Defects and defect engineering are at the core of many regimes of material research, including the field of thermoelectric study. The 60-year history of V$_2$VI$_3$ thermoelectric materials is a prime example of how a class of semiconductor material, considered mature several times, can be rejuvenated by better understanding and manipulation of defects. This review aims to provide a systematic account of the underexplored intrinsic point defects in V$_2$VI$_3$ compounds, with regard to (i) their formation and control, and (ii) their interplay with other types of defects towards higher thermoelectric performance. We herein present a convincing case that intrinsic point defects can be actively controlled by extrinsic doping and also via compositional, mechanical, and thermal control at various stages of material synthesis. An up-to-date understanding of intrinsic point defects in V$_2$VI$_3$ compounds is summarized in a ($\chi$, r)-model and applied to elucidating the donor-like effect. These new insights not only enable more innovative defect engineering in other thermoelectric materials but also, in a broad context, contribute to rational defect design in advanced functional materials at large.

1. Introduction

V$_2$VI$_3$ compounds ($V =$ Group V elements Sb and Bi, and $VI =$ Group VI elements S, Se and Te) and their derivatives constitute an important class of semiconductor material in renewable energy and next generation information technology. For decades these compounds have been the benchmark thermoelectric (TE) materials.[1] Recently they became a focus in the study of bulk quantum topological insulators.[2] In this review we intend to address the fundamental yet underexplored role of intrinsic point defects in V$_2$VI$_3$ compounds. While this gap of knowledge has led to ambiguities in the synthesis-structure-property correlation, it is the area of research that holds the promise of further improving the material performance.

In V$_2$VI$_3$ materials intrinsic point defects specifically refer to vacancies and antisite defects while extrinsic point defects refer to guest atoms. Strictly speaking, intrinsic point defects are thermally created in an otherwise perfect crystal in which case the stoichiometry is retained. In practice, the condition of stoichiometry is often relaxed, so the nomenclature “intrinsic point defects” and “native point defects” can be used interchangeably. One should not confuse the nature of a point defect (i.e., intrinsic or extrinsic) with the character of the procedure of creating such defects (e.g., equilibrium or off-equilibrium).

This review is written from a thermoelectric perspective in that we study the TE properties of the material in its totality to characterize intrinsic point defects and their interplay with other defects in V$_2$VI$_3$ materials; reversely, a better understanding of intrinsic point defects and their interplay with other defects enables us to further optimize the TE performance of V$_2$VI$_3$ compounds. The TE performance of a material is gauged by its dimensionless figure of merit $zT = \alpha^2T/\kappa = PF/\kappa$,[3] where $\alpha$, $\sigma$, $\kappa$, $T$ and $PF$ are the Seebeck coefficient (i.e., thermopower), electrical conductivity, total thermal conductivity (including the lattice component, $\kappa_l$, and carrier component, $\kappa_c$), the absolute temperature, and the power factor ($PF$), respectively. The overarching goal of TE research is to develop higher $zT$ materials.[4–8] To this end, no TE material would have achieved its best performance without defects.[9] The canonical “phonon-glass electron-crystal” strategy is implemented via coherently engineering point defects, textures, grain boundaries, and nano-inclusions to reduce the $\kappa_l$[18–17] and enhance the $PF$.[18–25]

Bi$_2$Te$_3$ is customarily regarded as the representative of V$_2$VI$_3$ compounds. The crystal structure of this compound is trigonal (space group R-3m) and consists of atomic layers stacked in the order of Te$^{(1)}$-Bi$^{(2)}$-Te$^{(3)}$-Bi$^{(2)}$-Te$^{(1)}$ along the c-axis. The Te atoms in site (2) have Te$^{(2)}$-Bi bonds that are covalent and ionic, while the Te$^{(1)}$-Te$^{(1)}$ layers are weakly bound with van der Waals force. This conveys to the Bi$_2$Te$_3$ an almost two-dimensional nature, with a strong anisotropy between the properties in the plane and those along the c-axis. The pioneer work in Bi$_2$Te$_3$ by Goldsmid et al.,[26] the first TE refrigerator using p- and n-type Bi$_2$Te$_3$.[27]
and the classic alloying (solid solution) approach by Ioffe et al.\textsuperscript{[38]} dated back to 1950’s. The outstanding TE performance and the wide range of composition in both p-type and n-type attained by alloying Bi$_2$Te$_3$ with isostructural Sb$_2$Te$_3$ or Bi$_2$Se$_3$ showcases the efficacy of defect engineering.\textsuperscript{[29–31]} In addition, V$_2$VI$_3$ compounds have been a test bed for novel material fabrication methods.\textsuperscript{[10]} These methods, in turn, govern the type, amount, and topology of defects. The history of TE study of V$_2$VI$_3$ compounds is a prime example of how a class of material can be rejuvenated by better understanding and manipulation of defects, ranging from 0D point defects,\textsuperscript{[32]} 1D dislocations,\textsuperscript{[33–35]} 2D grain boundaries,\textsuperscript{[36,37]} to 3D nanoinclinations.\textsuperscript{[38]} This review focuses on intrinsic point defects in V$_2$VI$_3$ compounds.

Understanding the role of intrinsic point defects is a prerequisite for establishing the fundamental synthesis-structure-property correlation in V$_2$VI$_3$ semiconductors, however, it is challenging to correlate specific atomic level defects and macroscopic TE properties given the complex crystal structure, especially when heavily doped and/or in the presence of other types of defects. For example, the best commercial TE materials near room temperature are ternary p-type Bi$_2$Sb$_2$Te$_5$ and n-type Bi$_x$Sb$_{3–x}$Se$_{2–x}$.\textsuperscript{[27]} The TE properties of these heavily extrinsically doped Bi$_2$Te$_3$ are actually governed by intrinsic point defects, the causal chain follows: extrinsic point defects $\rightarrow$ intrinsic point defects $\rightarrow$ TE properties (cf. Section 3.1).

