Synergistic Compositional–Mechanical–Thermal Effects Leading to a Record High $zT$ in n-Type V$_2$VI$_3$ Alloys Through Progressive Hot Deformation

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Here a progressive hot deformation procedure that endows the benchmark n-type V$_2$VI$_3$ thermoelectric materials with short range disorder (multiple defects), long range order (crystallinity), and strong texture (nearly orientation order) is reported. Not only it is rare for these structural features to coexist but also these structural features elicit the synergistic compositional–mechanical–thermal effects, i.e., a profound interplay among the counts, magnitude, and temperature of hot deformation in relation to the as formed point defects, dislocations, textures, strain clusters, and distortions. Using progressively larger die sets and relatively low hot deformation temperature, rich multiscale microstructures concurrently with a high level of texture comparable to that of zone melted ingot are obtained. The strong donor-like effect significantly increases the majority carrier concentration, suppressing the detrimental bipolar effect. In addition, the multiscale microstructures yield an ultralow lattice thermal conductivity $\approx 0.31$ W m$^{-1}$ K$^{-1}$ at 405 K. A record $zT = 1.3$ at 450 K are attained in progressively hot deformed n-type Bi$_{1.95}$Sb$_{0.05}$Te$_{2.3}$Se$_{0.7}$ through the synergistic effects. These results not only promise a better pairing between n-type and p-type legs in device fabrication but also bring our understanding of n-type V$_2$VI$_3$ alloys and hot deformation technique to a new level.

1. Introduction

With the capability of direct heat-electricity energy conversion without greenhouse emissions, thermoelectrics provides a solution to the global energy and environmental crisis.[1] The efficiency of a thermoelectric (TE) device is governed by the device material’s figure of merit, $zT = \sigma S^2 T/\kappa$, where $T$, $\sigma$, $S$, and $\kappa$ are the absolute temperature, the electrical conductivity, the Seebeck coefficient, and the total thermal conductivity (including the lattice component $\kappa_{\text{ph}}$ and the charge carrier component $\kappa_{\text{el}}$), respectively. Toward higher $zT$, defect engineering is invoked to (i) improve the power factor $PF = \sigma S^2$ through tuning band structure,[2,3] texture,[4,5] and grain boundary;[6,7] and (ii) suppress the $\kappa_{\text{ph}}$ through multiscale microstructures.[8,9] While point defects are of vital importance,[10,11] it is the synergy among various kinds of defects in defect engineering that underlies the high $zT$.

The rhombohedral V$_2$VI$_3$ materials are a hotbed of defect engineering,[12] the success of which make them the benchmark TE materials for solid-state cooling[8,13,14] and low/mid temperature waste heat harvesting.[15–24] In particular, the high performance of n-type V$_2$VI$_3$ alloys is subject to a delicate balance between strong textures and multiscale microstructures, which is a challenge for materials synthesis and processing. Making the task more challenging, the performance-enhancing mechanisms proved effective in p-type V$_2$VI$_3$ alloys turned out to be less so in n-type V$_2$VI$_3$ alloys. Compared to the p-type counterpart, the n-type V$_2$VI$_3$ material tends to be electrically more anisotropic: the electrical conductivity anisotropy of...
n-type $V_2VI_3$ single crystal ($\sim 4$–$7$) is higher than that of the p-type counterpart ($\sim 3$).\cite{25} A high level of (00l) texture in n-type $V_2VI_3$ alloys is indispensable for a high charge carrier mobility $\mu_H$ and a large PF ($\approx 4$ W m$^{-1}$ K$^{-1}$).\cite{8,13} For example, n-type $V_2VI_3$ alloys prepared by hot pressing (HP) or spark plasma sintering (SPS) are not highly (00l)-textured, their maximum $zT$ values are no higher than 1.0.\cite{8,13,14} Due to a nanoscale carrier mean free path in n-type $V_2VI_3$ alloys,\cite{8} the grain refinement or nanostucturing approach, which effectively suppresses the $\kappa_{ph}$ severely degrades the $\mu_H$ and the PF.

There are several other peculiarities about n-type $V_2VI_3$ alloys. First, the optimal composition varies drastically with the micromorphology. The optimal composition for mechanically deformed polycrystalline n-type Bi$_2$Te$_{2.7}$Se$_{0.3}$ (typically via grinding or ball milling) is Bi$_2$Te$_2$Se$_{0.7}$ while the counterpart for single crystals (SC) or zone melted (ZM) ingots is Bi$_2$Te$_2$Se$_{0.9}$.\cite{10} Second, the carrier concentration $n_H$, the key transport parameter for high $zT$, is directly governed by the intrinsic point defects (mainly antisites and anion vacancies) that can be further regulated chemically, mechanically, and thermally.\cite{10} This causal chain is in that tuning the intrinsic point defects affords a way to optimize the $n_H$ without invoking the use of unstable (Ag and Cu) and expensive donors (Sb$_1$ or Te$_1$) dopants.\cite{8,10} Third, the texture of $V_2VI_3$ alloys relies on crystal slip along the basal plane with the aid of dislocation movement under pressure, which is accompanied by the generation and annihilation of intrinsic point defects.\cite{25} High density dislocations can effectively scatter the mid-wavelength phonons that are less effectively affected by point defects and grain boundaries.\cite{8,17}

