

Pressure-driven electronic topology and structural phase transitions in $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$

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ABSTRACT

Synchrotron angle-dispersive X-ray diffraction (ADXRD), Raman scattering, and difference-Fourier electron-density mapping were conducted to track a canonical cascade phase transition of $R\bar{3}m \rightarrow C2/m \rightarrow C2/c \rightarrow Im\bar{3}m$ in $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ up to 45.0(2) GPa. The phase sequence resembles that reported for the Se-dominant counterpart $\text{Bi}_2\text{Se}_{2.1}\text{Te}_{0.9}$, except that each transition onset is systematically shifted to higher pressures by ~ 2 –6 GPa, emphasizing the pronounced compositional sensitivity of phase stability in Bi–Te–Se solid solutions. Notably, these structural transformations are preceded by a Lifshitz-type electronic-topological transition (ETT) at ~ 2.9 GPa, as evidenced by concurrent anomalies in the A_{1g}^2 breathing mode and the axial modulus. This indicates that the ETT is closely linked to pressure-induced carrier redistribution and the accompanying lattice distortion that ultimately drives van der Waals (vdW) gap collapse. Difference-Fourier electron-density mapping further reveals a progressive charge transfer from Bi-6p states toward antibonding Te/Se-derived states, followed by charge accumulation in interstitial regions that stabilizes the high-pressure cubic network. Equation-of-state fits yield bulk moduli of 32.3 ± 0.1 , 77.1 ± 1.4 , 233.9 ± 8.8 , and 153.1 ± 2.2 GPa for the $R\bar{3}m$, $C2/m$, $C2/c$, and $Im\bar{3}m$ phases, respectively, documenting systematic stiffening upon progressive suppression of vdW-layer compressibility. Increasing Se content stiffens the rhombohedral phonons of parent Bi_2Te_3 , elevates the Lifshitz pressure, and stabilizes complex nine-/ten-layer polytypes absent in Te-doped Bi_2Se_3 . These elastic, structural, and vibrational benchmarks provide quantitative constraints for modeling lattice dynamics and transport in alloyed Bi-chalcogenides and clarify how targeted substitution modulates the interplay between electronic and structural instabilities under pressure.

1. Introduction

Topological insulators (TIs) have attracted significant attention due to their unique electronic structure, characterized by symmetry-

protected surface states that remain robust against perturbations such as non-magnetic impurities [1,2]. An intriguing avenue for modifying these surface states and inducing exotic phases, including superconductivity, involves applying external pressure or introducing chemical

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dopants [3,4]. Among the known TIs, compounds consisted of (Bi, Sb)-(Te, Se) constituents are of particular interest owing to their amenable band structure tunability and relatively lower critical pressures required for inducing phase transitions [5,6].

The layered compound Bi_2Te_3 is a benchmark thermoelectric and a prototypical topological insulator. At ambient pressure it crystallizes in the rhombohedral $R\bar{3}m$ structure, where quintuple layers stack along the c -axis through weak van der Waals (vdW) gaps. Hydrostatic compression closes these gaps and drives a sequential polymorphic transformation that can profoundly alter both the lattice thermal conductivity and the electronic band topology [7,8]. Selenium (Se) alloying provides an additional degree of freedom: replacing Te with the smaller and more electronegative Se expands the stability field of certain high-pressure phases while suppressing others, thereby offering a viable route for tuning the structure-property relationships that govern thermoelectric efficiency. Fig. S1 collates the transition sequences reported for a series of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ alloys examined by different groups over the past decade. Although each composition departs from the same $R\bar{3}m$ parent phase, the subsequent evolution is highly composition-dependent. For pure Bi_2Te_3 , Zhu et al. observed an $R\bar{3}m \rightarrow C2/m$ transition near 8 GPa, followed by $C2/m \rightarrow C2/c$ at ~ 14 GPa and a final conversion to cubic $Im\bar{3}m$ beyond 25 GPa [9]. With moderate Se content ($\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$) the monoclinic window widens and the transition to the cubic phase is delayed to ~ 28 GPa [10]. Near-stoichiometric Bi_2SeTe_2 exhibits an even richer pathway: Nielsen et al. [11] reported the emergence of a nine- or ten-layer $C2/m$ polytype, followed by a tetragonal $I4/mmm$ phase that persists above 45 GPa. At higher Se fractions the monoclinic polymorphs are truncated and the $I4/mmm$ structure stabilizes at lower pressures, as demonstrated in $\text{Bi}_2\text{Se}_{1.19}\text{Te}_{1.75}$ [11] and $\text{Bi}_2\text{Se}_{2.1}\text{Te}_{0.9}$ [12]. These disparate results underscore the delicate and intricate interplays between chemical pressure, layer stacking, and electronic instabilities in the Bi-Te-Se system. As is evident from Fig. S1, despite of intensive efforts, two key questions remain unresolved. First, the reported transition pressures for nominally similar compositions diverge by several gigapascals, reflecting the possible influences imposed by the pressure-transmitting media used, differences in sample's grain size, and even refinement protocols adapted in data analyses [10–15]. Second, only a few studies have correlated structural changes with simultaneous measurements of phonon dynamics or electronic transport, leaving the microscopic mechanism that dictates the selection between competing monoclinic variants or triggers the formation of the $I4/mmm$ phase remains largely speculative [16–18]. Resolving these pivotal issues is essential, because each structural rearrangement can be accompanied by an electronic-topological transition that modifies carrier concentration and scattering, thereby influencing both thermoelectric performance and the possibility of pressure-induced superconductivity.

