

Atomic-Scale Chemical Inhomogeneity as a Determinant of Thermoelectric Transport in Bi_2Te_3 -Based Materials

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The local structure and chemical environment critically govern transport properties in quantum and energy materials, but their atomic-scale manifestations remain elusive. Here we uncovered the atomic characteristics, intrinsic origin, and thermoelectric implications of chemical inhomogeneity in Bi_2Te_3 -based materials with varying Se alloying. Using aberration-corrected electron microscopy, chemical bonding analysis, and thermodynamic modeling, we revealed pronounced Se enrichment in the central layer of a quintuple structure and constructed precise atomic models for this intrinsic inhomogeneity. Atomic-scale charge-density and valence-state measurements provided direct experimental evidence for chemical bonding disparity in Bi_2Te_3 , with more covalent bonding in central layers and greater ionic bonding in outer layers. We also showed that this bonding disparity, coupled with entropy-enthalpy competition, drove the observed site preference and local chemical segregation in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ ($x = 0.5, 1.0, 1.5, 2.0$, and 2.5). The site-resolved bonding analyses further demonstrated that selective Se occupation tuned both ionic and covalent components of Bi–X bonds in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$. Therefore, this intrinsic chemical inhomogeneity modulated bonding polarity, the electronic band gap, and the Seebeck coefficient, serving as a fundamental determinant of thermoelectric performance. Our findings highlight atomic-scale chemical inhomogeneity as a key factor in tailoring functional properties of layered quantum materials beyond thermoelectrics.

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I. INTRODUCTION

Bi_2Te_3 -based materials have been at the forefront of multifunctional inorganic semiconductors for a long time,

given their exceptional thermoelectric performance near room temperature [1,2], realization as prototypical three-dimensional topological insulators [3–5], and, more recently, transformation from intrinsically brittle crystals to mechanically ductile and flexible forms [6–8]. These diverse functionalities originate from their rhombohedral structure with quintuple layers (QLs) of $\text{Te}^{(1)}\text{–Bi–Te}^{(2)}\text{–Bi–Te}^{(1)}$ separated by van der Waals gaps, in which the $\text{Bi–Te}^{(1)}$ bond is relatively ionic, and the $\text{Bi–Te}^{(2)}$ bond is more covalent and weaker, as conventionally assumed [9–12].

Alloying Bi_2Te_3 with Sb_2Te_3 or Bi_2Se_3 has been found to be an effective approach to tune its thermoelectric, topological, and mechanical performance by modulating

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the band structure, thermal stabilization, bonding environment, and defect structures [13–15]. In the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ system ($0 \leq x \leq 3$), a continuous solid solution between Bi_2Te_3 and Bi_2Se_3 , provides compositional control over electronic and thermal transport behaviors [16,17]. Varying the Te/Se ratio adjusts the band gap and induces band convergence, thereby altering the carrier concentration and effective mass. Around the intermediate composition $\text{Bi}_2\text{Te}_2\text{Se}$, the alloy exhibited a maximum band gap. Additionally, the mixing of Te and Se on the anion sublattice was found to introduce point defects causing phonon scattering, leading to a global minimum in lattice thermal conductivity near $\text{Bi}_2\text{Te}_{2.5}\text{Se}_{0.5}$ and a local maximum at $\text{Bi}_2\text{Te}_{1.5}\text{Se}_{1.5}$ [18]. Moreover, the plasticity of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ crystals was found to degrade with an increasing Se content and saturated beyond a ratio of 1.2 [19]. The infrared active vibrations and single-Dirac-cone-like surface states were also tuned with Se and Te substituted in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ topological insulators [20–22]. The ability to modulate these diverse properties in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ materials is strongly governed by the local structure and chemical environment [23–26]. These underlying effects require atomically resolved analysis of defects, elemental distributions, site occupancies, and related features. However, most existing studies relied on density-functional-theory calculations and macroscopic characterizations [13,27,28] such as x-ray diffraction, Hall measurements, and bulk transport analysis, which, despite offering insights into defect energetics, electronic structure, and averaged properties, lacked the atomic resolution and site-specific sensitivity required to resolve the local structural and chemical complexities.

To address this issue, we employed aberration-corrected transmission electron microscopy to investigate local structural and chemical variations in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, with particular emphasis on site occupancy, elemental distribution, and local bonding environments at the atomic scale. Across all examined compositions, we identified a pronounced local chemical inhomogeneity that arose from the preferential Se enrichment at $\text{Te}^{(2)}$ sites within the QLs. This inhomogeneity was found to be primarily driven by chemical bonding disparities and thermodynamic stability. Furthermore, we explored the impact of local chemical inhomogeneity on the thermoelectric performance and revealed a direct correlation between the site-specific Se content, chemical bonding polarity, band gap, and Seebeck coefficient.

II. RESULTS AND DISCUSSION

After introducing Se into bismuth telluride, we obtained a series of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ materials, with $x = 0.5, 1.0, 1.5, 2.0$ and 2.5 . X-ray powder diffraction (XRD) patterns indicated a single phase of the samples with a rhombohedral structure between that of Bi_2Te_3 and Bi_2Se_3 (Supplemental Material Fig. S1 [29]). Scanning-transmission-electron-microscopy (STEM) measurements with high-angle annular dark-field

(HAADF) imaging showed a uniform microstructure contrast in the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ materials, and energy-dispersive x-ray spectroscopy (EDS) analysis also displayed a homogeneous distribution of the elements at the nanoscale (Supplemental Material Fig. S2 [29]). However, STEM analysis at the atomic scale showed local chemical inhomogeneity at all compositions of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ (Fig. 1). The atomic-resolution HAADF-STEM images along the [100] direction of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ [Fig. 1(a)] clearly showed the QL structure with a sequence of $\text{Te}^{(1)}\text{-Bi-Te}^{(2)}\text{-Bi-Te}^{(1)}$ and van der Waals gaps between the $\text{Te}^{(1)}$ sites. In the case of $\text{Bi}_2\text{Te}_{2.5}\text{Se}_{0.5}$, the $\text{Te}^{(2)}$ sites located in the central layer of the QLs were found to have a lower intensity compared to that of the $\text{Te}^{(1)}$ sites in the outer layers (Supplemental Material Fig. S3 [29]), indicating a discrepancy in the element type or content at two chalcogen sites with respect to the local chemical inhomogeneity [30]. We further quantified the intensity variation of the HAADF-STEM images (Z-contrast image) in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ by statistically analyzing the separated Bi, $\text{Te}^{(1)}$, and $\text{Te}^{(2)}$ sites, as shown in Supplemental Material Fig. S4 [29]. With increasing Se content, both the $\text{Te}^{(1)}$ and $\text{Te}^{(2)}$ sites shifted toward lower-intensity regions due to the alloying effect of Se with a lower atomic number (Z). More importantly, we found that the intensity of the $\text{Te}^{(2)}$ site consistently exhibited lower intensity than the $\text{Te}^{(1)}$ site across all $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ compositions, suggesting the possibility of Se enrichment at the central-layer $\text{Te}^{(2)}$ site within the quintuple layers.