Hence, implementing desired microstructures, optimizing intrinsic point defects while retaining a high level of (00l) texture pose a challenge in material synthesis and processing of n-type $V_2VI_3$ alloys. To this end, hot deformation (HD) is a promising approach.\cite{10} HD has been implemented in p- and n-type $V_2VI_3$ solid solutions, which enhanced the (00l) textures to some extent, induced atomic scale point/line defects and nanoscale distortions, and also tuned the $n_H$ through the donor-like effect.\cite{8,10,18,20,27} Despite the progress, there are at least three specific barriers impeding HD from further improving the $zT$ of n-type $V_2VI_3$ alloys. The first barrier is that the texture nearly remains unchanged when the number of times of HD process is more than twice using the same size die set.\cite{14,28} Second, in view of the small band gap of $V_2VI_3$ alloys and the PF, the purpose of waste heat harvesting at elevated temperature, the donor-like effect needs to be strong enough to afford a higher majority carrier concentration to suppress the detrimental bipolar effect.\cite{20,29} Previous studies showed that at a low degree of deformation, the donor-like effect is quickly saturated with increasing number of HD (aka the HD count); deformation at high temperature induces the recovery effect that weakens the donor-like effect.\cite{15} High HD temperatures (773 or 823 K) also lead to grain coarsening that is less favored for suppressing the $\kappa_{ph}$.\cite{8} Furthermore, high energy ball milling yields a strong donor like effect, but the high degree of texture is irreversibly lost.

We herein adopt a strategy based on the hot deformation induced “synergistic compositional–mechanical–thermal effects” in n-type polycrystalline $V_2VI_3$ alloys. This strategy aims at the peculiarities of n-type $V_2VI_3$ alloys and those specific barriers of traditional HD process. The additive-based (chemical), deformation-based (mechanical), and thermal-based (thermal) effects and the resulting interplay among the intrinsic and extrinsic point defects, textures, dislocations, nanoscale strain clusters and distortions constitute the core of synergistic compositional–mechanical–thermal effects. These synergistic effects are implemented through an innovative HD procedure with progressively greater degree of deformation, higher HD counts, but lower HD temperature. We found that the optimal HD temperature 723 K is the balance point between the donor-like effect and the recovery effect.\cite{10} The innovative hot deformation process endows $V_2VI_3$ alloys with short range disorder (rich multiscale microstructures), long range order (good crystallinity), and strong texture (preferred orientation), which tend to be counter related in a material. The derived strong (00l) texture, comparable to that of ZM ingots, ensures a large PF. The purpose of Sb alloying in the present work is twofold: (i) enhancing mass fluctuation scattering of phonons; and (ii) facilitating the formation of antisite defects and thus enhances the donor-like effect at a relatively low HD temperature. The derived $\kappa_{ph}$ ($\approx 0.31$ W m$^{-1}$ K$^{-1}$ at 405 K) is one of the lowest values reported in $V_2VI_3$ alloys due to the multiscale microstructures. The resulting record $zT \approx 1.3$ at 430 K and high average $zT$ values of 1.2 between 300 and 500 K for five-time hot deformed Bi$_{1.95}$Sb$_{0.05}$Te$_{2.3}$Se$_{0.7}$ promise a better leg pairing of the p-type $V_2VI_3$ compounds that have $zT$ values in the range of 1.3–1.8\cite{15,18} in device fabrications.

2. Results and Discussion

The results and discussion are organized as follows. Subsection 2.1 covers the detailed texture evolution as a function of HD conditions. The main theme of Subsection 2.2 is the HD induced multiscale microstructures. Subsection 2.3 addresses the chemistry of intrinsic point defects. In Subsection 2.4, we present the state-of-the-art TE properties in relation to the synergistic compositional–mechanical–thermal effects.