In addition, the pressure response of Bi-based layered chalcogenides is governed not only by lattice-packing constraints but also by subtle changes in the Fermi-surface topology that occur when particular extremal orbits cross the chemical potential. Such electronic topological transitions (ETTs, or Lifshitz transitions) often preceded or accompany structural transformations, modifying the concentration and scattering of carriers and thereby feeding back on phonon stability. In pristine Bi_2Te_3 an ETT has been identified near 3 GPa by anomalies in the Seebeck coefficient and in the pressure coefficients of Raman modes [15]. Fig. S1 indicates these events with solid black horizontal bars superimposed on the structural sequence reported by each research group. The collective data reveal two systematic trends. First, the ETT pressure rises steadily with selenium content, from ~ 2 GPa in Bi_2Te_3 to ~ 2.7 GPa in $\text{Bi}_2\text{Se}_{0.9}\text{Te}_{2.1}$ and beyond 3.1 GPa in Se-rich members such as Bi_2SeTe_2 . Second, whenever the ETT occurs within the stability field of rhombohedral $R\bar{3}m$, it is immediately followed (within 2–3 GPa) by the onset of the first monoclinic $C2/m$ phase. This temporal proximity supports the view that the Lifshitz transition softens specific shear

modes that facilitate layer sliding and octahedral distortion [19]. Despite these correlations, the microscopic mechanism linking the ETT to monoclinic nucleation remains under debate. Attempt of using angle-resolved photoemission under pressure proved to be challenging, and transport signatures were often masked by grain-boundary effects in polycrystalline samples [20]. Consequently, only a handful of studies have tracked both the Fermi-surface reconstruction and the concomitant structural change in the same specimen. For $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$, Chen et al. [10] observed a sharp resistivity minimum at 6.8 GPa that coincides with the disappearance of the (003) Bragg peak of the $R\bar{3}m$ phase, signaling the loss of long-range quintuple-layer stacking order. Similar coincidences have been reported for $\text{Bi}_2\text{Se}_{1.19}\text{Te}_{1.75}$ and $\text{Bi}_2\text{Se}_{2.1}\text{Te}_{0.9}$, where Raman anomalies in the A_{1g}^2 mode track the ETT while XRD confirmed the emergence of the 9/10-layer polytype or the tetragonal $I4/mmm$ phase [11,12].