The significance of intrinsic point defects in V$_2$VI$_3$ compounds is justified by a simple argument. The carrier concentration $n$ is the material parameter of utmost importance in V$_2$VI$_3$ compounds as the $\sigma$, $\alpha$, and $\kappa_e$ depend closely on the value of $n$, intrinsic point defects are on a par with extrinsic point defects in the capacity of contributing charge carriers. Experimental and theoretical studies corroborated that the optimal carrier concentration $n$ of V$_2$VI$_3$ materials is on the order of $10^{19}$ cm$^{-3}$,\textsuperscript{[32,33,39]} while intrinsic point defects alone can contribute $10^{18}$–$10^{20}$ cm$^{-3}$.\textsuperscript{[40]} In a proof-of-principle study, we devised an intrinsic point defect engineering (IPDE) approach in n-type Bi$_x$Te$_2$Se$_{0.7}$, which simultaneously optimized the $PF$, $\kappa_{ph}$ and $zT$.\textsuperscript{[32]} The success of the IPDE approach is reflected in the $zT$ peak value of above 1.2 at 445 K and also high averaged $zT$ values of 1.1 between 300 K and 500 K.

The significance of intrinsic point defects is also confirmed in other state-of-the-art TE materials. For example, vacancies modulate the carrier concentration $n$ in Zintl compounds.\textsuperscript{[40]} In Mg$_{2-x}$Sb$_x$Sn$_{0.6}$Ge$_{0.4}$, Sb doping at low ratios tunes the $n$ while it facilitates the formation of Mg vacancies at high Sb doping ratios, Mg vacancies effectively scatter heat-carrying phonons; in addition, excess Mg in the starting material facilitates the formation of Mg interstitials that also alter the $n$. In ZrNiSn-based half-Heusler (HH) materials, the band gap is modulated by the content of Zr/Sn antisite defects.\textsuperscript{[42]}

The rest of the article is organized as follows. We discuss the creation and control of intrinsic point defects in V$_2$VI$_3$ semiconductors in Section 2 and 3, respectively. As shown, intrinsic point defects can be created and manipulated compositionally, mechanically (via “the donor-like effect”), and thermally (via “the recovery effect”). We propose a simple ($\chi$, $r$)-model and discuss the donor-like effect. Section 4 and 5 are devoted to the impact of intrinsic point defects on the TE properties and how to engineer intrinsic point defects to tailor the material performance in different temperature ranges, respectively. In Section 6, we address the underheded role of intrinsic point defects in nanostructured and texturing process. Finally we conclude, in Section 7, with perspective remarks.
2. Formation of Intrinsic Point Defects in V₂VI₃ Binary Compounds

The V₂VI₃ binary compounds grown from stoichiometric melts tend to have Group V element excess because Group VI element often precipitates as a secondary phase (mainly Te) or is volatile (mainly S or Se). Satterthwaite et al. reported that the as-grown Bi₂Te₃ ingot is p-type when the actual Te content is less than 62.8 at% (namely, Te-deficient), and the hole concentration n rapidly decreases with Te excess; at the other end, the ingot exhibits n-type (Figure 1a). These less intuitive observations can be explained by intrinsic point defects. Harman et al. proposed that the dominant intrinsic point defects in the as-grown Bi₂Te₃ ingot are negatively charged antisite defects Bi₄ on the Te-deficient side and positively charged antisite defects Te₄ on the Te-rich side. This scenario is supported by the results of packing density measurements and the density values calculated for various defect models (Figure 1b). The presence of antisite defects in Bi₂Te₃ thin film is confirmed by high precision chemical analysis. In the same vein, the dominant intrinsic point defects in p-type Sb₂Te₃ are Sb₄ and V₄ while V₄ are the dominant point defects in n-type Bi₂Se₃. Horak et al. pointed out that V₄ coexists with V₄ in n-type Bi₂Se₃. The predominance of these intrinsic point defects has been confirmed by first-principles calculations. Table 1 lists the type and the concentration of dominant intrinsic point defects in Sb₂Te₃, Bi₂Te₃, and Bi₂Se₃.

In addition to intrinsic point defects, Bi excess (Te deficiency) may create extended defects such as the seven-layer-lamella defect Bi₄Te₄ with the sequence Te¹–Bi–Te¹–Bi–Te¹–Bi–Te¹. The presence of Bi₄Te₄ is confirmed by high resolution electron microscopy measurements in bulk crystals, films, and nanowires of Bi₂Te₃. First-principles calculations suggest that the low formation energy of the nearest neighbor XBi–Te¹ (i.e., the exchange of a Bi atom with a Te¹ atom in the same supercell) facilitates the formation of Bi₄Te₄. Furthermore, Horak et al. proposed that Bi₄ and Bi₄ are favored at low and high Bi excess, respectively.

3. Manipulation of Intrinsic Point Defects

In Section 3, we address how to implement intrinsic point defects in V₂VI₃ compounds, following the order of pre-synthesis control (Section 3.1), in-synthesis control (Section 3.2), and post-synthesis control (Section 3.3 and Section 3.4). Alternatively, these controls can be categorized into compositional/chemical control (Section 3.1 and 3.2), mechanical control (Section 3.3), and thermal control (Section 3.4).

3.1. Compositional Control in Cation-Rich V₂VI₃ Compounds

As mentioned in Section 2, V₂VI₃ binary compounds synthesized from stoichiometric starting composition tend to be cation rich. There is an important correlation between the conduction type and the carrier concentration of intrinsic point defects and the electronegativity χ and covalent radius r of cations and anions. We hereafter call this correlation the (χ, r)-mechanism or the (χ, r)-model. As shown in Figure 2a, the smaller the difference in χ and r between the cation and the anion the easier for antisite defects to form. At the other end, increasing the difference in χ and r between the cation and the anion will favor the formation of anion vacancies. We present the χ, r of constituent elements in binary V₂VI₃ compounds in Table 2. The formation energy of antisite defect E₁ can be enumerated in ascending order as:

Table 1. Conduction type and the calculated concentration of dominant intrinsic point defect in Sb₂Te₃, Bi₂Te₃, and Bi₂Se₃. The concentration of defect depends on the formation energy and thus the position of Fermi level, which is fixed at the midgap in calculations.

| Compounds | Sb₂Te₃ | Bi₂Te₃ | Bi₂Se₃ |
|-----------|--------|--------|--------|
| Conduction type | p | p | n |
| Point defect type | Sb₄ | Bi₄ | V₄ |
| Point defect concentration (cm⁻³) | 2 × 10⁻¹¹ | 8 × 10⁻¹⁹ | 3 × 10⁻¹⁹ |

Figure 1. a) Room temperature carrier concentration of Bi₂Te₃ ingots as a function of Te content. b) Room temperature mass density of Bi₂Te₃ ingots as a function of Te content.
in cation-rich binary Bi$_2$Te$_3$ can make the carrier concentration in p-type Bi$_2$Te$_3$... 1600004