2.1. Evolution of Texture with Hot Deformation

In light of the quaternary Bi–Sb–Se–Te phase diagram (Figure 1a) and as shown in Figure 1b, single-phased Bi$_{3-x}$Sb$_x$Te$_{2.3}$Se$_{0.7}$ ($0 \leq x \leq 0.25$) samples with HD count $\approx 1$ were obtained, they all adopted a hexagonal crystal structure (JCPDS# 29-0247). All peaks shift toward higher angles with increasing Sb content, indicating the formation of solid solutions. The basal lattice parameter is nearly unchanged, while the axial lattice parameter drops gradually with increasing Sb content, consistent with the smaller radius of Sb atom (1.45 Å) compared to that of Bi atom (1.60 Å) (Figure S1, Supporting Information). The progressive heat deformed Bi$_{1.95}$Sb$_{0.05}$Te$_{2.3}$Se$_{0.7}$ samples still retain a hexagonal structure without discernible secondary phases (Figure 1c).

As mentioned above, retaining a high level of texture is vital for the high $zT$ of n-type polycrystalline $V_2VI_3$ alloys. The degree of texture and the textural evolution with Sb content and
HD count can be gauged by the orientation degree $F$ of (00$l$) planes (Figure S2, Supporting Information and Figure 1d).\(^\text{[43]}\) Ideally, $F = 1$ for single crystal and $F = 0$ for complete random orientation. The $F$ value is nearly unchanged with varying Sb content, while rapidly rises with increasing HD count. It is known that the grains easily slip and rotate along the basal planes under pressure and the $c$-axis tends to be aligned parallel to the pressing direction during the plastic deformation process, thereby leading to a substantially enhanced (00$l$) textures. Though such phenomena were observed in early works of Bi$_2$Te$_3$–xSe$_x$ alloys,\(^\text{[4,8,32,33]}\) the degree of texture obtained therein is generally weaker than that is derived in this work. The cause of this discrepancy allows us to have a deeper understanding of the HD process and also the n-type V$_2$VI$_3$ alloys.

The HD count, degree and temperature are three pivotal parameters to obtain strong (00$l$) texture. Table 1 summarizes the major HD parameters and the derived $F$ values in the present and some prior works.\(^\text{[4,8,28,32,33]}\) There are some interesting findings. First of all, deformation in a larger graphite die is generally beneficial for texture enhancement. In this work, a progressively larger magnitude of deformation (in progressively larger die sets) led to consistently enhanced texture with increasing HD count. Second, comparing the present work with ref.\(^\text{[28]}\), the derived (00$l$) texture or the $F$ value is not solely
Table 1. Majority deformation parameters and F values in this and prior work.

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<td>723</td>
<td>0.67</td>
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<td>HD5</td>
<td>25–30</td>
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determined by the initial and final die size but also subject to the details of intermediate deformations. Third, plastic deformation and dynamic recrystallization (aka the recovery effect) are two counter effects in the HD process, the HD temperature is the key control parameter to attain the balance. A low HD temperature (e.g., 603 K in ref. [32]) failed to reach a uniform plastic deformation and a high degree of texture. On the other hand, a high HD temperature (e.g., 823 K in refs. [4] and [28]) facilitated uniform plastic deformation and thereby significantly enhanced the (00l) texture. However, such a high HD temperature also promoted dynamic recrystallization that weakened the texture to some extent because of the reconstruction and rearrangement of grain boundaries. In this work, we found an optimized the HD temperature at 723 K, which balanced the plastic deformation and dynamic recrystallization. As a result, the derived F value is higher than those of n-type V2VI3 polycrystalline alloys, and is close to that of Bi2Te3 thin film and single crystal.[25] Figure 4 shows three types of nanoscale structures: strain clusters, polycrystals, and distortions. Figure 4a,b is the low- and medium-magnification TEM images of the HD5 sample, plastic deformation induced a high density of nanoscale strain clusters are observed. As shown in Figure 4c, nanocrystals with the size of ≈60 nm embedded in the matrix can be readily observed through the sample, similar to previous report.[8] These embedded nanocrystals come from the dynamic recrystallization during the hot deformation process. Meanwhile, the highly deformed sample displays a mass of nanoscale distorted regions, because amounts of slips form to comply with strain compatibility during severe deformation (Figure 4d).

2.2. Multiscale Microstructures

Strong (00l) texture facilitates charge transport but the same also boosts phonon transport that is undesired for high zT values. In order to suppress the Kph while retaining the μH, forming multiscale microstructures with a strong degree of texture via HD is perceived as a feasible way. To showcase the as formed microstructures, the HD5 sample was subject to more detailed microstructural analysis using transmission electron microscopy (TEM). Figure 4 shows three types of nanoscale structures: strain clusters, polycrystals, and distortions.