To further characterize the local chemical inhomogeneity in the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ materials, atomic-resolution STEM-EDS mapping was performed to determine the distribution of elements at the crystallographic sites [31,32]. As shown in Fig. 1(a), the atomic locations of the Bi, Te, and Se elements in the QLs were well observed in the STEM-EDS elemental images after denoising by applying a nonlocal principal component analysis (NL-PCA) method (see Sec. IV) [33,34]. As shown in the raw and denoised STEM-EDS images (Supplemental Material Fig. S5 [29]), we found that this NL-PCA method significantly improved image quality while preserving the intrinsic lattice features. In the Se elemental images, we found an apparent high intensity in the central layer of the QLs, particularly in the $\text{Bi}_2\text{Te}_{2.5}\text{Se}_{0.5}$ and $\text{Bi}_2\text{Te}_{2.0}\text{Se}_{1.0}$ samples. The intensity in the STEM-EDS maps was approximately proportional to the concentration of each specific element at the atomic sites. Thus, the observed variation of the Se signal at different locations indicated the enrichment of the Se element in the central layer of the QLs, which was found throughout the entire series of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, even the alloying element Se increased to 2.5. On the other hand, the Te elemental maps showed the opposite behavior, with a lower intensity in the central layer and a higher intensity in the outer layer of the QLs. The features of Se and Te elemental distribution in different layers of the QLs were also confirmed by the integrated intensity profiles

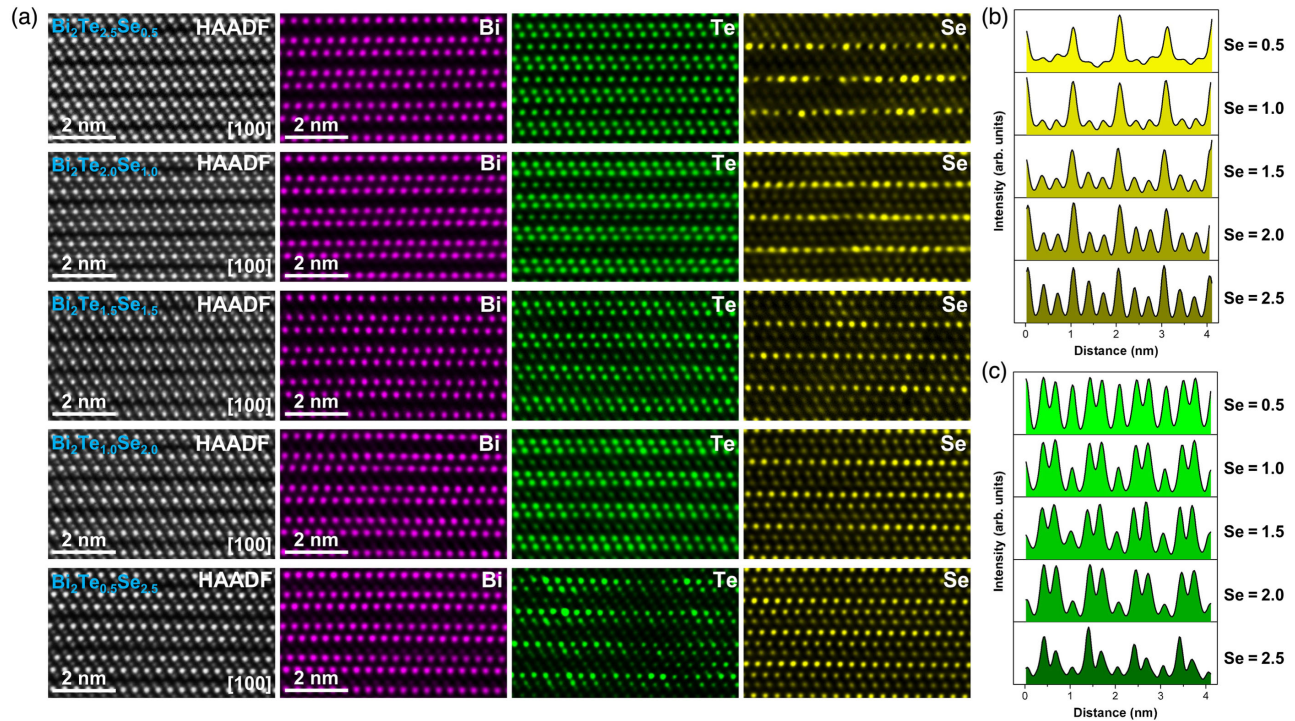


FIG. 1. Local chemical structures of the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ materials. (a) Atomic-resolution HAADF-STEM images and EDS elemental mappings of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, with $x = 0.5, 1.0, 1.5, 2.0$, and 2.5 . Horizontal integrated intensity profiles of (b) Se and (c) Te elements.

of corresponding EDS elemental images, as shown in Figs. 1(b) and 1(c). Moreover, we observed a similar local chemical inhomogeneity in single-crystal $\text{Bi}_2\text{Te}_2\text{Se}$ (Supplemental Material Fig. S6 [29]), with Se enriched in the central layer of the QLs. This indicated that local chemical inhomogeneity was an intrinsic structure of a $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ system, regardless of the synthesis conditions or methods. In addition, the observations of $\text{Bi}_2\text{Te}_2\text{Se}$ deviated from the long-standing consensus of this composition having an ordered Te–Bi–Se–Bi–Te structure [9,10,13,35,36], indicating a limitation of previous studies.

To quantify the concentrations of Se and Te, we analyzed the composition of the different layers in the QLs based on atomic-resolution STEM-EDS data. Supplemental Material Fig. S7 [29] shows an example of composition quantification in $\text{Bi}_2\text{Te}_{2.5}\text{Se}_{0.5}$, where the central layer has 28.0 at.% of Se and 72.0 at.% of Te, while the ratio of Se and Te reverses in the bottom (outer) layer, with 12.0 at.% of Se and 88.0 at.% of Te. Similarly, the composition quantification of seven QLs was performed on other $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ materials, as summarized in Fig. 2(a). With more Se element introduced into the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ materials, the content of Se gradually increases in both the central and outer layers of the QLs, while the content of Te showed the opposite change. However, it should be noted that the amount of Se in the central layer is always higher than in the outer layer, confirming the preferred occupation of Se atoms in the QL center. The average Te and Se contents obtained from this composition quantification were