Figure 2. a) Schematic of the formation of intrinsic point defects in cation-rich case. The size of circle represents the covalent radius. b) The calculated formation energies of intrinsic point defect considering spin-orbit interactions in the cation-rich case. $V_C$, $A_C$, $V_A$, and $C_A$ represent cation vacancies, anion antisite defects, anion vacancies, and cation antisite defects, respectively.

$$E_{AS}(\text{Sb–Te}) < E_{AS}(\text{Bi–Te}) < E_{AS}(\text{Sb–Se}) < E_{AS}(\text{Bi–S})$$ \hspace{1cm} (1)

Meanwhile, the formation energy of anion vacancies $E_V$ is listed in descending order as:

$$E_V(\text{Sb–Te}) > E_V(\text{Bi–Te}) > E_V(\text{Sb–Se}) > E_V(\text{Bi–S})$$ \hspace{1cm} (2)

These two inequalities can be used to semi-quantitatively explain the composition dependence of the conduction type and that of the carrier concentration in cation-rich V$_2$VI$_3$ single crystals and zone-melted ingots. For example, the difference in $E_{AS}$ explains why Bi$_2$Te$_3$ exhibits a strong p-type characteristic whereas Bi$_2$Se$_3$ is weakly p-type in light of inequality (1). Inequality (2) can explain the strong n-type characteristic of Bi$_2$Se$_3$ in terms of the low $E_V$.

The formation energy of Bi$_{1x}$ in cation-rich binary Bi$_2$Te$_3$ can be calculated by the following formula derived from statistical thermodynamics:

$$E_{Bi_{1x}} = -k_B T_m \left( \ln \frac{n_{Bi_{1x}}}{N_T} + 1 \right)$$ \hspace{1cm} (3)

where $k_B$ is the Boltzmann constant, $T_m$ the melting point, $n_{Bi_{1x}}$ the number of Bi$_{1x}$ per cm$^3$, and $N_T$ the number of available Te sites per cm$^3$, respectively. The typical value of $E_{AS}$ is 0.35 eV, 0.50 eV, 0.64 eV for binary Sb$_2$Te$_3$, Bi$_2$Te$_3$, and Bi$_2$Se$_3$, respectively$^{[47,49,50,51]}$. These values are confirmed by first-principles calculations (Figure 2b). Generally, cation antisite defects and anion vacancies are energetically more favorable than anion antisite defects and cation vacancies under the cation-rich condition.$^{[58]}

The ($\chi$, $r$)-model can be extended to ternary and quaternary V$_2$VI$_3$ materials. In general, substituting more electronegative or smaller atoms of the same valence on the anion site tends to drive the material towards hole-like (p-type) conduction, while substituting more electronegative or smaller atoms of the same valence on the anion site tends to drive the system towards electron-like (n-type) conduction. For instance, increasing Sb content in p-type Bi$_{2-x}$Sb$_{x}$Te$_3$ reduces the $E_{AS}$, thereby increasing the hole concentration $n_h$ owing to a smaller difference in $\chi$ and $r$ between Sb and Te than the counterpart between Bi and Te (Figure 3a)$^{[29,50,72]}$. Similarly, substituting Te by Se in Bi$_2$Te$_3$ increases the $E_{AS}$ and suppresses the $E_V$, resulting in a n-type conduction.$^{[32]}$ When the concentration of anion vacancies ([V$_{Te}^-$]) exceeds the concentration of antisite defects ([Bi$_{Te}^-$] and [Bi$_{Se}^-$]), a p-type to n-type crossover occurs (Figure 3b)$^{[32,73]}$. Notably, S substitution on the Se-site quickly shifts the p–n crossover point down to $x = 0.13$$^{[68,74,75]}$. Doping n-type Bi$_2$S$_x$Te$_{3-x}$ with Sb$^{[76]}$ or doping p-type Bi$_2$Se$_3$ with Se$^{[77,79]}$ rapidly diminish the carrier concentration (Figure 3c).

An important implication of these results is that intrinsic point defects can be actively tuned by isoelectronic extrinsic dopants. The best commercial room temperature TE materials p-type Bi$_{2-x}$Sb$_x$Te$_3$ and n-type Bi$_{2}$Te$_{3-x}$Se$_x$ alloys are good examples. These results also serve as a caveat when we try to derive the causal chain in data analysis: implementing isoelectronic extrinsic dopants leads to the formation of intrinsically point defects, then the latter govern the observed conduction type and the magnitude of carrier concentration.

Comparing to the case of isoelectronic extrinsic doping, the interplay between intrinsic point defects and heteroelectron extrinsic dopants is more complex. Nonetheless, it is known

Table 2. Boiling point, electronegativity, covalent radius, and atomic mass of constituent elements in V$_2$VI$_3$ compounds.

| Elements | Bi | Sb | Te | Se | S |
|----------|----|----|----|----|---|
| Boiling point [K] | 1837 | 1860 | 1261 | 1231 | 991 |
| Electronegativity | 2.02 | 2.05 | 2.1 | 2.55 | 2.58 |
| Covalent radius [Å] | 1.46 | 1.40 | 1.36 | 1.16 | 1.02 |
| Atomic mass | 208.98 | 121.75 | 127.60 | 78.96 | 32.07 |
That heteroelectron dopants such as Li, Ag, Cu, Pb, Sn, I, Mn, Ge affect the formation of intrinsic point defects. For example, Te loss can be suppressed by adding a small amount of Cu to increase the formation energy of $iiVTe$.

Indium (In) doping is a manifestation of the significance of intrinsic point defects in the presence of heteroelectron extrinsic dopants. Doping by indium modulates the formation energy of intrinsic point defects and thus alters the carrier concentration, shifting the optimal operation regime from room temperature to higher temperature. Indium (5s$^2$5p$^1$) occupying the Sb (5s$^2$5p$^3$)-site is expected to form a negatively charged substitutional point defect and thus increases the hole concentration $n_h$ (In$_{5s^25p^1}$ → $^\text{ii}$In$_{5s^25p^1}$). However, Figure 4a shows the opposite: indium substitution moderately decreases the $n_h$ in Sb$_2$Te$_3$, $\text{Se}_{x}$, in contrast to iodine doping and Ti doping.