To gain more general insights from the vast information disclosed in Fig. S1, we specifically compare the detailed high-pressure structural phase transformation results for the two samples $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ and $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$. Firstly, Tseng et al. [12] performed a comprehensive investigation of the pressure-driven structural and electronic evolution in $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ using *in situ* ADXRD and Raman spectroscopy with pressure up to 30 GPa. The results revealed a sequential structural transition from the initial rhombohedral phase ($R\bar{3}m$) to two monoclinic phases ($C2/m$, then $C2/c$), subsequently followed by a body-centered cubic ($Im\bar{3}m$) phase and, at higher pressures, a body-centered tetragonal ($I4/mmm$) structure. Crucially, signature of ETT emerges at approximately 6 GPa, marked by a deviation in the pressure dependence of the c/a ratio and pronounced phonon mode softening in the E_g^2 and A_{1g}^2 modes. It strongly indicates that changes in electronic compressibility and band topology might have prevailed as a precursor preceding the actual structural transformation. These observations have been attributed to the scenario that, in contrast to the conventional alloying rule of random mixing based on the Vegard's law, the alloying Te ions are preferentially occupying the outer layer of the quintuple units in $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$. Since the size of Te ion is larger than that of Se ion, such site-specific occupation of Te ions would consequently lead to substantial compressive stress in the top and bottom Bi-Se bilayers of the Bi_2Se_3 quintuple structure. These findings underscore the critical role of site-specific occupation and internal chemical pressure in shaping the behavior of phase transformation and electronic properties in topological materials under extreme conditions. In comparison, Kang et al. [13] investigated how hydrostatic pressure alters the crystal structure, electronic topological features, and superconducting properties of $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$. Their experimental results revealed the appearance of an ETT at approximately 2.5 GPa, evidenced by anomalies in the c/a ratio and the full width at half maximum (FWHM) of the A_{1g}^1 Raman mode. Similarly, this ETT occurs prior to any detectable structural phase transformation, as $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ remains in the $R\bar{3}m$ phase up to around 8.4 GPa. Concomitant with the ETT, Kang et al. [13] observed the emergence of superconductivity near 2.4 GPa, suggesting a strong correlation between changes in the electronic band structure and the onset of superconductivity. This observation highlights again the crucial role of subtle electronic reconstructions, e.g. the Lifshitz transitions, in driving novel physical phenomena under pressure [21]. Above 8.4 GPa, $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ undergoes successive structural transformations to the $C2/m$, $C2/c$, and eventually to a bcc-like phase at around 22.9 GPa, as were confirmed by both synchrotron X-ray diffraction (XRD) and Raman spectroscopy [13]. At approximately 36.3 GPa, the system forms a disordered bcc alloy, highlighting the progressive collapse of its layered structure as pressure was further increased. Detailed analyses on the lattice parameters using the Birch-Murnaghan Equation of State revealed an apparent compressibility anisotropy, with the c -axis exhibiting a marked change around the same pressure range where superconductivity and ETT signatures appear. Notably, a comparison with the

related TIs, such as Bi_2Te_3 , Sb_2Te_3 , and Bi_2Se_3 , reveals that $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ undergoes its ETT and superconducting transition at substantially lower pressures. By the same token, as discussed above for $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$, this result may be understood as, in $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$, the smaller alloying Se ions are preferentially occupying the central layer, leading to a tensile stress in the top and bottom Bi–Te bilayers and making the system more susceptible to the applied hydrostatic pressures. In any case, both studies clearly highlight the pivotal roles played by the chemical composition and compositional disorder in influencing the pressure-driven structural and electronic transitions, in particular in tuning the threshold pressure needed for these intriguing phenomena [13]. It is noted that, however, the underlying mechanisms of exactly why and how the compositional stoichiometry and disorder affect these intriguing physical properties are still awaiting explanations.

In this work, we aim to address these issues by investigating $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$, a composition located near the midpoint of the Bi_2Te_3 – Bi_2Se_3 solid-solution line and therefore serving as a sensitive probe of the structural competition summarized in Fig. S1. By combining synchrotron ADXRD measurements up to 45.0(5) GPa with careful Rietveld refinement, we construct a detailed high-pressure phase diagram, quantify phase coexistence regimes, and systematically compare our transition pressures with previous reports. Furthermore, by correlating high-resolution diffraction with *in situ* Raman spectroscopy and difference-Fourier electron-density mapping, we directly track how electronic reconstruction and lattice rearrangement evolve across the Lifshitz-type ETT [22] and the subsequent polymorphic transitions. This integrated experimental dataset enables us to clarify whether the ETT merely precedes or actively promotes the onset of the monoclinic phases through lattice softening and interlayer collapse. Beyond resolving the compositional dependence of transition pressures, the structural and vibrational benchmarks reported here provide quantitative constraints for modeling carrier-phonon coupling and pressure-tuned transport in Bi-based topological chalcogenides.