summarized in Supplemental Material Table S1 [29], showing the largest compositional difference for $\text{Bi}_2\text{Te}_2\text{Se}$. This observation was consistent with the average intensity ratio of the $\text{Te}^{(1)}/\text{Te}^{(2)}$ sites to the Bi site in the HAADF-STEM analysis (Supplemental Material Figs. S4 and S8 [29]). With this composition quantification, we have proposed atomic models for the local chemical inhomogeneity in the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ series, as illustrated in Fig. 2(b). The Se content in the central layer of the QLs is determined to be 0.3, 0.6, 0.7, 0.8 and 0.9, indicating that the central layer is not fully occupied by Se atoms even through the overall Se content up to 2.5 in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$. STEM-EDS simulation based on the atomic model was further performed to verify the reliability of the quantified composition in the $\text{Bi}_2\text{Te}_2\text{Se}$ (Supplemental Material Fig. S9 [29]), showing excellent agreement between the experimental and simulated Te and Se intensity profiles. Moreover, Rietveld refinement of XRD served as an independent validation of the STEM-derived site occupancies, where two representative compositions ($\text{Bi}_2\text{Te}_2\text{Se}$ and Bi_2TeSe_2) were refined with the fitted patterns and parameters presented in Supplemental Material Fig. S10 and Table S2 [29]. The calculated profiles well reproduced all major Bragg peaks with satisfactory reliability factors, demonstrating that the atomic models derived from our STEM analysis accurately described the crystal structures of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$.

Our analysis of atomic-resolution chemical mapping and quantification have clearly revealed the existence of local chemical inhomogeneity in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, with pronounced

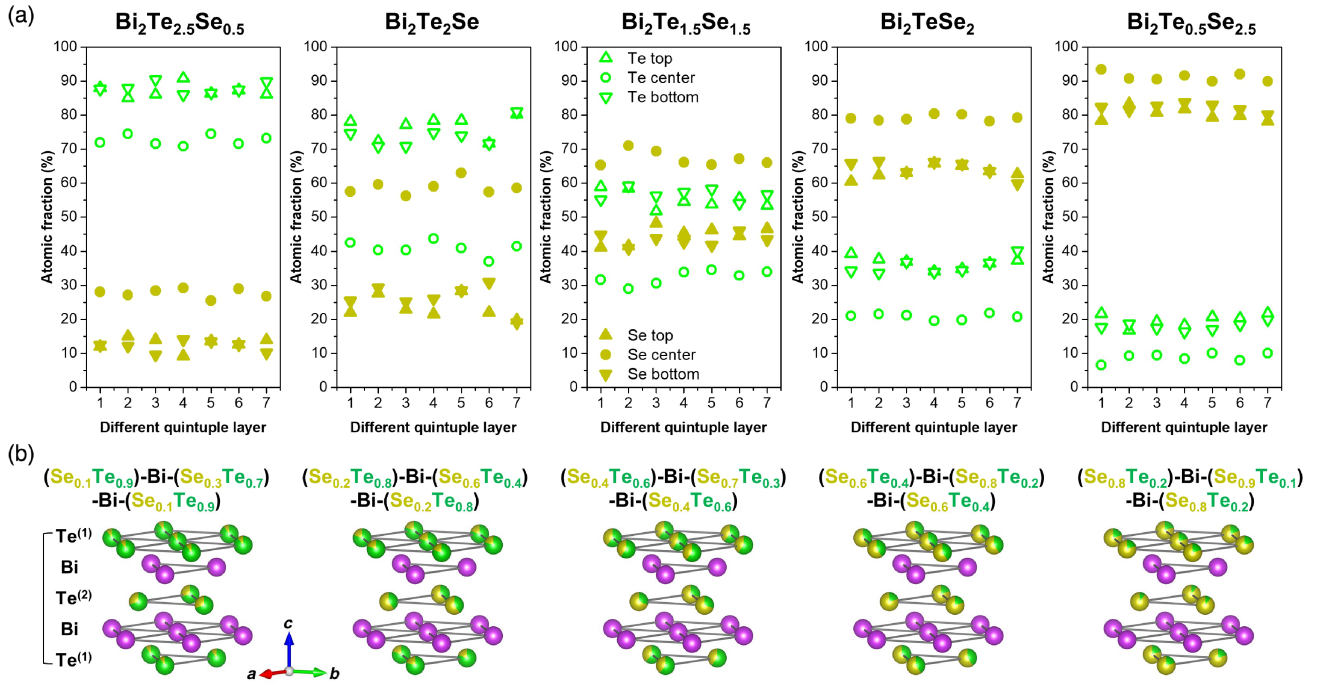


FIG. 2. Composition quantification of the quintuple layer in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$. (a) Quantification of Se and Te in the different quintuple layers of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, with $x = 0.5, 1.0, 1.5, 2.0$, and 2.5 . (b) Atomic models of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ constructed using the average compositions from (a).

Se enrichment in the central layer of the QLs. The underlying formation mechanism was further elucidated through a chemical bonding analysis, as atomic interactions serve as the basis for the chemical and structural organization of materials [37,38]. Atomic-scale charge density, a fundamental solid-state property determining chemical bonding, was obtained using a differential phase contrast (DPC) STEM technique (see Sec. IV), in which the shift of the electron probe induced by local positive and negative charge can be determined by a segmented detector or pixelated detector, and then converted to projected charge-density maps according to Ehrenfest's theorem and Gauss's law [39–41]. Figure 3(a) shows the atomic-scale charge-density map of the pristine Bi_2Te_3 . Positive values are observed at atomic sites due to the screened nuclear charge, while the surrounding negative values arise from electronic contributions. With the determined charge distribution of QL [Fig. 3(b)], we found that the negative charge pockets between the Bi and $\text{Te}^{(2)}$ sites were more pronounced than those between the Bi and $\text{Te}^{(1)}$ sites, indicating a difference in bonding characteristics within the QLs. This was further investigated by the chemical shift measurement of the Te sites using electron-energy-loss spectroscopy (EELS) in STEM [Fig. 3(c)]. EELS arose from the inelastic scattering of electrons with the specimen and provided information on the valence states of the elements through the analysis of core-loss edges, as demonstrated in various materials [42–44]. The energy position of these core-loss edges served as an effective probe of the valence state, where a shift toward

higher energy loss generally indicated an increase in the oxidation state. Using the standard first-derivative method to determine the edge onsets, we found that the Te signal from the central layer ($\text{Te}^{(2)}$) exhibited a larger chemical shift (approximately equal to 1.2 eV) relative to the outer layer ($\text{Te}^{(1)}$), suggesting that the $\text{Te}^{(1)}$ atoms were more negatively charged than the $\text{Te}^{(2)}$ atoms. This provided another experimental evidence for the bonding disparity between the central and outer layers of the QLs in Bi_2Te_3 .