To explain this counter-intuitive observation, Horak proposed that incorporation of indium into Sb$_2$Te$_3$ creates charge neutral point defects $\text{InSb}$, accompanied by a $\text{In}^{5s^25p^1}$ → $\text{In}^{5s^25p^3}$ electronic transition. In this scenario, the substitution of Sb by In does not directly alter the $n_h$, rather, it raises the $E_{AS}$ due to the greater difference in $\chi$ between In and Te than that between Sb and Te, thereby reducing the $n_h$. A similar scenario has been proposed for Ti, $\text{Bi}_{5}$, or Se$^{27}$-doped Sb$_2$Te$_3$. The relative reduction of $n_h$ due to the doping on the Te-site is enumerated in descending order as: Ti $>$ In $>$ Se $>$ Bi.

To elucidate the effect of indium doping on the $n_h$, the $E_{AS}$ of Sb$_2$Te$_3$ is estimated by the following relation:

$$N_{AS} \propto (C_{SB} - C_{In}) \exp\left(-\frac{E_{AS}}{k_bT_m}\right)$$

where $N_{AS}$ is the concentration of antisite, $C_{SB}$ the Sb concentration, $C_{In}$ the In concentration, $k_b$ the Boltzmann constant, $T_m$ the melting point (assuming a linear relationship between $T_m$(Sb$_2$Te$_3$) = 902 K and $T_m$(In$_2$Te$_3$) = 940 K), respectively. $E_{AS} = E_0 + \Delta E$, where $E_0$ = 0.35 eV is the activation energy of Sb$_2$Te$_3$ in undoped Sb$_2$Te$_3$, $\Delta E$ the activation energy increment of Sb$_2$Te$_3$ due to indium doping. As shown in Figure 4b, the $\Delta E$ rapidly increases with increasing indium content, a reflection of the fact that the formation energy of Sb$_2$Te$_3$ in indium-doped Sb$_2$Te$_3$ is higher than that of undoped one.

3.2. Synthesis Environment Control

We in Section 3.2 discuss the control of intrinsic point defects in the case of off-stoichiometric starting materials. We hereafter call this mechanism “synthesis environment control”. Under a cation-rich growth condition, $V_{\text{Te}}$, $\text{Bi}_{5}^{\text{In}}$, and Sb$_{x}^{\text{Te}}$ are responsible for the native n-, p-, and p-type conduction in Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Bi$_2$Te$_3$. 

![Figure 3](https://www.MaterialsViews.com)
and Sb$_2$Te$_3$ ingots, respectively. Under an anion-rich condition, Se$_{Bi}$, Te$_{Bi}$, and V$_{Sb}^{‴}$ are responsible for the native n-type, n-type, and p-type conduction in Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ ingots, respectively. [58,98] In the zone-melted (ZM) p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ ingots, it is found that the formation of antisite defects can be suppressed by adding extra Te (>60 at%) to the melts because the $E_{AS}$ is higher under a Te-rich condition (Figure 5a). [27,43] Meanwhile, excess Bi (>40 at%) in Bi$_2$Te$_3$ and Bi$_2$Se$_3$ facilitates the formation of Bi$_{Te}$ and Bi$_{Se}$.

Controlling intrinsic point defects in V$_2$VI$_3$ compounds now has an impact beyond the field of TE material research. Bi$_2$Te$_2$Se becomes the subject of crystal growth research owing to its topological insulator properties. [2,29,32] In the study of 3D topological insulators a grand challenge is to minimize the bulk electrical conduction to help discern the surface electrical conduction. However, stoichiometric Bi$_2$Te$_2$Se grown by a modified Bridgman method is metal-like, with a $n_e$ on the order of $10^{19}$ cm$^{-3}$. To suppress the bulk electrical conduction, Jia et al. fabricated highly bulk resistive Bi$_{2-x}$Te$_2$-x-Se samples under a slightly Bi-rich condition in which the Bi excess introduces Bi$_{Te}$ (Figure 5b). [99] In another study of topological insulator, Jiang et al. fabricated high-quality Sb$_2$Te$_3$ films by molecular beam epitaxy and observed the intrinsic point defects by in situ scanning tunneling microscopy and spectroscopy. They found that in a strong Te-rich environment V$_{Sb}^{‴}$ is the defect with lowest formation energy while Sb$_{Te}$ becomes the lowest energy defect in a less Te-rich environment. [100]

3.3. Mechanical Control: Deformation and the Donor-like Effect

In addition to compositional control (Section 3.1) and synthesis environment control (Section 3.2), mechanical control via post-synthesis deformation is another approach. [101–108] It is well known that the p-type Bi$_2$Te$_3$ ingots can be inverted to n-type.
simply by pressing.\cite{109} and the pressed n-type material can be re-inverted to p-type via sintering at sufficiently high temperatures.\cite{110} Heavy plastic deformation of Bi$_2$Te$_3$ ingots produces non-basal slips and V$^{\prime\prime\prime}_{\text{Te}}$, changing the conduction type from p-type to n-type, and simultaneously enhancing the electrical conductivity (Figure 6).\cite{101} Ionescu et al. suggested that non-basal slip produces 3 Bi to 2 Te vacancy–interstitial pairs during heavy deformation processing.\cite{111} In presence of Bi vacancies, Bi atoms diffuse from Te sites back to their original sublattice sites, extra Te vacancies and excess electrons are thus produced. This important mechanism is called "the donor-like effect", expressed as:

$$2V^{\prime\prime\prime}_{\text{Te}} + 3V^{\prime\prime\prime}_{\text{Bi}} + 3V^{\prime}_{\text{Te}} \rightarrow 4V^{\prime\prime\prime}_{\text{Bi}} + 4V^{\prime\prime\prime}_{\text{Te}} + 6e'$$

(5)

where V$^{\prime\prime\prime}_{\text{Te}}$ and V$^{\prime\prime\prime}_{\text{Bi}}$ are the Bi and Te vacancies, V$^{\prime}_{\text{Te}}$, the antisite defects, and e' the excess electrons, respectively. Similar formulae like (5) hold for V$^{\prime\prime\prime}_{\text{Se}}$, V$^{\prime\prime}_{\text{Se}}$, V$^{\prime}_{\text{Se}}$, and V$^{\prime\prime}_{\text{Se}}$.

The donor-like effect is a delicate multiple-stage n-type doping mechanism involving multiple intrinsic point defects. The study of donor-like effect is warranted because grinding, ball milling, hot/cold deformation, and hot pressing processes have been extensively used for various purposes in TE research. The past decade has witnessed great strides toward understanding and utilizing the donor-like effect in V$_2$VI$_3$ compounds.