The other characteristic structural feature is the high density of dislocations as shown in Figure 4e. A larger degree of HD at a lower temperature would induce more severe plastic deformation, which creates a large number of dislocations inside the distorted regions as well as at the interfaces between the distorted regions and the matrix. Dislocation scattering has been proved to be effective in scattering midwavelength phonons,[17] thus dense dislocations induced by innovative HD promise a significant reduction of Kph. Furthermore, hot deformation also produces atomic-scale intrinsic point defects (i.e., vacancies) into the lattice that further impede the transport of short-wavelength phonons. As such, the progressive HD creates multiscale structural defects, including microscale grain boundaries, nanoscale strain clusters, polycrystals, and distortions, as well as atomic-scale point and line defects, which work synergistically to realize full-spectrum phonon scatterings, thereby substantially suppressing the Kph over a wide temperature range.
2.3. Carrier Concentration in Relation to Intrinsic Point Defects

The $\mu_H$ of Bi$_{1.95}$Sb$_{0.05}$Te$_{2.3}$Se$_{0.7}$ is remarkably increased upon enhanced (00l) texture despite the formation of multiscale microstructures after progressive HD process (Figure 1f). The room temperature $\mu_H$ substantially increases from 71 cm$^2$ V$^{-1}$ S$^{-1}$ at $n_H = 6.9 \times 10^{19}$ cm$^{-3}$ for the HD1 sample to 100 cm$^2$ V$^{-1}$ S$^{-1}$ at $n_H = 9.7 \times 10^{19}$ cm$^{-3}$ for the HD5 sample. For comparison, the $\mu_H$ of SC Bi$_2$Te$_{2.4}$Se$_{0.6}$ is 149 cm$^2$ V$^{-1}$ S$^{-1}$ at a $n_H = 4.1 \times 10^{19}$ cm$^{-3}$.[44]

With a strong textures and multiscale microstructures, we shift our focus to the optimization of $n_H$, another key electrical transport parameter. Previous works demonstrated that the $n_H$ of V$_2$VI$_3$ compounds is directly governed by the type and...
amount of intrinsic point defect (Figure 5a). As shown Figure 5b, the \( n_{\text{hi}} \) of n-type polycrystalline Bi\(_{2-x}\)Sb\(_x\)Te\(_2.3\)Se\(_{0.7}\) initially rises and then drops with increasing Sb content (i.e., the \( x \) value), pointing toward the interplay between the extrinsic and intrinsic point defects. There are two major sources of intrinsic point defects in deformed Bi\(_{2-x}\)Sb\(_x\)Te\(_2.3\)Se\(_{0.7}\). The first source is of chemical origin: the antisite defects (Bi\(^{\prime}\)Te or Bi\(^{\prime}\)Se) are formed during the growth of Bi\(_2\)Te\(_3\)–Se from the melts. Reducing the difference in electronegativity \( \Delta \chi \) between the cation and the anion facilitates the formation of antisite defects. Hence, the addition of Sb into Bi\(_2\)Te\(_3\)–Se increases the concentration of antisites [Bi\(^{\prime}\)Te] on account of the smaller \( \Delta \chi \) of Sb–Te (\( \Delta \chi = 0.05 \)) than that of Bi–Te (\( \Delta \chi = 0.08 \)). The other source is of mechanical origin: the deformation induced nonbasal slips yield, on the average, pairs of 2V\(^{\prime\prime\prime}\)Bi and 3V\(^\cdot\cdot\)Te. In the presence of abundant Bi vacancies, the antisites Bi\(^{\prime}\)Te readily diffuse back.
into the Bi sublattice, creating excess anion vacancies $V^\text{Te}_{\text{Bi}}$ (i.e., the donor-like defects) and electrons. This is referred as the donor-like effect \cite{10}.

$$2V^\text{Bi}_{\text{Te}} + 3V^\text{Te}_{\text{Te}} + \text{Bi}^\text{Te}_{\text{Te}} \rightarrow V^\text{Bi}_{\text{Te}} + \text{Bi}^\text{Te}_{\text{Te}} + 4V^\text{Te}_{\text{Te}} + 6e^- \quad (1)$$

The same formula is valid for $V^\text{Sb}_{\text{Te}}$, $V^\text{Se}_{\text{Te}}$, $\text{Sb}^\text{Te}_{\text{Te}}$, and $\text{Bi}^\text{Se}_{\text{Te}}$.