Both the charge-density and chemical shift measurements revealed the discrepancy in the chemical bonding in Bi_2Te_3 , with more covalent bonding of $\text{Bi}-\text{Te}^{(2)}$ and more ionic bonding of $\text{Bi}-\text{Te}^{(1)}$. This provided compelling atomic-scale experimental evidence to confirm the long-standing assumption of bonding inhomogeneity in Bi_2X_3 ($X = \text{Te}, \text{Se}$), as initially proposed over 60 years ago [10,11]. On this basis, with Se introduced into Bi_2Te_3 , the more weakly bound $\text{Te}^{(2)}$ site was preferentially occupied by the more electronegative Se atoms due to the lower formation energy of this substitution [14,15]. This chemical bonding disparity induced the observed Se enrichment in the central layer of the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ QLs. To further confirm the key roles of chemical bonding and elemental electronegativity, we examined the site preferences of Te and S in the Bi_2Se_3 system, with the Pauling electronegativities 2.58 (S), 2.55 (Se), and 2.10 (Te). Atomic-resolution STEM-EDS maps of $\text{Bi}_2\text{Se}_{2.5}\text{Te}_{0.5}$ and $\text{Bi}_2\text{Se}_{2.5}\text{S}_{0.5}$ (Supplemental Material Fig. S11 [29]) showed that the less electronegative Te preferentially occupied the outer layers ($X^{(1)}$ sites),

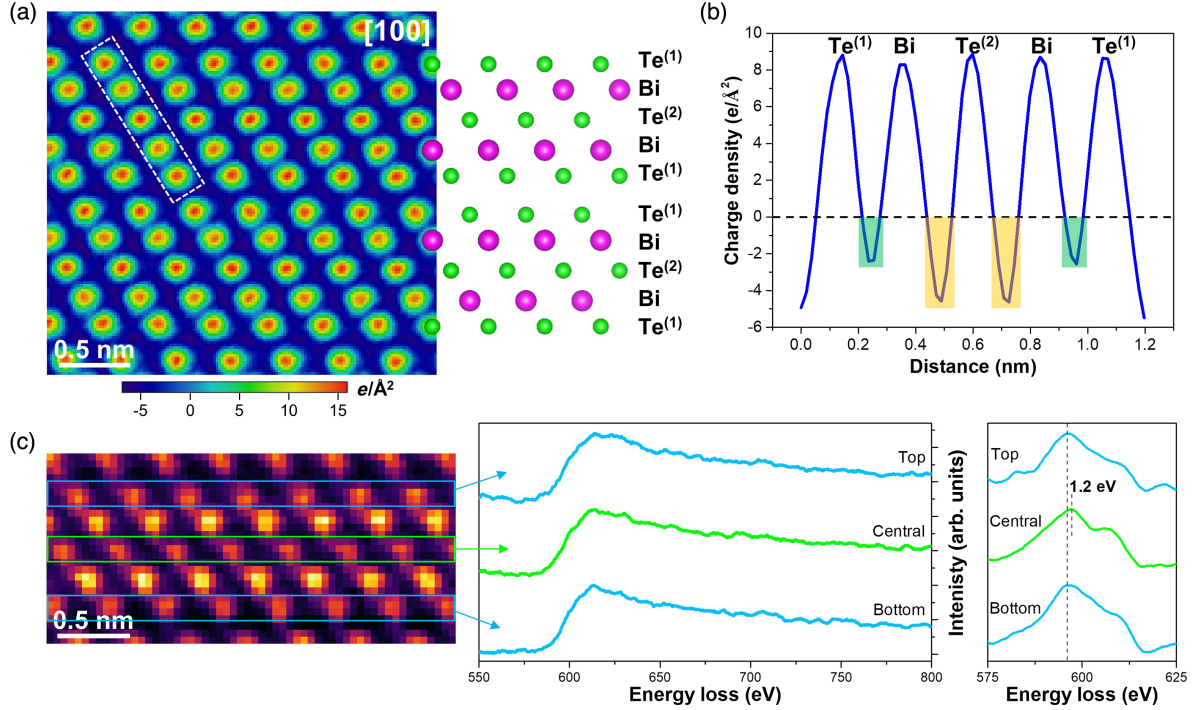


FIG. 3. Chemical bonding heterogeneity of Bi_2Te_3 . (a) Atomic-scale charge-density mapping of Bi_2Te_3 and (b) charge distribution profile of quintuple layer as marked in (a). (c) Chemical shift of different Te sites in Bi_2Te_3 measured by atomic-resolution EELS.

while the more electronegative S tended to locate in the central layers ($X^{(2)}$ sites). These observations explained the preferential occupation of Se in the central $\text{Te}^{(2)}$ layer of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ in terms of bonding disparity and electronegativity differences. However, the reason for the notably low Se concentration in the outer $\text{Te}^{(1)}$ layer remains unclear in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, particularly for $x \leq 1.0$. Therefore, thermodynamic calculations of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ alloying (see Sec. IV)

were performed to further clarify the formation of local chemical inhomogeneities. We obtained the configurational entropy, enthalpy, and Gibbs free energy of the alloys with varied Se contents in the calculations, as summarized in Fig. 4(a). The minimum Gibbs free energy corresponded to stabilized structures with a specific Se concentration in the central layer ($X^{(2)}$ site): 0.31, 0.55, 0.73, 0.85, and 0.94 for $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ ($x = 0.5, 1.0, 1.5, 2.0$, and 2.5), as marked