Despite extensive high-pressure studies on $\text{Bi}_2(\text{Te},\text{Se})_3$ -based compounds, a unified experimental picture that directly correlates the pressure-induced structural sequence with electronic-topological reconstruction and real-space charge redistribution remains limited, particularly for $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$. In this work, we address this gap by integrating synchrotron ADXRD, Raman spectroscopy, and difference-Fourier electron-density mapping within a single, consistent high-pressure dataset. This combined approach allows us to (i) determine the full structural phase sequence up to the dense Im-3m phase, (ii) identify an ETT near ~ 2.9 GPa through concurrent elastic and phonon anomalies, and (iii) provide quantitative equation-of-state parameters while explicitly discussing the influence of stress effects in the high-pressure regime. Furthermore, by comparing transition pressures with previous reports on compositionally related Bi-chalcogenides, we highlight how Te/Se substitution systematically shifts structural stability windows. Our results establish a coherent structural-vibrational-electronic framework for understanding pressure-driven topology and phase evolution in $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ and related layered quantum materials.

2. Experiment details

Nominally stoichiometric $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ single crystals were prepared by a modified Bridgman technique with high-purity (99.9999%) Bi, Te, and Se. The starting materials were mixed according to the desired compositions and then encapsulated in a quartz ampoule of 20 mm in diameter. The mixture was melted at 875 °C and kept at the same temperature for 2 days prior to being cooled down slowly to 670 °C at a cooling rate of 0.5 °C/h and finally cooled down to room temperature at a rate of 10 °C/h. Shiny, plate-like crystals with a typical size of $\sim 5 \times 3 \times 0.1$ mm³ were extracted from the synthesized products and ultrasonically cleaned in diluted acetic acid and acetone sequentially. The picked $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ crystals were ground into powders and loaded in a membrane-driven symmetric diamond anvil cell (DAC) with a pair of

450 μm culet diamonds. ADXRD measurements were performed under various pressures up to 45.0(5) GPa at beamline 13-BMC, Advanced Photon Source (APS). The X-ray beam with a wavelength of 0.434 Å (28.0 KeV) was focused into a $26 \times 28 \mu\text{m}^2$ spot using Kirkpatrick-Baez mirrors. Diffraction patterns were collected using a Dectris Pilatus3 1 M pixel array detector. The sample-detector distance and detector orientation were calibrated using a CeO_2 standard. In this study, we used the ruby scale for pressure standard by overlapping the diffraction peaks of the standard with those obtained in the experiment [23]. Fine ruby spheres were used in this study because they are easier to identify than the ruby chips or powder. The ruby spheres were loaded simultaneously with the $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ powder and evenly distributed around the sample. The pressure-transmitting medium (PTM) for ADXRD measurements was Neon gas, which was loaded by Core Lab gas loading system GLS1500.

The high-pressure Raman scattering spectroscopy (HP-RSS) was employed to characterize the in-plane and out-of-plane vibration modes of various bonding configurations. The pressure-dependent Raman measurements were performed with a confocal micro-Raman system (TRIAx 550) with JOBIN-YVON SPEX SPECTRUM ONE liquid nitrogen cooled charge-coupled diode (CCD) detector. The 5320 Å line from a solid-state Nd:YAG laser was focused to about 2–4 μm in diameter on the sample surface. All spectra were recorded in the back-scattering geometry at room temperature with a Leitz UM 32 microscope objective. The laser power was ~ 0.5 mW, and for each ruby fluorescence and Raman spectrum, the data were taken with 3 accumulations, and the integration time was 1200 s. The laser beam was focused to about 2–4 μm in diameter on the sample surface, giving rise to an excitation power density of about $4 \times 10^3 \sim 1.6 \times 10^4$ W/cm². The wavenumbers of the laser beam are accurate to ± 1 cm^{−1}, as determined from plasma emission lines. The frequency of each Raman band reported in this study was obtained using Lorentzian curve fitting. The pressure was measured *in situ* using the same laser light and confocal micro-Raman system to excite and analyze the ruby fluorescence, respectively, as was used to measure the HP-RSS. Under ambient conditions, the wavelength of R_1 line of ruby is 6942 Å. The precision of the pressure determination with a corresponding resolution of DAC pressure of about 0.1–0.2 GPa was achieved by reading the peak position of the embedded ruby R_1 fluorescence. The PTM used for HP-RSS was Neon gas, which was loaded by Core Lab gas loading system GLS1500. The Jandel Scientific Peakfit is used to deconvolute and determine the peak position, intensity, and the FWHM of the Raman spectra. Lorentz-Gauss cross product functions were used throughout, and peak fitting was iterated until the attained correlation coefficient square (r^2) was greater than 0.995.

