu, X. Shi, F. F. Xu, L. L. Zhang, W. Q. Zhang, L. D. Chen, Q. Li, C. Uher, T. Day, G. J. Snyder, *Nat. Mater.* **2012**, *11*, 422.
- [13] W. Y. Zhao, Z. Y. Liu, P. Wei, Q. J. Zhang, W. T. Zhu, X. L. Su, X. F. Tang, J. H. Yang, Y. Liu, J. Shi, Y. Chao, S. Q. Lin, Y. Z. Pei, *Nat. Nanotechnol.* **2017**, *12*, 55.
- [14] H. Z. Zhao, J. E. Sui, Z. J. Tang, Y. C. Lan, Q. Jie, D. Kraemer, K. McEnaney, A. Guloy, G. Chen, Z. F. Ren, *Nano Energy* **2014**, *7*, 97.
- [15] L. D. Zhao, S. H. Lo, Y. S. Zhang, H. Sun, G. J. Tan, C. Uher, C. Wolverton, V. P. Dravid, M. G. Kanatzidis, *Nature* **2014**, *508*, 373.
- [16] L. D. Zhao, J. Q. He, D. Berardan, Y. H. Lin, J. F. Li, C. W. Nan, N. Dragoe, *Energy Environ. Sci.* 2014, *7*, 2900.



- [17] W. Liu, X. J. Tan, K. Yin, H. J. Liu, X. F. Tang, J. Shi, Q. J. Zhang, C. Uher, Phys. Rev. Lett. 2012, 108, 5.
- [18] W. S. Liu, H. S. Kim, S. Chen, Q. Jie, B. Lv, M. Yao, Z. Ren, C. Y. Opeil, S. Wilson, C. W. Chu, Z. F. Ren, *Proc. Natl. Acad. Sci.* USA 2015, 112, 3269.
- [19] G. D. Mahan, J. Appl. Phys. 1989, 65, 1578.
- [20] S. Öğüt, K. M. Rabe, Phys. Rev. B 1995, 51, 10443.
- [21] C. Fu, T. Zhu, Y. Liu, H. Xie, X. Zhao, Energy Environ. Sci. 2015, 8, 216.
- [22] Y. Z. Pei, H. Wang, G. J. Snyder, Adv. Mater. 2012, 24, 6125.
- [23] S. Chen, K. C. Lukas, W. S. Liu, C. P. Opeil, G. Chen, Z. F. Ren, Adv. Energy Mater. 2013, 3, 1210.
- [24] R. He, D. Kraemer, J. Mao, L. P. Zeng, Q. Jie, Y. Lan, C. Li, J. Shuai, H. S. Kim, Y. Liu, D. Broido, C. W. Chu, G. Chen, Z. F. Ren, *Proc. Natl. Acad. Sci. USA* **2016**, *113*, 13576.
- [25] L. D. Zhao, G. Tan, S. Hao, J. He, Y. Pei, H. Chi, H. Wang, S. Gong, H. Xu, V. P. Dravid, C. Uher, G. J. Snyder, C. Wolverton, M. G. Kanatzidis, *Science* **2015**, *351*, 141.
- [26] G. Rogl, A. Grytsiv, M. Gürth, A. Tavassoli, C. Ebner, A. Wünschek, S. Puchegger, V. Soprunyuk, W. Schranz, E. Bauer, H. Müller, M. Zehetbauer, P. Rogl, *Acta Mater.* **2016**, *107*, 178.
- [27] R. He, S. Gahlawat, C. F. Guo, S. Chen, T. Dahal, H. Zhang,
 W. S. Liu, Q. Zhang, E. Chere, K. White, Z. F. Ren, *Phys. Status Solidi* A 2015, 212, 2191.
- [28] C. Fu, H. Xie, T. J. Zhu, J. Xie, X. B. Zhao, J. Appl. Phys. 2012, 112, 124915.
- [29] J. Callaway, Phys. Rev. 1959, 113, 1046.
- [30] C. Fu, H. Wu, Y. Liu, J. He, X. Zhao, T. J. Zhu, Adv. Sci. 2016, 3, 1600035.
- [31] C. Yu, T. J. Zhu, R. Z. Shi, Y. Zhang, X. B. Zhao, J. He, Acta Mater. 2009, 57, 2757.
- [32] D. G. Cahill, S. K. Watson, R. O. Pohl, Phys. Rev. B 1992, 46, 6131.
- [33] V. I. Fistul, *Heavily Doped Semiconductors*, Plenum Press, New York **1995**.
- [34] Z. W. Chen, B. H. Ge, W. Li, S. Q. Lin, J. W. Shen, Y. Chang, R. Hanus, G. J. Snyder, Y. Z. Pei, *Nat. Commun.* 2017, 8, 13828.
- [35] F. Casper, T. Graf, S. Chadov, B. Balke, C. Felser, Semicond. Sci. Technol. 2012, 27, 063001.
- [36] F. J. Humphreys, M. Hatherly, Recrystallization and Related Annealing Phenomena, Elsevier, Oxford 2004.
- [37] M. Nader, F. Aldinger, M. J. Hoffmann, J. Mater. Sci. 1999, 34, 1197.
- [38] P. J. Jorgensen, J. Appl. Phys. 1973, 44, 2876.
- [39] H. S. Kim, S. D. Kang, Y. L. Tang, R. Hanus, G. J. Snyder, Mater. Horiz. 2016, 3, 234.
- [40] M. Jonson, G. D. Mahan, Phys. Rev. B 1980, 21, 4223.
- [41] T. Zhu, C. Fu, H. Xie, Y. Liu, X. Zhao, Adv. Energy Mater. 2015, 5, 1500588.
- [42] H. H. Xie, H. Wang, Y. Z. Pei, C. G. Fu, X. H. Liu, G. J. Snyder, X. B. Zhao, T. J. Zhu, Adv. Funct. Mater. 2013, 23, 5123.
- [43] T. M. Tritt, Annu. Rev. Mater. Res. 2011, 41, 433.
- [44] H. S. Kim, W. Liu, G. Chen, C. W. Chu, Z. F. Ren, Proc. Natl. Acad. Sci. USA 2015, 112, 8205.
- [45] C. G. Fu, Y. T. Liu, X. B. Zhao, T. J. Zhu, Adv. Electron. Mater. 2016, 2, 1600394.