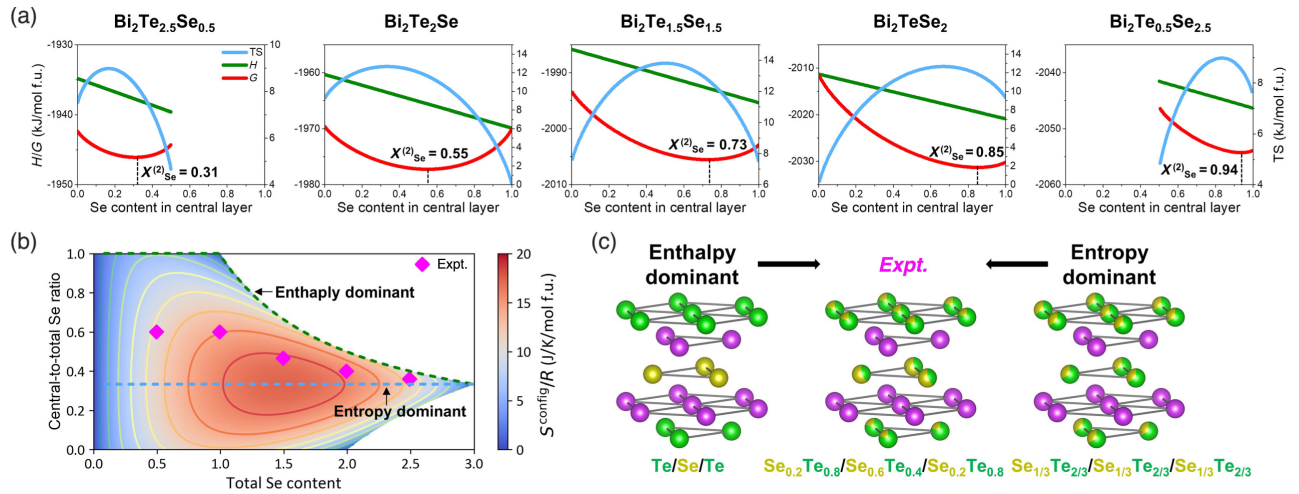


FIG. 4. Thermodynamic calculations of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$. (a) Entropy, enthalpy, and Gibbs free energy as a function of the Se content in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, with $x = 0.5, 1.0, 1.5, 2.0$, and 2.5 . (b) Contour map of the configurational entropy with the central-to-total Se ratio in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, including enthalpy- and entropy-dominant conditions. (c) Demonstration of enthalpy and entropy competition in $\text{Bi}_2\text{Te}_2\text{Se}$ with corresponding atomic models.

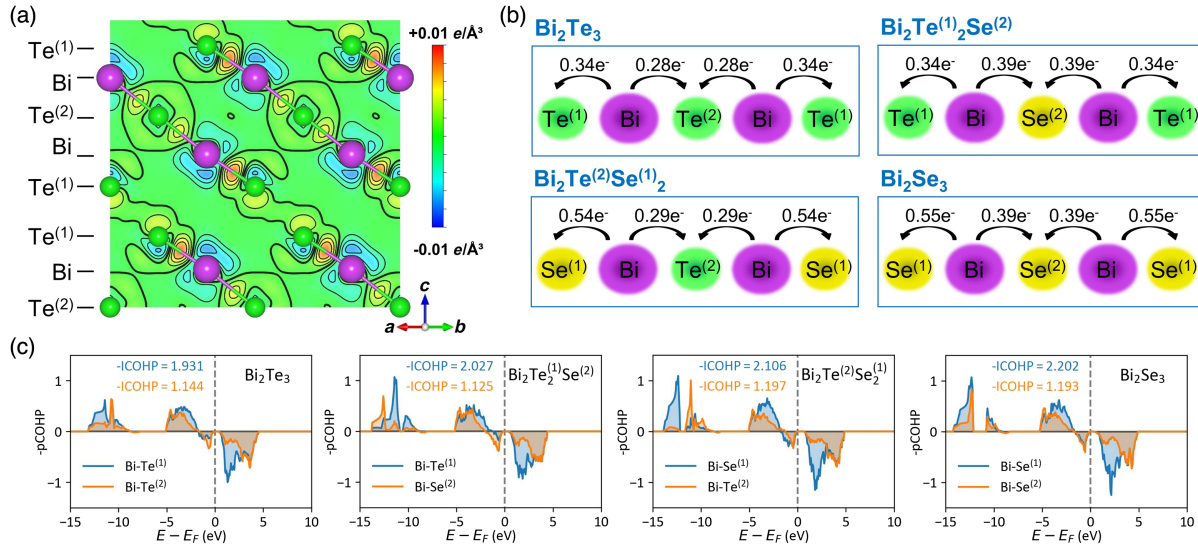


FIG. 5. Site-resolved bonding analyses for $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$. (a) The deformation charge density of the (110) plane of Bi_2Te_3 . (b) The results of Bader charge analysis and (c) crystal-orbital Hamilton population for Bi_2Te_3 , $\text{Bi}_2\text{Te}_2^{(1)}\text{Se}^{(2)}$, $\text{Bi}_2\text{Te}^{(2)}\text{Se}_2^{(1)}$, and Bi_2Se_3 .

in Fig. 4(a). These values matched well with our experimental quantifications (Supplemental Material Fig. S12 [29]) and were explained by the competition between entropy and enthalpy [Figs. 4(b) and 4(c)]. When enthalpy dominated, the Se first occupied the central layer until the Se concentration exceeded 1.0, and then Se moved to the outer layers. In contrast, when entropy dominated, Se distributed evenly across the central and outer layers (1/3 in each layer), producing in a highly disordered structure. The experimentally observed Se distributions in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ fell between these two limiting regimes, as shown in Fig. 4(b). Atomic models of $\text{Bi}_2\text{Te}_2\text{Se}$ further provided an intuitive illustration of the Se arrangement that resulted from the competition between entropy and enthalpy [Fig. 4(c)]. Taken together with the analysis shown in Figs. 3 and 4, we demonstrated that the local chemical inhomogeneity in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ originated from the combined effects of chemical bonding and thermodynamic stability. Moreover, we performed a series of site-resolved bonding analyses for $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, as shown in Fig. 5. In pristine Bi_2Te_3 , the deformation charge-density map [Fig. 5(a)] exhibited a pronounced accumulation of charge around the $\text{Te}^{(1)}$ sites and a correspondingly stronger depletion on neighboring Bi atoms, indicating a larger net charge transfer from Bi to $\text{Te}^{(1)}$ than to $\text{Te}^{(2)}$. This observation was corroborated by the electron localization function calculations (Supplemental Material Fig. S13 [29]). Bader charge analysis [45] [Fig. 5(b)] and crystal-orbital Hamilton population (COHP) analysis [Fig. 5(c) and Supplemental Material Table S3 [29]] further revealed a larger charge transfer to the outer-layer $\text{Te}^{(1)}$ site (approximately $0.34 e$) compared to the central-layer $\text{Te}^{(2)}$ site (approximately $0.28 e$), and the integrated COHP ($-ICOHP$) for $\text{Bi}-\text{Te}^{(1)}$ was also markedly greater than for $\text{Bi}-\text{Te}^{(2)}$.

This well clarified the feature of bond disparity in Bi_2Te_3 , consistent with atomic-scale experimental observations (Fig. 3).

By comparing the Bader charge and COHP results for the four representative structures (Bi_2Te_3 , $\text{Bi}_2\text{Te}_2^{(1)}\text{Se}^{(2)}$, $\text{Bi}_2\text{Te}^{(2)}\text{Se}_2^{(1)}$, and Bi_2Se_3), we further evaluated the effect of site-specific Se substitution on the chemical bonding in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$. Se substitution consistently increased the charge transfer to the substituted chalcogen site [Fig. 5(b)], thereby enhancing the ionic character of the corresponding Bi-X bond, but the effect on the covalent bonding was site dependent [Fig. 5(c)]. Substitution at the $X^{(1)}$ site tended to increase $-ICOHP$ for the $\text{Bi}-X^{(1)}$ interaction (strengthening its covalent contribution), whereas substitution at the $X^{(2)}$ site slightly reduced the $-ICOHP$ for $\text{Bi}-X^{(2)}$ (weakening its covalent contribution). These site-dependent trends demonstrated that selective Se occupation modulated both ionic and covalent components of Bi-X bonds and thus controlled the bond disparity in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$. In addition, the bonding disparity in the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ system was not a fixed intrinsic property but rather a temperature-dependent outcome governed by the Gibbs-equilibrium distribution of Se (Fig. 4). Therefore, the finite-temperature Se distribution both reflected and determined the magnitude of the bonding disparity.