3. Result and discussion

Fig. 1 shows the evolution of synchrotron XRD patterns for $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ collected from ambient pressure to 45.0(5) GPa. At ambient, all the reflections can be perfectly indexed to the $R\bar{3}m$ structure, the same as that of both Bi_2Te_3 and Bi_2Se_3 at ambient conditions [9]. The raw data obtained at ambient and a series of applied pressures in DAC are reported in the Supplementary Information and displayed in Fig. S2. The patterns obtained at 4.5(1) GPa and 8.9(1) GPa exhibit a progressively uniform shift of all peaks toward higher 2θ with only minor broadening, indicating a purely elastic response of the quintuple-layer framework. The first discernible structural change appears at 14.5(2) GPa, where new Bragg peaks (marked in cyan) emerge while the parent reflections weaken. Rietveld analysis indicates that these additional lines can be assigned to a monoclinic $C2/m$ phase, similar to that reported for Bi_2Te_3 at 8–10 GPa [24]. The presence of Se apparently significantly raises onset pressure for the $R\bar{3}m \rightarrow C2/m$ transition. Interestingly, the pressure window over which $R\bar{3}m$ and $C2/m$ coexisting is quite narrow (approximately from 14.5 to 16.7 GPa), suggesting a first-order transition driven by the collapse of vdW gaps

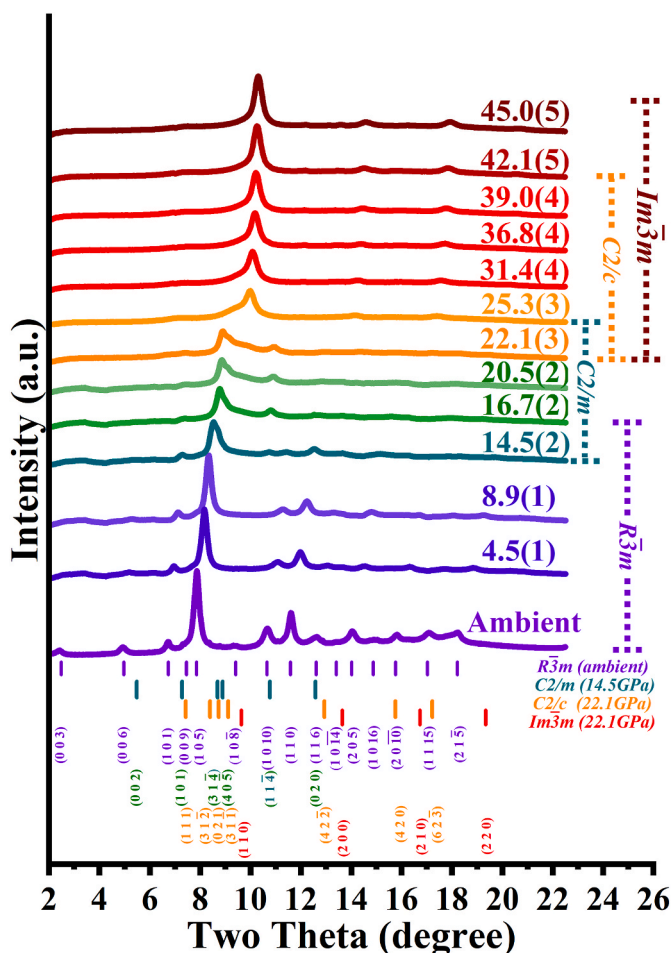


Fig. 1. Synchrotron ADXRD (0–45 GPa) shows $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ retaining rhombohedral $R\bar{3}m$ until 14.5(2) GPa, then successively converting to $C2/m$, $C2/c$ (22.1(3) GPa), and cubic $Im\bar{3}m$ (>31.4(4) GPa); color-coded ticks mark calculated Bragg peaks and (hkl) indices, evidencing the classic layered-to-cubic route, shifted to higher pressures by the elevated Te/Se ratio.