Equation (1) correlates the chemically created antisites $\text{Bi}^\text{Te}_{\text{Te}}$ and mechanically created donor-like defects $V^\text{Te}_{\text{Te}}$, allowing us to interpret the results presented in Figure 5a. For the ease of discussion, it is plausible to assume that all Bi$_{2-x}$Sb$_x$Te$_{2.3}$Se$_{0.7}$ samples have the same $[\text{Bi}^\text{Te}_{\text{Te}}]$ and $[V^\text{Te}_{\text{Te}}]$ as they were subject to the same grain refinement and HD process. At $x = 0$, the $[\text{Bi}^\text{Te}_{\text{Te}}]$ is relatively low, the donor-like effect is thus weak in view of Equation (1), giving rise to a low $n_{\text{HI}}$. \cite{45} The initial Sb alloying ($0 < x < 0.10$) increases the $[\text{Bi}^\text{Te}_{\text{Te}}]$ and thus promotes the donor-like effect, yielding an increased $n_{\text{HI}}$ (Figure 5a). At a higher Sb content ($x \geq 0.15$), however, a higher $[\text{Bi}^\text{Te}_{\text{Te}}]$ is attained but only part of it contributes to the donor-like effect, the reminder of $\text{Bi}^\text{Te}_{\text{Te}}$ compensates $V^\text{Te}_{\text{Te}}$, yielding a drastic reduction in $n_{\text{HI}}$. Similar phenomena can be found in polycrystalline Bi$_2$Te$_3$,Se$_2$, and Bi$_2$Te$_2.3$Se$_{0.7-x}$ systems. \cite{10,45}

As depicted in Figure S9 of the Supporting Information, a small amount of Sb alloying increases the concentration of antisite defects and promotes the donor-like effect, thereby enhancing the $\sigma$ and PF. At the same time, the initial incorporation of Sb enhances the scattering of phonons via the lattice distortion and mass fluctuation, which leads to the slight reduction in the $\kappa_{ph}$. The double effects of simple Sb alloying yield a highest $zT$ of 1.1 at 405 K for once hot deformed Bi$_{1.95}$Sb$_{0.05}$Te$_{2.3}$Se$_{0.7}$, which is much higher than the HP Bi$_2$Te$_2$,Se$_{0.7}$, and comparable to the HD3 Bi$_2$Te$_2$,Se$_{0.7}$, especially at low temperatures. \cite{10} This $zT$ enhancement is ascribed to the simultaneously increased $n_{\text{HI}}$ and reduced $\kappa_{ph}$ through Sb alloying.

As known, the optimal carrier concentration ($n_{\text{opt}}$) depends on temperature as $n_{\text{opt}} \propto T^{3/2}$. Previous reports suggested that the $n_{\text{opt}}$ near room temperature is about $5 \times 10^{19}$ cm$^{-3}$ in V$_2$VI$_3$ solid solutions. \cite{8,14} For the application of low-temperature power generation at 450 K, the $n_{\text{opt}}$ should be raised above $9.2 \times 10^{19}$ cm$^{-3}$. Notably, the $n_{\text{HI}}$ of $x = 0.05$ HD1 sample is only $6.9 \times 10^{19}$ cm$^{-3}$, not high enough for TE application above 450 K. These samples need to be subject to further deformation.

In the following, we focus on the further optimization of $n_{\text{HI}}$ for the $x = 0.05$ HD1 sample, which possesses the highest $zT$ value through progressive HD process. As shown in Table S1 of the Supporting Information, the results of energy-dispersive X-ray spectroscopy (EDS) measurements show that the compositions of all the $x = 0.05$ samples slightly deviated from their nominal counterparts due to the Se loss in the growth-from-the-melt process; importantly, the composition is practically unchanged through the progressive HD process. Hence, the observed variation of $n_{\text{HI}}$ with the progressive HD process (Figure 5c) is mainly ascribed to the donor-like effect rather than the change of chemical composition.
In view of Equation (1), more severe deformation produces higher $[\text{V}''\text{Bi}]$ and $[\text{V}''\text{Te}]$ and thus leads to stronger donor-like effect. In this work, our approach is using progressively larger degree of deformation and more deformation times than previous reports (Table 1).\[4,8,32\] Furthermore, note that the donor-like effect can be mediated by the HD temperature. Below 723 K, the higher the HD temperature the stronger the donor-like effect is. Above 773 K, the recovery effect will offset the donor-like defects to some extent.\[30\] Variable temperature program (773 K for first time HD and 723 K for the following HDs) is implemented into this work to ensure consistently enhanced donor-like effect. For comparison, the detrimental effect of unoptimized HD temperature on the TE performance is presented in Figure S10 of the Supporting Information.

As depicted in Figure 5c, the room temperature $n_H$ rapidly rises with increasing HD count, substantially higher than those of prior works.\[4,8,32\] Specially, the HD5 sample owns a room-temperature $n_H \approx 9.7 \times 10^{19} \text{ cm}^{-3}$, around 41% increment over the HD1 one. In Figure 5d, we plot the $zT$ values at 450 K as a function of carrier concentration in n-type $V_2VI_3$ system in this and prior work.\[4,8,10,45\]

2.4. The Synergistic Compositional–Mechanical–Thermal Effects and a Record $zT$

With optimized texture (Section 2.1), multiscale microstructures (Section 2.2), and $n_H$ (Section 2.3), we discuss the electrical transport properties of progressively hot deformed $x = 0.05$ sample. As displayed in Figure 6a, the $\sigma$ decreases with temperature for all the samples, typical of degenerate semiconductor behavior. Progressively hot deforming the $x = 0.05$ sample increases the $\sigma$ because of the simultaneously enhanced textures and donor-like effect. Typically, the room temperature $\sigma$ of $154 \times 10^3 \text{ Sm}^{-1}$ was attained for the HD5 sample, which is a 66% increase than the HD1 one. In addition, the $\sigma$ for all the samples exhibits a $T^{-3/2}$ dependence, indicative of dominant acoustic phonon scattering.