The difference in bonding at chalcogen sites and the occupancy preference of the elements play a key role in determining the electrical and thermal transport properties [46]. Thus, we further investigated the effect of local chemical inhomogeneity on the thermoelectric properties of the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ materials (Supplemental Material Fig. S14 [29]). As shown in Fig. 6, we found the same trends of the central-to-outer Se variation, chemical bonding polarity, band gap, and Seebeck coefficient.

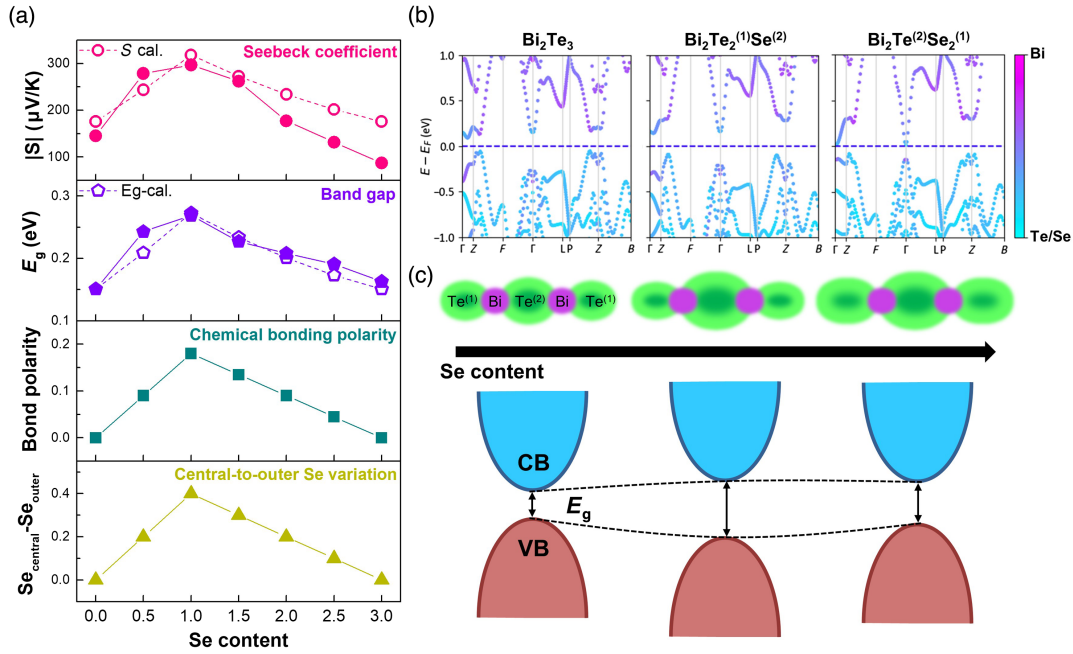


FIG. 6. Correlation of the chemical structure and electrical properties of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$. (a) Central-to-outer Se content variation, chemical bond polarity, band gap, and Seebeck coefficient of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, with $x = 0, 0.5, 1.0, 1.5, 2.0, 2.5$, and 3.0 . (b) Band structures of Bi_2Te_3 -based materials from theoretical calculations. (c) Schematic diagram of chemical bond-polarity and band-gap variations as the Se content was increased in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$.

The chemical bonding polarity, reflected by the electronegativity difference between the $\text{Bi}-\text{Te}^{(2)}$ and $\text{Bi}-\text{Te}^{(1)}$ bonds (see Sec. IV), arose from the concentration discrepancy between Te and Se at the two chalcogen sites (outer-layer site $X^{(1)}$ and central-layer site $X^{(2)}$) as determined by the quantitative analysis of local chemical inhomogeneity. As shown in Fig. 6(a), in the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ series ($x = 0, 0.5, 1.0, 1.5, 2.0, 2.5$, and 3.0), the chemical bonding polarity initially increased to reach a maximum at $\text{Bi}_2\text{Te}_2\text{Se}$ and then decreased. This was supported by the site-resolved bonding analyses for $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ (Fig. 5), where the Se occupying the $X^{(2)}$ site increased valence-electron transfer into the central layer and thereby enhanced the ionic character (bond polarity) of the $\text{Bi}-X^{(2)}$ bond. As a result, the overall bonding polarity of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ followed the relative Se concentration between the central and outer sublayers, as shown in Fig. 6(a).

We also observed a composition-dependent change in the band gap of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ [Fig. 6(a) and Supplemental Material Fig. S15 [29]]. In the simple tight-binding model [47,48], larger bond polarity increased the site-energy difference and weakened orbital hybridization, which localized the occupied states and raised the unoccupied states, thereby widening the band gap. The role of the Se site occupancy was further elucidated through theoretical calculations [Fig. 6(b) and Supplemental Material Fig. S16 [29]]. As indicated in previous studies [13,49,50], spin-orbit coupling (SOC) was crucial for the band structure of Bi_2Te_3 and induced the anticrossing of valence and

conduction bands to open the gap. By analyzing the contributions of the two Te sites to the band dispersion (Supplemental Material Fig. S16 [29]), we found that the electronic states along $\Gamma-Z$ were predominantly governed by the $\text{Te}^{(1)}$ site. Substituting Se at the $\text{Te}^{(2)}$ site had a minor effect on the overall SOC and primarily increased anion electronegativity and bond polarity, which shifted the band-edge energies and widened the band gap. In contrast, Se substitution at the $\text{Te}^{(1)}$ site directly affected SOC-active orbital hybridization and weakened SOC-driven anticrossing at the Γ point, thus lowering the energy level and narrowing the gap. Therefore, the band gap was highly related to the Se content in the $X^{(1)}$ and $X^{(2)}$ sites in the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ system, showing the same trends as those of the central-to-outer Se variation and chemical bonding polarity. These correlations were schematically illustrated in Fig. 6(c). Moreover, a larger slope near the Fermi level in the density-of-states calculation was also found in the Se occupying in the $\text{Te}^{(2)}$ site (Supplemental Material Fig. S17 [29]), indicating the effect of the Se location on the effective mass of the carriers. This was consistent with the variation of the effective mass extracted experimentally across the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ series, as shown in Supplemental Material Fig. S18 [29]. Since the carrier concentration remained in the same order of magnitude in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, the Seebeck coefficient primarily followed the change in the effective mass and thus exhibited the same trend as the chemical bonding polarity and band gap. This correlation indicated that the site-specific Se distribution altered the

bonding polarity and consequently modified the band gap, which in turn enhanced the Seebeck coefficient through an increased effective mass. In addition, thermal conductivity exhibited a pronounced composition-dependent variation across the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ (Fig. S14 [29]), which can be attributed to stronger phonon scattering arising from mass and strain fluctuations as well as local bonding discrepancy induced by Se and Te mixing [51–54].