between quintuple layers. With further compression, the $R\bar{3}m$ reflections vanish completely and a single $C2/m$ lattice describes the pattern at 20.5(2) GPa. At 22.1(3) GPa, additional splitting appears on the low-angle side of the principal peaks. These features are ascribed to an iso-symmetric distortion toward $C2/c$, indicating that layer sliding and octahedral tilting become energetically favorable once the inter-layer distance falls below ~ 3.2 Å. A similar monoclinic-to-monoclinic crossover has been observed in $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$, albeit at a pressure about 4 GPa lower. The observation underscores the role of Se content in stabilizing the competing monoclinic variants [10]. Above 31.4(4) GPa, the diffraction pattern exhibits abrupt changes. Namely, the broad $C2/c$ multiples collapse into a dominant doublet at $2\theta \approx 9.4^\circ$ and a set of weaker peaks that can fit a cubic $Im\bar{3}m$ unit cell. At 39.0(4) GPa, the reflections of the cubic structure sharpen, and no residual peaks of the monoclinic phase can be detected, indicating a complete reconstruction into a body-centered arrangement of Bi and chalcogen atoms. The phase transition sequence of $R\bar{3}m \rightarrow C2/m \rightarrow C2/c \rightarrow Im\bar{3}m$ matches the progression reported for $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ [10] with each transition occurring at pressures about 2–3 GPa higher, which appears to have intimate relevance to the Te/Se ratio in the sample. The final $Im\bar{3}m$ phase persists to at least 45.0(5) GPa, in agreement with the high-pressure stability field previously established for Se-rich analogues [11]. It is noted that between 14.5(2) and 25.3(3) GPa the widths of the diffraction peaks broaden substantially, which might be reflecting the non-hydrostatic

stress that develops as the sample densifies. Nevertheless, the refinement residuals ($R_p < 3\%$) remain low throughout the pressure range, attesting to the robustness of the structural assignments. In fact, the behavior of progressive suppression in the layered motifs followed by the eventual adoption of a cubic network appears to be ubiquitously observed in many layer-structured vdW chalcogenides, wherein the applied pressure first triggers shear of adjacent layers and subsequently drives cations to re-ordering into close-packed frameworks [15]. Considering that the ETTs in Bi-chalcogenides are commonly preceding or accompanying such structural changes [9,14,15,24], the marked intensity redistribution seen at 14.5(2)–16.7(2) GPa is likely coupled to a Lifshitz transition that modifies carrier pocket multiplicity. Future high-pressure transport and Raman measurements on the same crystals will be required to confirm this conjecture. In short, the ADXRD data displayed in Fig. 1 evidently establish that $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ follows the same canonical rhombohedral $\rightarrow$ monoclinic $\rightarrow$ cubic pathway observed in other Bi–Te–Se alloys, albeit that, with increasing Te concentration, the onset pressures for each transition are systematically elevated to higher values. A quantitative comparison with previously reported Bi–Te–Se compositions reveals a clear and systematic compositional trend in the pressure-driven phase evolution. As summarized in Fig. S1, $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ follows the same overall structural cascade ($R\bar{3}m \rightarrow C2/m \rightarrow C2/c \rightarrow Im\bar{3}m$) as its Se-dominant counterpart $\text{Bi}_2\text{Se}_{2.1}\text{Te}_{0.9}$; however, the onset pressure of each transition is consistently shifted to higher values by approximately 2–6 GPa. This upward shift is observed for the first monoclinic transition as well as for the subsequent transformations into the $C2/c$ and cubic $Im\bar{3}m$ phases, indicating that Te-rich compositions exhibit enhanced resistance against pressure-induced layer sliding and densification. Such systematic pressure offsets cannot be attributed to the experimental uncertainties alone and instead reflect the intrinsic role of chemical substitution in modifying internal strain, bonding hierarchy, and electronic compressibility. The present results therefore provide a quantitative benchmark for compositional tuning of phase stability in the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ system and demonstrate that alloying offers a controlled route to shift structural and electronic instability thresholds without altering the fundamental transformation pathway. This trend highlights the competing influences of chemical pressure and electro-negativity on the stability of monoclinic intermediates. It provides a quantitative framework for correlating structural evolution with the thermoelectric and topological properties of Bi-based chalcogenides. The Angular-dispersive X-ray Diffraction pattern obtained in this experiment is demonstrated in Fig. S2. Nevertheless, Table S1 presents the GSAS-EXPGUI well refinement lattice constant for each applied pressure.