The influence of HD count on the $S$ is illustrated in Figure 6b. As shown, the room temperature $S$ reduces from $-182 \mu\text{V K}^{-1}$ for the HD1 sample to $-169 \mu\text{V K}^{-1}$ for the HD3 sample, and $-155 \mu\text{V K}^{-1}$ for the HD5 sample, as expected from the increasing $n_H$.\[8\] We also note that the peak $S$ shifts from 450 K for the HD1 sample to 480 K for the HD3 sample, and then to 525 K for HD5 one, demonstrating that the adverse impact of intrinsic conduction on the $S$ at the elevated temperature is effectively suppressed. Interestingly, all the HD samples show a similar $S$ value above 550 K. The band gap $E_g$ of Bi$_{2-x}$Sb$_x$Te$_{2.3}$Se$_{0.7}$ was estimated by the Goldsmid–Sharp relationship: $E_g = 2eS_{\text{max}}T_{\text{max}}^{-2}$.\[20\] It is noteworthy that the derived $E_g$ value of Bi$_{2-x}$Sb$_x$Te$_{2.3}$Se$_{0.7}$ alloys is nearly unchanged upon Sb alloying and progressive HD (Tables S2 and S3, Supporting Information). Thus, the suppression of the bipolar effect with increasing HD count is ascribed to the significantly increased majority carriers induced by the donor-like effect. To our best knowledge, this is the first time suppression of intrinsic conduction by donor-like effect without relying on a broadened $E_g$ is reported in $V_2VI_3$ solid solutions.
Progressive HD enhances the PF owing to the increased $\sigma$ (Figure 6c). Specifically, the PF value at 300 K is $3.04 \times 10^{-3}$ W m$^{-1}$ K$^{-1}$ for the HD1 sample, and it sharply increases to $3.72 \times 10^{-3}$ W m$^{-1}$ K$^{-1}$ for the HD5 sample. The PF attained here was higher than those reported previously in n-type V$_2$VI$_3$ polycrystalline alloys [8,10,45] and but lower than $PF = 4.25 \times 10^{-3}$ W m$^{-1}$ K$^{-1}$ for the ZM Bi$_2$Te$_2.79$Se$_{0.21}$ [8] which is ascribed to the stronger texture of the latter. It is also found that HD5 sample exhibit the highest PF above 450 K because the detrimental effect of minority carriers on the $S$ is suppressed by promoting the donor-like effect without enlarging the $E_g$.

Figure 6d depicts the temperature dependence of $\kappa$ and $\kappa_{ph}$ for Bi$_{1.95}$Sb$_{0.05}$Te$_{2.3}$Se$_{0.7}$ samples with different HD count. As shown in Figure S11 of the Supporting Information, the heat capacity $C_p$ values are practically unchanged with increasing hot deformation count, because HD itself does not change the chemical compositions (Table S1, Supporting Information). The $\kappa$ shows small differences with the increase of hot deformation number. The $\kappa_{ph}$ is calculated by the Wiedemann–Franz law, $\kappa_{ph} = L\sigma T$, where the Lorenz number $L$ was roughly estimated using the formula $L = 1.5 \exp(-|S|/116)$ [47] (Figure S12, Supporting Information). Notably, progressive HD processing by itself can effectively diminish the $\kappa_{ph}$ through complex microstructures. As mentioned above, the HD sample exhibits multiscale microstructures including atomic-scale point and line defects, nanoscale strain clusters, polycrystals, and distortions and micrometer-scale grain boundaries that can effectively
scatter a wide spectrum of heat-carrying phonons. The $\kappa_{ph}$ dramatically falls with increasing HD count. Typically, the room temperature $\kappa_{ph}$ slightly drops from 0.6 W m$^{-1}$ K$^{-1}$ for the HD1 sample to 0.51 W m$^{-1}$ K$^{-1}$ for the HD3 sample, and then sharply decreases to 0.38 W m$^{-1}$ K$^{-1}$ for the HD5 one. It is concluded that larger deformation degree, more count and lower temperature leads to a lower $\kappa_{ph}$. In particular, the minimum $\kappa_{ph}$ is only 0.31 W m$^{-1}$ K$^{-1}$ at 405 K for the HD5 sample, almost 40% reduction than that of HD1 counterpart. A careful comparison of $\kappa_{ph}$ between this work and other results is plotted in Figure 6e. The observed $\kappa_{ph}$ is one of the minimum values in $\text{V}_2\text{VI}_3$ alloys,$[8,10,22,36,37,44–46]$ and close to those state-of-the-art TE materials with complex crystal structures and strong anharmonicity (Figure S13, Supporting Information).[48]