Experimentally, the impact of donor-like effect is reflected in the large difference in $\alpha$, which is inversely correlated to the $n$, between (Bi,Sb)$_2$(Te,Se)$_3$ single crystal and hot pressed (HP) sample (Figure 6b).\cite{101} The (Bi,Sb)$_2$(Te,Se)$_3$ single crystal shows a p-type conduction for all compositions of Bi$_2$Sb$_x$Te$_3$ and a p–n transition at Bi$_2$Te$_{2.1}$Se$_{0.9}$, in contrast, the HP sample exhibits a p–n transition at Bi$_{0.66}$Sb$_{1.34}$Te$_3$ and a n-type conduction for all compositions of Bi$_2$Te$_{3-x}$Se$_x$. The donor-like effect can explain these observations. Importantly, hot deformation (HD) processes promote the donor-like effect.\cite{2,32,33,66,67,112} Different from the strong donor-like effect created by heavy deformation such as grinding, ball milling (BM), and extrusion, HD produces weaker donor-like effect due to mild deformation.

More severe deformation produces finer powders and a greater decrease in the $n_p$ in p-type Bi$_2$Sb$_x$Te$_3$ and a larger increase in the $n_e$ in n-type Bi$_2$Te$_{3-x}$Se$_x$.\cite{114} Shin et al. deformed the p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ ingot by cold pressing at 700 MPa from one to eleven times using the tool steel mold.\cite{115} They showed that the $\alpha$ increases with the increasing number of times of cold pressing, which correlates with a stronger donor-like effect. Similarly, increasing the number of times of HD or prolonging the BM time facilitates the donor-like effect and hence increased the $n_e$ in n-type Bi$_2$Te$_{3-x}$Se$_x$ (Figure 6c and 6d). The donor-like effect gets marginal above a certain level of deformation.

### 3.4. Thermal Control via the Recovery Effect

The recovery effect can be regarded as a post-deformation thermal relaxation process, which basically counters the donor-like
effect regarding the carrier concentration change. The microscopic picture of the recovery effect posits that anion vacancies are annihilated by dislocation climb and array formation upon annealing. As expected, the recovery effect has a strong dependence on the annealing temperature (Figure 6a).\textsuperscript{[101]}

Low-temperature annealing only slightly mitigates the donor-like effect and thus slightly reduces the $n_\text{e}$. As a result, the $\sigma$ is reduced while the $\alpha$ is somewhat enhanced. At the other end, when the deformed samples are annealed at high temperatures for a long time, the donor-like effect can be nearly removed, as a result, the electrical properties revert slowly back to the original ones. Studies also showed that raising HP or SPS temperatures also mitigates the donor-like effect (i.e., $V_\text{Te}^-$ or $V_\text{Bi}^-$) due to the recovery effect.\textsuperscript{[32,116–118]} It should be pointed out that the HD and annealing temperaturae are substantially higher than the operation temperature of $V_\text{Bi}V_\text{I}_3$ TE materials so the thermal stability of as formed intrinsic point defects is not an issue in operation. This has been confirmed by our repetitive test measurements.

4. Role of Intrinsic Point Defect towards Higher $zT$

In Section 4 we address how intrinsic point defects generally impact the TE properties $\sigma$, $\alpha$, and $\kappa$, which sets the stage for elucidating intrinsic point defect engineering in Section 5.

4.1. Optimizing Electron Band Structure

Optimizing electron band structure involves two basic tasks: (i) tuning the band filling to attain an optimal carrier concentration $n$; and (ii) enhancing the electron density of states (DOS) near the Fermi level $E_F$ to increase the $\alpha$. While implementing extrinsic point defects by doping remains the mainstream methodology to optimize the value of $n$, we recently showed that intrinsic point defects alone can attain an optimal $n$ value $\approx 5 \times 10^{19}$ cm$^{-3}$ in both p- and n-type $V_2V_\text{I}_3$ materials.\textsuperscript{[32]} To enhance the DOS near $E_F$, theoretical calculations by Hashibon et al. showed that the $E_F$ is shifted into the valence band by $Bi'^\text{r}_\text{I}$, and into the conduction band by $Te'^\text{r}_\text{Bi}$,\textsuperscript{[56]} forming resonant (defect) states.\textsuperscript{[21]} On the other hand, the band structure tuning by intrinsic point defects in $V_2V_\text{I}_3$ compounds will strongly interplay with composition optimization, which results in the change in band gap. The discussion on this topic is specially presented in Section 5.2.

4.2. Reduced Lattice Thermal Conductivity

Compared to the closely inter-dependent $\sigma$, $\alpha$, $\kappa_{\text{Si}}$, the $\kappa_{\text{Bi}}$ is the only TE property that can be tuned independently. To date, the basic strategy to reduce the $\kappa_{\text{Bi}}$ is to introduce more and diverse phonon scattering centers because heat-carrying phonons have a wide distribution in energy (frequency) and momentum (wavelength). Intrinsic point defects are effective phonon scatterers above room temperature because the average wavelength of heat-carrying phonons gets shorter at elevated temperatures. Termentzdis et al. studied the effects of vacancies and antisite defects on the $\kappa_{\text{Bi}}$ by non-equilibrium molecular dynamics simulations (NEMD).\textsuperscript{[119]} The reduction of $\kappa_{\text{Bi}}$ is $>60\%$ for $5\% [V_{\text{Te}}']$ and $>70\%$ for $4\% [V_{\text{Bi}}']$ in $Bi_2Te_3$ (Figure 7a). In contrast, the reduction in $\kappa_{\text{Bi}}$ is about $20\%$ regardless of the concentration of $Bi'^\text{r}_\text{Te}$ or $Te'^\text{r}_\text{Bi}$ (Figure 7b). These results are understandable in that the vacancies possess larger mass difference and larger strain fluctuation than the antisite defects, thus more effectively scattering heat-carrying phonons.