Fig. 2 displays the Rietveld refinement results of ADXRD patterns for $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ at selected pressures, as analyzed using the GSAS software package [25]. At ambient conditions (Fig. 2(a)) and 12.0(2) GPa (Fig. 2(b)), the crystal structure corresponds to the rhombohedral $R\bar{3}m$ phase, in line with other Bi–Se–Te compounds [9]. The low values of R_p and χ^2 suggest that this structural model accurately reproduces the observed Bragg peaks. As pressure increases to 14.5(2) GPa (Fig. 2(c)), new diffraction features become evident, reflecting the progressive emergence of a monoclinic $C2/m$ phase. Although $R\bar{3}m$ remains dominant at 14.5(2) GPa, the refinements confirm the coexistence of $C2/m$, with an estimated fraction ratio ($I_{C2/m}/I_{R\bar{3}m}$) of nearly 78.5%. By 16.9(2) GPa and 20.0(3) GPa (Fig. 2(d) and (e)), the $C2/m$ phase prevails substantially, although minor residuals of $R\bar{3}m$ may persist, depending on the exact pressure conditions and potential deviations from hydrostatic compression [15]. In the vicinity of 22.1(3) GPa (Fig. 2(f)), another transition occurs, as the $C2/c$ phase appears alongside $C2/m$, suggesting a partial rearrangement of the layers driven by increased compression. Simultaneously, the first signatures of a cubic $Im\bar{3}m$ phase can be detected, albeit at a relatively low percentage (<2%). At still higher pressures, such as 25.3(3) GPa and beyond (Fig. 2(g) and (h)), the $Im\bar{3}m$ phase becomes increasingly prevalent, eventually constituting over 30%