The flexion of $\kappa$–$\kappa_{el}$ for all the samples was attributed to the thermally excited minority carriers, which is consistent with the change in $S$ (Figure 6b). The bipolar effect is especially pronounced in narrow band gap $\text{V}_2\text{VI}_3$ materials, thereby limiting the $zT$ values at high temperatures.$[18,19]$ Again, suppressing the detrimental effect of intrinsic conduction is pivotal for high-temperature TE performance. The inflection point of $\kappa$–$\kappa_{el}$ shifts to a higher temperature with increasing HD count, indicating that donor-like effect induced majority carrier concentration increment suppresses the bipolar effects.

In order to clarify the contribution of bipolar thermal conductivity $\kappa_b$ at elevated temperatures, the $\kappa_b$ as a function of temperature need to be identified. In cases where $\kappa_b$ has no contribution, the relationship between the $\kappa_{ph}$ and the reciprocal of temperature ($1/T$) is theoretically linear. Assuming a negligible effect of $\kappa_b$ on $\kappa$ before intrinsic excitation, the difference between the calculated $\kappa_{ph}$ and experimental $\kappa$–$\kappa_{el}$ is approximately equal to $\kappa_b$.[20] The $\kappa_b$ of the representative samples (HD1-$x = 0$, HD1-$x = 0.05$, and HD5-$x = 0.05$) are presented in Figure 6f. With rising temperature, $\kappa_b$ sharply increases because tremendous electron–hole pairs are thermally excited. The HD1-$x = 0$ sample shows a maximum $\kappa_b$ of 0.56 W m$^{-1}$ K$^{-1}$ at 525 K, accounting for about 43% the total $\kappa$ at corresponding temperature. After suitable doping Sb on Bi sites, slight reduction of $\kappa_b$ is observed. Progressive HD further substantially depresses the $\kappa_b$. For HD5, the $\kappa_b$ at 525 K is diminished to only 0.24 W m$^{-1}$ K$^{-1}$, with a great decrease of 57% as compared with the $x = 0$ sample. As shown, promoting donor-like effect is an effective way to suppress $\kappa_b$ instead of band gap enlargement.

Based on the analysis of texture evolution, intrinsic point defect, and multiscale microstructures, a question arises as to whether the synergistic compositional–mechanical–thermal effects created by progressive hot deformation combined with Sb-alloying lead to better TE properties? In progressively hot deformed $x = 0.05$ sample, the peak $zT$ is further increased to 1.3 at 450 K for HD5 one, around 30% increment over the pristine $\text{Bi}_2\text{Te}_{2.3}\text{Se}_{0.7}$ counterpart (Figure 7a). This is a record $zT$ value reported for the n-type $\text{V}_2\text{VI}_3$ materials (Figure 7b) with both the thermal and electrical properties measured along

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure7.png}
\caption{a) $zT$ values as a function of temperature for $\text{Bi}_{1–x}\text{Sb}_x\text{Te}_{2.3}\text{Se}_{0.7}$ with different HD count. b) Temperature dependent $zT$ for HD5 $x = 0.05$ sample, comparing with those of other high-$zT$ n-type $\text{V}_2\text{VI}_3$ materials.$[8,14,21,22,28,36,37,48,52,55]$ c) The main contributors to the average $zT_{ave}$ advances between 300 and 500 K of the $\text{Bi}_2\text{Sb}_x\text{Te}_{2.3}\text{Se}_{0.7}$ alloys in this work. d) Compatibility factor as a function of temperature for $\text{Bi}_{2–x}\text{Sb}_x\text{Te}_{2.3}\text{Se}_{0.7}$ alloys.}
\end{figure}
the in-plane direction.\cite{8,14,21,22,28,36,37,45,46} Compared with other n-type materials with high $zT$, our sample is more competitive in the vicinity of 450 K, indicating promising application potential in low-temperature TE power generation. More importantly, the average $z_{\text{ave}}$ value is substantially improved via synergistic compositional–mechanical–thermal effects (Figure 7c). Typically, the average $z_{\text{ave}}$ value of HD5 is 1.2 in the range of 300–500 K. In addition, the compatibility factor is also enhanced during the progressive HD process (Figure 7d).

As illustrated in Figure 8, this work demonstrates the success of enhancing $zT$ of n-type $V_2VI_3$ alloys, which match their p-type counterparts, by the synergy of point defect engineering, texture engineering, and multiscale microstructures. The efficacy of synergistic compositional–mechanical–thermal effects induced by innovative HD is thereby proved.