Grain boundaries provide us with another effective phonon scattering mechanism. At first glance, grain boundaries are irrelevant to intrinsic point defects. However, the routine powder metallurgy methods used to refine grain size often involve deformation processes that create vacancies (c.f. Section 3.3).\textsuperscript{[32,120]} The specific contribution of vacancies to the reduction of $\kappa_{\text{Bi}}$ is about unaccounted or mistakenly attributed to grain boundaries. He et al. recently studied the relation between point defects, grain boundaries, and the reduction $\kappa_{\text{Bi}}$ in $Bi_2Te_3$ nanocrystals by means of thermal conductivity, electron microscopy, and positron annihilation measurements.\textsuperscript{[120]} It is instructive to note that the $\kappa_{\text{Bi}}$ of $Bi_2Te_3$ nanocrystals increases with an increasing annealing temperature but the grain size barely changes upon annealing (Figure 7c). Positron annihilation lifetime measurements indicated a gradual reduction of vacancy concentration upon annealing (Figure 7d). Hence the reduction of $\kappa_{\text{Bi}}$ in $Bi_2Te_3$ nanocrystals is due to phonon scattering by vacancies rather than grain boundaries.

5. Intrinsic Point Defect Engineering

In this section, we discuss how to engineer intrinsic point defect to optimize the material’s TE performance in different temperature ranges. In view of the donor-like effect and the recovery effect, it is imperative to compare the behavior of single crystal, ZM ingot, HP and HD sample in relation to their synthesis and deformation conditions. All the HP samples are prepared from ballmilled powder, if not otherwise noted.

5.1. Reassessment of Optimal Compositions

$V_2V_\text{I}_3$-based compounds are often subject to powder metallurgy processes such as BM, HP, and HD etc. The donor-like effect (cf. Section 3.3) and the recovery effect (cf. Section 3.4) thus make the optimal composition of n- and p-type HP and HD $V_2V_\text{I}_3$ materials different from that of a single crystal or a ZM ingot.

5.1.1. n-type Ternary $Bi_2Te_{3-x}Se_x$

In light of the ($\chi$, $r$)-mechanism (cf. Section 2), and the greater difference in $\chi$ and $r$ between Bi and Se than that between Bi and Te (cf. Table 2), substituting Te by Se in $Bi_2Te_3$ single crystal increases the $E_{\text{AS}}$ and decreases the $E_\text{F}$ resulting in a $p$-type conduction. A p–n crossover occurs when the electrons contributed by anion vacancies ($V_{\text{Te}}'$ and $V_{\text{Bi}}'$) outnumber the holes created by antisite defects ($Bi'^\text{r}_\text{Te}$ and $Bi'^\text{r}_\text{Bi}$) (Figure 8a). Unidirectionally grown $Bi_2Te_{3-x}Se_x$ ZM ingots have optimal compositions at...
$x = 0.15$–$0.3$, showing a weak p-type conduction because of the predominance of $\text{BiTe}^\prime$ and $\text{BiSe}^\prime$. \cite{29,73} Electron doping by halide inhibits the p–n crossover and attains an optimal electron concentration $n_e \approx 5 \times 10^{19} \text{ cm}^{-3}$. \cite{32,33} Notably, inhibiting the p–n crossover can be achieved by the donor-like effect. \cite{101,103} Figure 8a shows that the donor-like effect gives rise to a high $n_e$ value, all the HP and HD samples are n-type conductive, especially at the traditional optimal compositions $x = 0.15$–$0.3$. \cite{32}

Figure 8 showcases the effects of compositional, mechanical, and thermal control of intrinsic point defects in n-type ternary $\text{Bi}_2\text{Te}_3$–$\text{Se}_x$. As shown in Figure 8a, the $n_e$ value of the HP and HD samples is n-type conductive, especially at the traditional optimal compositions $x = 0.15$–$0.3$.\cite{32} The deformation-induced vacancies $\text{VBi}''''$ and $\text{VTe}''$ (or $\text{VSe}''$) in the HD sample strongly scatter the heat-carrying phonons and effectively reduce the $\kappa_{\text{ph}}$. The high-density lattice defects such as the lattice distortions and dislocations generated during the HD process also contribute to the reduction of $\kappa_{\text{ph}}$.\cite{32–34} Our recent work showcases the efficacy of intrinsic point defect engineering via tuning the Se content and the HD condition. The HD $\text{Bi}_2\text{Te}_{2.3}\text{Se}_{0.7}$ sample attains a $zT = 1.0$ at 500 K (Figure 8b). In contrast to the ZM ingot with an optimal

\begin{align*}
x = 0.15 & \text{–} 0.3,
\end{align*}

showing a weak p-type conduction because of the predominance of $\text{BiTe}^\prime$ and $\text{BiSe}^\prime$. \cite{29,73} Electron doping by halide inhibits the p–n crossover and attains an optimal electron concentration $n_e \approx 5 \times 10^{19} \text{ cm}^{-3}$. \cite{32,33} Notably, inhibiting the p–n crossover can be achieved by the donor-like effect. \cite{101,103} Figure 8a shows that the donor-like effect gives rise to a high $n_e$ value, all the HP and HD samples are n-type conductive, especially at the traditional optimal compositions $x = 0.15$–$0.3$. \cite{32}

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the same as in n-type Bi$_2$Te$_{3-x}$Se$_x$. Increasing the Sb content in p-type Bi$_{2-x}$Sb$_x$Te$_3$ reduces $E_A$ and thereby rapidly increases the $n_h$ because of the smaller difference in $\chi$ and $r$ between Sb and Te than that between Bi and Te (Figure 9a). Compared to single crystalline Bi$_{0.5}$Sb$_{1.5}$Te$_3$, the donor-like effect in the BM sample partially compensates the holes and causes the reduction of $n_h$ at all Sb contents (Figure 9a). Notably, the HD process can further reduce the $n_h$ at $x < 1.7$, while the impact of HD on the $n_h$ is insignificant at $x > 1.7$ (Figure 9a). We infer that at high Sb contents ($x > 1.7$) the deformation induced V$_{\text{Bi}}$’’’ (or V$_{\text{Te}}$’’’) and iiV$_{\text{Te}}$ are depleted during the BM process, thus the donor-like effect is less pronounced.