We further established a quantitative framework linking the Se site distribution, bonding polarity, band gap, and Seebeck coefficient in the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ system (see calculation details in Supplemental Material Note S1 [29]). The Se content variation (C) between the central-layer $X^{(2)}$ and outer-layer $X^{(1)}$ sites was quantified as follows:

$$C = f_2 - f_1. \quad (1)$$

The bond-polarity discrepancy (P) was defined by the site electronegativity difference:

$$P = C(\chi_{\text{Se}} - \chi_{\text{Te}}). \quad (2)$$

The band-gap energy (E_g) was then modeled by a semi-empirical relation incorporating polarity and alloy bowing effects [56–58]:

$$E_g = E_0 + \alpha P - b \frac{x}{3} \left(1 - \frac{x}{3}\right). \quad (3)$$

Finally, the Seebeck coefficient (S) was estimated using the Goldsmid-Sharp relation [59–61]:

$$S \approx \eta \frac{E_g}{2eT}, \quad (4)$$

where f_2 and f_1 are the Se fractions in the $X^{(2)}$ and $X^{(1)}$ sites, respectively, with the composition balance $x = f_2 + 2f_1$ for $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$. χ represents the Pauling electronegativity ($\chi_{\text{Bi}} = 2.02, \chi_{\text{Te}} = 2.10, \chi_{\text{Se}} = 2.55$), E_0 is the reference gap of pristine Bi_2Te_3 , α reflects the sensitivity to bond polarity, b is the band-gap bowing parameter for alloying, η is an empirical correction factor for nonideal carrier statistics, T is the absolute temperature, and e denotes the elementary charge. All numerical parameters, corresponding values, and their physical interpretations were summarized in Supplemental Material Tables S4 and S5 [29]. With this quantitative correlation, the band gap and Seebeck coefficient of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ were directly estimated from the site-specific Se occupancy. As shown in Fig. 6(a), the calculated E_g and S values closely matched the experimental data across all compositions, indicating the reliability of the established correlation. Importantly, this constitutes the first quantitative coupling between local chemical inhomogeneity and thermoelectric transport in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, allowing electronic transport properties to be

directly estimated from atomic-resolution electron-microscopy observations.

III. CONCLUSIONS

In this study, we have elucidated the features, formation mechanism, and impact of local chemical inhomogeneity in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ materials. Atomic-resolution chemical mapping in STEM revealed the presence of local chemical inhomogeneities with Se enriched in the central layer of the QLs, constituting an intrinsic structural feature in the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ system. The atomic-scale composition was further quantified to determine the discrepancy between Te and Se within the QLs, which was then used to develop precise atomic models incorporating local chemical inhomogeneity of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$. Moreover, we found that chemical bonding and thermodynamic stability critically governed the formation of local chemical inhomogeneities in the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ materials. Our analysis of charge density and chemical shift, to the best of our knowledge, offers the first atomic-scale experimental evidence on the chemical bonding disparity in Bi_2Te_3 , thus revealing greater covalent bonding of $\text{Bi}-\text{Te}^{(2)}$ and greater ionic bonding of $\text{Bi}-\text{Te}^{(1)}$. This bond discrepancy accounted for the preferential occupation of the more electronegative Se atoms at the $\text{Te}^{(2)}$ site (the central layer) from the perspective of formation energy. The balance between entropy and enthalpy further clarified the distribution and concentration of Se in both the central and outer layers of the QLs based on thermodynamic stability. The site-resolved bonding analyses also elucidated the effect of Se substitution on the chemical bonding in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$. Se occupying the $X^{(2)}$ site increased the ionicity but reduced the covalency of the $\text{Bi}-X^{(2)}$ bond, while Se occupying the $X^{(1)}$ site enhanced both ionic and covalent indicators of $\text{Bi}-X^{(1)}$. This demonstrated that selective Se occupation modulated both ionic and covalent components of $\text{Bi}-X$ bonds and thus controlled the bond disparity. Furthermore, we identified a direct correlation among the site-specific Se concentration, bonding polarity, band gap, and Seebeck coefficient, and developed a predictive framework to estimate thermoelectric transport from atomic-scale chemical inhomogeneities. This demonstrated the critical role of local chemical inhomogeneity in determining the thermoelectric properties of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ materials. Our findings on local chemical inhomogeneity are expected to advance the thermoelectric optimization of Bi_2Te_3 -based materials, and also inspire future studies to explore their unique plasticity and topological behaviors.

IV. METHODS

A. Material synthesis

High-purity elements Bi, Te, Se, and S (shots, 99.999%, Alfa Aesar) weighed according to the nominal stoichiometry of $\text{Bi}_2\text{Te}_x\text{Se}_{3-x}$ ($x = 0, 0.5, 1, 1.5, 2, 2.5, 3$) and

$\text{Bi}_2\text{Se}_{2.5}\text{Y}_{0.5}$ ($\text{Y} = \text{Te}, \text{S}$). The weighed elements were sealed in evacuated quartz ampoules under high vacuum (approximately 10^{-4} Pa). The sealed ampoules were then heated to 1023 K over a period of 10 h, held at 1023 K for 12 h, and subsequently quenched in cold water. The samples were then annealed at 773 K for 72 h, followed by a second quenching in cold water. The produced ingots were ground into fine powders by hand in a glove box, then sintered in a 10-mm-diameter graphite mold using a spark plasma sintering system (SPS-211LX) at 723 K for 5 min under a pressure of 50 MPa. The synthesis of single-crystal $\text{Bi}_2\text{Te}_2\text{Se}$ was performed using the Bridgman method in a three-temperature-zone furnace. The furnace temperatures in the three zones were first raised to 1123, 1123, 1123 K over a period of 10 h, and then maintained at those temperatures for 12 h to ensure that the raw materials fully melted. Then, the temperature was gradually lowered in the three zones to 1003, 983, 673 K for crystal growth, with a growth rate of 1 mm h^{-1} and the crucible rotation speed of 15 rpm. The crystal growth stopped after the descent distance reached 120 mm, and then the system was cooled to room temperature within 24 h.