### 3. Conclusion

In this work, we implemented synergistic compositional–mechanical–thermal effects through progressive hot deformation toward a delicate balance between texture, extrinsic and intrinsic point defects, and multiscale microstructures in n-type quaternary $V_2VI_3$ alloys. These synergistic compositional–mechanical–thermal effects afforded a significantly extended parameter space for performance optimization. The details of texture evolution were systematically studied by X-ray powder diffraction, pole figures, and orientation distribution function. The integrated actions of larger magnitude, more counts and lower temperature of hot deformation gives rise to a stronger texture, which is comparable to that of zone melted ingots. The progressive hot deformation in conjunction with proper Sb alloying also facilitated the donor-like effect and increased the majority carrier concentration, successfully suppressing the detrimental effect of intrinsic conduction in absence of band gap enlargement. Meanwhile, owing to the multiscale microstructures that include atomic-scale point and line defects, nanoscale strain clusters, polycrystals, and distortions and microscopic grain boundaries, an ultralow lattice thermal conductivity $\approx 0.31$ W m$^{-1}$ K$^{-1}$ at 405 K was attained. As a result, a record $zT$ of 1.3 at 450 K as well as high averaged $z_{\text{ave}}$ values of 1.2 between 300 and 500 K was achieved in five-time progressively hot deformed Bi$_{1.95}$Sb$_{0.05}$Te$_{2.3}$Se$_{0.7}$, which matches better with the p-type counterparts in device fabrication. The successful implementation of synergistic compositional–mechanical–thermal effects in benchmark n-type $V_2VI_3$ alloys marks a progress in both hot deformation technique and defect engineering.

### 4. Experimental Section

**Sample Synthesis and Preparation:** The n-type rhombohedral $V_2VI_3$ alloys were grown from the melt followed by hot deformation. Appropriate amounts of Bi (99.999%), Sb (99.999%), Te (99.999%), and Se (99.999%) were weighed according to the nominal compositions of Bi$_2$Sb$_2$Te$_2$Se$_0.7$ alloy ($x = 0, 0.05, 0.10, 0.15, 0.20,$ and 0.25) and sealed into 10 mm-diameter quartz tubes evacuated.
at 10⁻³ Pa. These tubes were slowly heated to 1073 K in 5 h, dwelt for 10 h, and furnace-cooled to room temperature. The as formed ingots were crushed, ground into fine powders and then densified into Φ10 mm cylinders by spark plasma sintering at 723 K for 5 min with a 60 MPa uniaxial pressure. In a typical hot deformation process, the SPS samples were repressed in a much larger graphite die at 773 K for 5 min using the same stress. To promote the donor-like effect and the texture, progressive HD procedure is performed at a lower temperature (723 K), more counts (up to five times, the die at 773 K for 5 min with a 60 MPa uniaxial pressure. In a typical hot deformation stage.

Sample Characterization: X-ray diffraction data and pole figure measurement taken on the polished surfaces were obtained on a Bruker D8 Advance SS/18 kW diffractometer with the Cu 40 Kα radiation. The lattice parameters were refined by the Rietveld method using Topas 3.1 software. The chemical compositions were analyzed by JEOL JXA-8100 EDS. The samples for TEM [JEOL ARM200F equipped with cold field emission gun, ASCOR probe corrector) were prepared by the conventional standard methods including cutting, grinding, dimpling, polishing and Ar-ion milling on a liquid nitrogen cooling stage.

A caveat in the determination of zT of textured V₂V₁₃ materials is that all three TE properties must be measured in the same direction. In this work, all three TE properties of all the samples were measured along the in-plane direction (i.e., perpendicular to the HD pressing direction), if not otherwise noted. To this end, the in-plane thermal conductivity was measured using the method described in ref. [4].

The in-plane electrical conductivity σ and Seebeck coefficient S were simultaneously measured under helium atmosphere by using ZEM-2 (ULvac-Riko, Japan). The thermal conductivity was calculated by using the equation κ = pC₀D, where p is the density of the bulk sample, C₀ is the heat capacity and D is the thermal diffusivity, respectively. The p was estimated by using the sample dimensions and mass, and the C₀ was measured on a Netzsch LFA-457 instrument in the argon atmosphere. The Hall coefficients R₉₃ were measured on a PPM5 system (Quantum Design) with magnetic fields sweeping from −5T to 5T. The carrier concentrations nₑ, carrier mobility μₑ were calculated using the relation nₑ = 1/(eRₑ₉₃) and μₑ = σ Rₑ₉₃, respectively.

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

microstructures, synergistic effects, textures, thermoelectrics, V₂V₁₃

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