Compared to a value of $zT=1$ near room temperature in the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ ZM ingot,[29,72] the HD Bi$_{0.3}$Sb$_{1.7}$Te$_3$ shows a higher $zT$ value $\approx 1.3$ at 380 K (Figure 9b). Our result is consistent

5.1.2. p-type Ternary Bi$_{2-x}$Sb$_x$Te$_3$

Intrinsic point defect engineering in p-type Bi$_{2-x}$Sb$_x$Te$_3$ follows the same principle, as the underlying mechanisms are basically

Figure 8. a) Room temperature carrier concentration of the undoped single crystals,[29,73] HP and HD polycrystalline[32] Bi$_2$Te$_{3-x}$Se$_x$ samples. The arrows are to help visualize the trend of carrier concentration variation upon BM and HD processing. b) Se content dependences of $zT$ of the ZM,[39] HP and HD[32] Bi$_2$Te$_{3-x}$Se$_x$ samples. All thermoelectric properties are measured along the in-plane direction. Reproduced with permission.[32]

Figure 9. a) Room temperature carrier concentration of the undoped single crystals,[50] HP and HD polycrystalline[32] Bi$_{2-x}$Sb$_x$Te$_3$ samples. The arrows are to help visualize the variation trend of carrier concentration upon BM and HD processing. b) Sb content dependence of $zT$ values for the ZM, HP, and HD Bi$_{2-x}$Sb$_x$Te$_3$ samples.[32] Reproduced with permission.[32]
with the recent work by Li et al.,[122] in which they reported a high $zT$ for the mechanical alloyed (MA) Bi$_{0.3}$Sb$_{1.7}$Te$_3$. Notably, there is a significant improvement in the average $zT_{av}$ over the temperature range studied, and the average $zT_{av}$ between 300 K and 480 K for the hot deformed Bi$_{0.3}$Sb$_{1.7}$Te$_3$ sample is 1.2. These results demonstrate again that the significance of donor-like effect and the efficacy of intrinsic point defect engineering.

5.2. Tailoring Intrinsic Point Defects for Applications in Different Temperature Ranges

In this Section, we discuss how to engineer intrinsic point defects to tailor the material performance[33,66,94,123] in different temperature regimes.

Figure 10. Room temperature carrier concentration and carrier mobility of a) n-type Bi$_2$Te$_{2.79}$Se$_{0.21}$ alloys,[33] and b) p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ alloys.[112] Temperature dependent lattice thermal conductivity of c) n-type Bi$_2$Te$_{2.79}$Se$_{0.21}$ alloys,[33] and d) p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ alloys.[112] Temperature dependence of $zT$ of e) n-type Bi$_2$Te$_{2.79}$Se$_{0.21}$ alloys,[33] and f) p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ alloys.[112] a,c,e) Reproduced with permission.[33] b,d,f) Reproduced with permission.[112] Copyright 2013, The Royal Society of Chemistry.

5.2.1. Room Temperature Refrigeration

The best commercial TE materials for refrigeration near room temperature are ZM n-type Bi$_2$Te$_{2.53}$Se$_x$ ($x = 0.15–0.3$) and ZM p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ ingots. We showed that hot deforming ZM ingots without intermediate BM process (namely, direct HD) is an effective way to enhance TE performance near room temperature.[31,112] The donor-like effect introduced by direct HD is weaker than that with intermediate BM process because of less deformation and a stronger recovery effect.[2,32,33,66,67] The carrier concentration slightly increases (decreases) for the n-type ZM Bi$_2$Te$_{2.79}$Se$_{0.21}$ (p-type ZM Bi$_{0.5}$Sb$_{1.5}$Te$_3$) sample upon direct HD, a high $\alpha$ value is thus retained (Figure 10a,b,[33,112]) In contrast, the $n_e$ of the n-type HP Bi$_2$Te$_{2.79}$Se$_{0.21}$ Sample is nearly tripled and the $n_h$ of the p-type HP Bi$_{0.5}$Sb$_{1.5}$Te$_3$ sample is reduced nearly by half due to a stronger donor-like effect introduced by HP.[33]
5.2.2. Low-Temperature Power Generation

The abundant low to mid-temperature (below 500 K) waste heat from industry sectors and automobile exhaust warrants the development of higher performance TE materials in this temperature range. However, the small band gap of n-type Bi$_{2}$Te$_{2.7}$Se$_{0.3}$ and p-type Bi$_{0.5}$Sb$_{1.5}$Te$_{3}$ inherently restricts their temperature range. However, the small band gap of n-type Bi$_{2}$Te$_{2.7}$Se$_{0.3}$ and p-type Bi$_{2–}$Sb$_{2}$Te$_{3}$ system, a high $zT$ value of $≈1.3$ was obtained near 380 K in HP-HD Bi$_{0.5}$Sb$_{1.5}$Te$_{3}$ (Figure 11a).[66] Li et al. also reported a $zT$ value of $≈1.33$ at 373 K in mechanically alloyed Bi$_{0.5}$Sb$_{1.5}$Te$_{3}$ with SiC nanoparticles.[122] Compared to HP-HD sample, less Sb ($x = 1.6$) is needed for the optimal carrier concentration in HD-ZM sample.[126]

As mentioned above, powder metallurgy processing leads to a strong donor-like effect and thus a high $n_s$, making n-type Bi$_{2}$Te$_{2.7}$Se$_{0.3}$ ($0 < x < 1$) more suitable for application of low-temperature power generation.[12] For instance, the n-type HD Bi$_{2}$Te$_{2.7}$Se$_{0.3}$ subject to BM has a peak $zT$ of 1.2 at 445 K[12] (Figure 11b). Combining melt-spinning (MS) and spark plasma sintering (SPS), Wang et al. reported a maximum $zT$ of 1.0 at 460 K for n-type Bi$_{1.9}$Sb$_{0.1}$Te$_{2.55}$Se$_{0.45}$.[127] Yan et al. reported an $≈22%$ improvement in peak $zT$ value from 0.85 to 1.04 at 398 K in n-type Bi$_{2}$Te$_{2.7}$Se$_{0.3}$ HD2 samples.[128]