B. Thermoelectric properties and band-gap measurements

The phase purity and crystal structure of the powder samples were examined using a Rigaku MiniFlex XRD instrument with $\text{Cu K}\alpha$ radiation at room temperature. The electrical-transport properties (electrical conductivity σ and Seebeck coefficient S) were measured using an Ulvac ZEM-3. The thermal conductivity was calculated using the relationship $\kappa = DC_p\rho$, with the thermal diffusivity (D) measured using the laser flash method (Netzsch LFA 467), specific heat capacity (C_p) determined by the Dulong-Petit law, and density (ρ) measured using the Archimedes method. Sound velocities were measured at room temperature by the ultrasonic pulse-echo method using an Olympus 5073PR pulser and receiver. The Hall carrier concentration (n) was estimated from $n = 1/(eR_H)$. The Hall coefficient R_H was measured using the four-probe method in a physical property measurement system. The carrier effective mass (m^*) was evaluated using the single-parabolic-band-based model [55], a widely adopted approach for thermoelectric semiconductors. The specific expression was

$$\left(\frac{m^* T/K}{m_e 300}\right)^{3/2} = \frac{n}{n_{m,0}} \left[\exp\left(\frac{S}{S_0}\right) - 2 \right] - 0.1455, \quad (5)$$

where m_e is the electron mass, $n_{m,0} = 2.5094 \times 10^{19} \text{ cm}^{-3}$, $S_0 = 86.17 \text{ } \mu\text{V/K}$, n is the carrier concentration, and S is the Seebeck coefficient. The measured parameters were input into this expression for modeling. The extracted m^* values for all $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ compositions were summarized in Supplemental Material Table S6 [29]. Room-temperature

infrared diffuse reflectance measurements of the powders were obtained to probe the optical band gap of the samples. The spectra were collected in the mid-IR range ($7900\text{--}500 \text{ cm}^{-1}$) using an IRAffinity-1S Fourier-transform infrared spectrophotometer. The band gaps were then derived from the reflectance spectra using the Kubelka-Munk equations, where the absorption edges were analyzed to extract the optical band-gap values.

C. Scanning transmission electron microscopy

The Bi_2Te_3 -based samples were prepared for STEM measurements using a standard procedure by grinding, polishing, and ion milling at the temperature of liquid nitrogen. STEM measurements were performed on an aberration-corrected transmission electron microscopy (FEI Titan Themis G2) operated at 300 kV, with a Super-X EDS detector. The structures of the samples were investigated by HAADF in the STEM mode, with a probe convergence angle of 25 mrad and a collection angle of 61–200 mrad. Atomic-resolution EDS mapping in STEM was acquired by 400×300 pixels, with a dwell time of 10 μs and a pixel size of 25.65 pm. The total acquisition time was around 30 min for EDS mapping. The beam current was approximately 50 pA for both the HAADF image and EDS mapping. Atomic-resolution differential-phase-contrast- (DPC) STEM imaging was performed with a four-quadrant annular detector. With the center-of-mass displacement of the diffraction pattern measured by DPC STEM, the charge-density map was generated using Ehrenfest's theorem and Gauss's law [39–41] based on the four-quadrant DPC images. High-resolution electron energy-loss spectroscopy measurements were conducted on a cold-field-emission double-Cs-corrected transmission electron microscopy (Thermo Scientific Spectra 300) operated at 300 kV, using a Gatan Continuum 1069 system with a K3 camera.

The raw STEM-EDS spectrum images were generated using VELOX software (version 3.11) with the characteristic x-ray signals of each element ($\text{Bi K}\alpha$, $\text{Te L}\alpha$, $\text{Se K}\alpha$, and $\text{S K}\alpha$). Then, the raw EDS maps were denoised using the nonlocal principal component analysis method (the detailed denoised procedure was described in previous studies) [31,33,34], which enabled the accurate determination of the atomic position and intensity in denoised EDS images. The composition of the quintuple layers in the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ materials was quantified with VELOX software using the STEM-EDS mapping results. The STEM-EDS simulation was performed using the multislice method in the μSTEM software package with parameters adopted from our experiment. This was used to verify the reliability of the quantified STEM-EDS composition in the case of $\text{Bi}_2\text{Te}_2\text{Se}$, as shown in Supplemental Material Fig. S9 [29].

D. Theoretical calculations

For thermodynamic calculations, a temperature of 800 K was used, consistent with the annealing temperature in the

experiment. We assumed y mol of Se occupied the central layer of $1\text{-mol Bi}_2\text{Te}_{3-x}\text{Se}_x$ and $(x-y)$ mol occupied the outer layer. The formula thus could be written as $\text{Bi}_2(\text{Se}_y\text{Te}_{1-y})_{\text{central}}(\text{Se}_{(x-y)/2}\text{Te}_{(2-x+y)/2})_{\text{outer2}}$ (a variant of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ highlighting the central and outer layers). The Gibbs free energy is defined as follows:

$$G = H - TS, \quad (6)$$

where H is the enthalpy, and S is the entropy of the alloyed system. Herein, only the configurational entropy was considered using the sublattice model [62], as follows:

$$S^{\text{config}} = -R \sum_S \sum_i a^S X_i^S \ln X_i^S, \quad (7)$$

where a^S is the number of sites in the sublattice, and X_i^S is the fraction of species i randomly distributed in the S sublattice. The units of S^{config} are J/K/mol f.u. The enthalpy of Bi_2Te_3 , $\text{Bi}_2\text{Se}_{\text{central}}\text{Te}_{\text{outer2}}$, and Bi_2Se_3 at 0 K were calculated by using the Vienna *ab initio* simulation package [63] and the Perdew-Burke-Ernzerhof generalized-gradient-approximation functional [64]. The van der Waals interactions were considered by using the DFT-D3 method [65]. A conventional 15-atom cell of was constructed for the calculations. The enthalpy of Bi_2Te_3 , $\text{Bi}_2\text{Se}_{\text{central}}\text{Te}_{\text{outer2}}$, and Bi_2Se_3 were -59.366 , -61.248 , and -64.417 eV, respectively. Therefore, assuming that the enthalpy value changed linearly as the Se content increased in certain positions, the enthalpy of $\text{Bi}_2(\text{Se}_y\text{Te}_{1-y})_{\text{central}} \times (\text{Se}_{(x-y)/2}\text{Te}_{(2-x+y)/2})_{\text{outer2}}$ was calculated as follows:

$$H = (-59.366 - 1.882 \times y - 1.5845 \times (x - y))/3 \times \text{NA}. \quad (8)$$

The band structures and the density of states were calculated using a primitive cell. We applied an energy cutoff of 500 eV, and the structures were fully relaxed before reaching the energy criterion of 10^{-6} eV. The SOC effect was considered in the self-consistent calculations. The crystal-orbital Hamilton population and its integration (COHP and ICOHP) were calculated by using the LOBSTER package [66].

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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