5.2.3. Mid-Temperature Power Generation

Using V$_2$VI$_3$ compounds in mid-temperature (above 500 K) applications demands a larger band gap $E_g$. The binary Sb$_2$Te$_3$ has the largest $E_g = 0.20$ eV among all the p-type Bi$_{2–}$Sb$_2$Te$_3$ materials.[129] However, the binary Sb$_2$Te$_3$ is plagued by the presence of numerous Sb$_{2}$Te$_6$ nanoscale distorted regions, and atomic scale line and point defects.[130] These multi-scale scattering centers can effectively scatter heat-carrying phonons with a wide wavelength range and thus effectively suppress the $\kappa_{ph}$ (Figure 10 c,d). As a result, the maximum $zT$ reaches $≈1.2$ at 357 K and $≈1.3$ near room temperature for n-type ZM-HD2 Bi$_{2}$Te$_{2.7}$Se$_{0.3}$ and p-type ZM-HD Bi$_{0.5}$Sb$_{1.5}$Te$_{3}$, respectively (Figure 10e,f). In comparison, the HP samples (subject to BM) show a lower $zT$ than the ZM ones owing to a larger $PF$ degradation than the reduction of $\kappa_{ph}$.[126]
In n-type Bi₂Te₃–Seₙ, increasing the Se content increases the Eₚ and it increases the nₑ in conjunction with doping by iodine. The iodine-doped ZM Bi₂Te₃–Seₙ shows a maximum zT of 0.86 at 600 K (Figure 11b).[13] We showed that the repetitive HD Bi₂Te₂Se₃ material has a zT value of 1.0 at 513 K.[67] As a comparison, single-crystalline Bi₁₊ₓTe₁₋ₓSeₓ is located right at the point of p–n transition that has the lowest zT and α[32] the Eₚ of single-crystalline Bi₁₊ₓTe₁₋ₓSeₓ happens to reach its maximum at x = 1.0, above which the Eₚ starts to decrease with increasing x value.[13] To ease this restriction, the HD process and thus the donor-like effect are utilized.[32] Liu et al. recently conducted a systematic study of n-type Bi₁₊ₓTe₁₋ₓBi₂Se₃–Bi₂S₃ system.[134] These results showed that Bi₁₋ₓTeₓSeₓSₙ has a peak zT value = 0.8 at 573 K and Bi₁₋ₓSeₓSₙ = 0.8 at 773 K upon high energy BM followed by the HP process. It is plausible to infer that the donor-like effect plays a key role in these materials.

### 6. Approaches beyond Intrinsic Point Defect Engineering

The focus of Section 6 is on the underused role of intrinsic point defects in the (i) nanostructuring approach and (ii) texturing approach. Extensively employed in V₂VI₃ materials but without explicitly containing “intrinsic point defects” in their names, the nanostructuring and texturing approach involve powder metallurgy processes such as BM, HD, HP. These processes are the same ones we employ to create intrinsic point defects (cf. Section 3.3 and 3.4). Hence the proper assessment of nanostructuring and texturing approach is subject to a proper assessment of donor-like effect and recovery effect.

While the nanostructuring approach was initially proposed to enhance the electrical properties of TE material via quantum confinement,[135,136] most advances in enhancing zT are attained by the reduction of κₐ in nanostructured TE material. On one hand, the nanostructuring process introduces numerous grain boundaries that strongly scatter heat-carrying phonons. On the other hand, it is risky to assert that grain boundary scattering is the primary mechanism underlying the reduction of κₐ. A good example is the reduction of κₐ in Bi₁₋ₓTeₓ nanocrystals (cf. Section 4.2).[120] In which the deformation-induced vacancies dominate over grain boundaries.

Nanostructuring approach can be categorized into two basic classes: bottom-up and top-down. In a typical bottom-up approach, nanostructures are firstly prepared by BM,[137–139] or MA[140–143] before consolidation to yield nanostructured bulk materials. A high zT value of 1.4 using ZM ingots as the feedstock[13] and a high zT value of 1.3 using elemental chunks as the feedstock[138] were attained in p-type Bi₂₋ₓSbₓTe₃ nanocomposites by a high-energy-BM-HP procedure. In comparison, HD is an effective top-down approach for creating nanostructures and enhancing the zT of both p- and n-type (Bi,Sb)₂(Se,Te)₃-based materials. The significant reduction in κₐ of HD-ZM sample is ascribed to effective phonon scattering by multi-scale microstructures.[33]

Texture refers to the misorientation between grains. To the first order approximation, texture is independent of intrinsic point defects. Texture is found to be crucial for the carrier mobility µ[144–152] intrinsic point defects are shown to affect the carrier concentration n (cf. Section 2 and 3) while they both control the anisotropy of (σ, α, κ). The commercial V₂VI₃ TE materials are fabricated by unidirectional crystal growth methods such as Bridgman,[152] Czochralsky,[153] and zone-melting (ZM)[154] technique, which lead to textures in the as-grown ingots. Advanced powder metallurgy methods, including HP,[155] SPS,[156] hot extrusion,[157–162] shear extrusion,[163,164] powder extrusion,[165] and equal channel angular extrusion[166,167] have been utilized to introduce textures in V₂VI₃ materials. It is plausible to assume that these deformation processes involves the donor-like effect (cf. Section 3.3). For example, Zhao et al. prepared fine-grained n-type Bi₁₋ₓTeₓ materials with preferred grain orientation by using SPS as a hot forging tool.[104] We have employed HD process to obtain high performance p- and n-type V₂VI₃ materials.[2,32,66,67] The degree of texture can be controlled by the HD temperature,[2] the number of times of HD,[67] and also the deformation strain.[66]

Notably, the carrier concentration n strongly affects the anisotropy of (σ, α, κ).[124,125] Increasing the n deforms the Fermi surface topology, making it more prolate and warped from an ellipsoidal shape. As a result, the anisotropy ratio in both σ and κ increases with increasing n given the same degree of texture.[124,125] As for the α, it is nearly isotropic in the extrinsic region,[168] and highly anisotropic in the intrinsic region.[169,170] The α anisotropy is attributed to the presence of minority carriers and the difference in the ratio of hole to electron mobility along the two principal directions.[169] Hence a synergistic implementation of texture and intrinsic point defects would help simultaneously attain an optimal µ and an optimized anisotropy of (σ, α, κ).

### 7. Conclusions

Defects, ubiquitous and often wrongly conceived as performance limiters, are the key performance enhancer in diverse functional materials upon proper implementation. This review focuses on the underexplored intrinsic point defects (i.e., vacancies and antisite defects) in V₂VI₃ semiconductors and their derivatives, regarding the compositional, mechanical and thermal control as well as their interplay with other defects towards higher thermoelectric performance. It is not our aim to emphasize the significance of intrinsic point defects over other types of defects; rather, we intend to clarify the causal chain in the synthesis-structure-property correlation. We summarized our understanding of intrinsic point defects in a (χ, τ)-model and discussed the donor-like effect and the recovery effect in V₂VI₃ compounds.

The study of intrinsic point defects in V₂VI₃ compounds is not yet complete, especially regarding the role of intrinsic point defects in nanostructuring and texturing approaches (cf. Section 6), which warrants further investigations. Nonetheless, the new insights derived herein open a promising avenue for further improving the thermoelectric performance of other compounds and, in a wider context, contribute to the development of advanced functional materials by rational defect design in the long run.

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