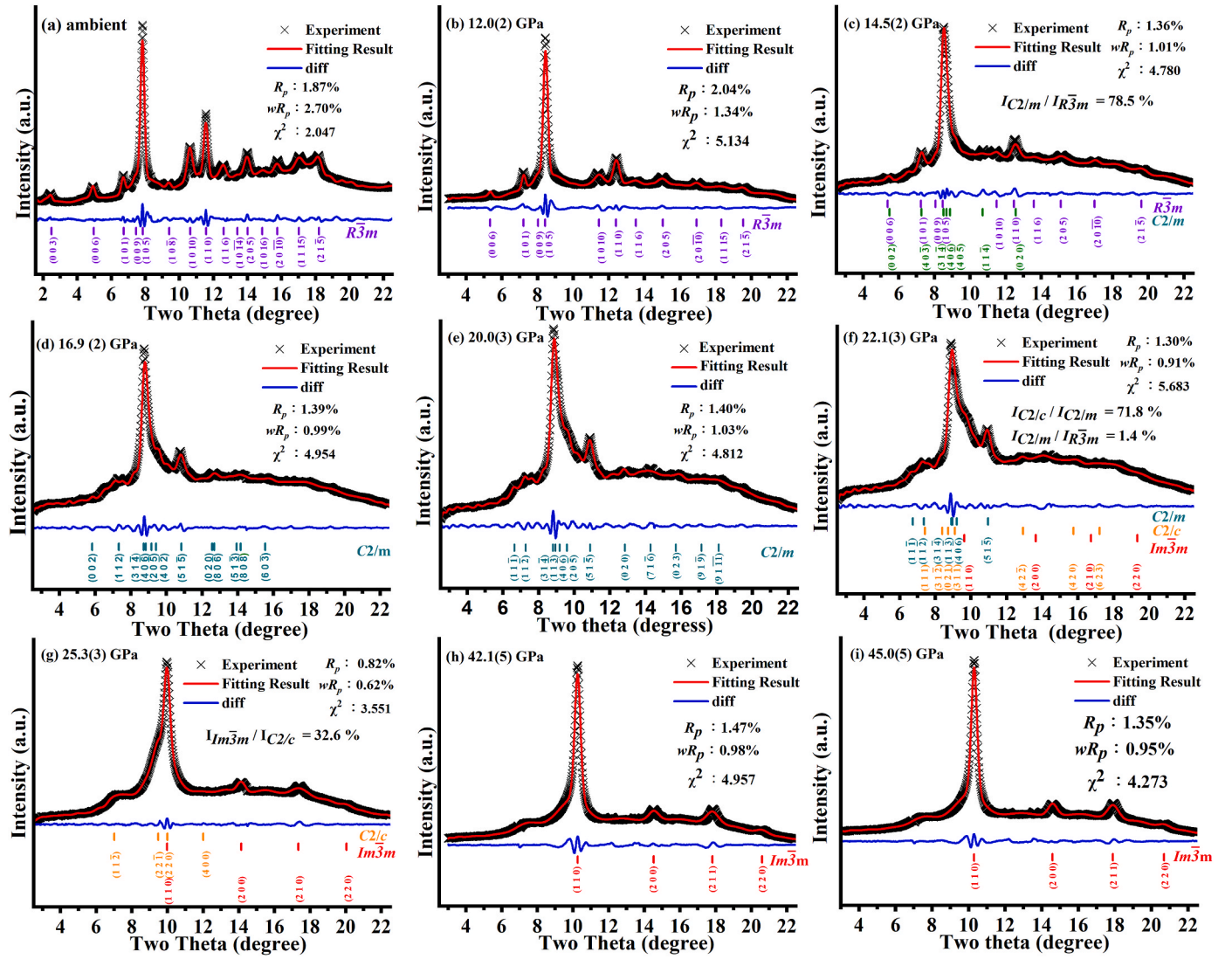


Fig. 2. Rietveld fits (red lines) to $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ ADXRD data (black; residuals blue) map a clear phase cascade. Panels (a)–(i), through mixed $R\bar{3}m/C2/m$ at 14.5(2) GPa, single-phase $C2/m$ at 16.9(2) and 20.0(3) GPa, the onset of $C2/c$ and incipient $Im\bar{3}m$ at 22.1(3) GPa, and the dominance of the cubic phase by 45.0(5) GPa. In-panel R_p , wR_p , and χ^2 values and phase-fractions verify excellent model-data agreement across the entire pressure range.

of the sample. This progression indicates that the layered chalcogenide lattice undergoes multiple structural transformations within a narrow pressure range. The Rietveld indicators remain acceptably low throughout all refinements (with $R_p < 2\%$ and $wR_p \approx 1\%$ in many cases), further confirming the reliability of the proposed phase assignments [25]. These findings align with previous studies of Bi-based chalcogenides, where sequential transitions from rhombohedral to monoclinic and, ultimately, cubic structures were observed under compression [12]. In addition, Table S2 summarizes the refinement lattice information at ambient and each phase-transition pressure. Rietveld refinement index, lattice parameter, bonding length, bonding angle and Wyckoff position are included. Doping with Te appears to shift the onsets of the high-pressure phases to pressures relatively higher than that of the undoped Bi_2Se_3 , which can concomitantly influence both the band topology and the thermoelectric properties [26,27]. Such phase evolution reflects the interplay of vdW gaps, layer stacking arrangements, and electronic band adjustments under strong compression, ultimately culminating in a more isotropic crystal structure at $Im\bar{3}m$. The analysis shown here provides deeper insight into how doping modifies the high-pressure stability fields of topological chalcogenides, an aspect of considerable interest for potential applications in quantum electronics

and high-performance thermoelectric materials [28,29]. To further elaborate on the above conjectures, it is heuristic to have some visualized pictures that can mimic how the electron density distribution (i.e., the bonding nature) evolves with increasing compressive pressures. Further discussion of site-selective occupation is therefore not repeated elsewhere. Fig. 3 displays the difference Fourier electron-density maps for $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ extracted from high-pressure single-crystal data at selected pressures. At ambient conditions, the maps reveal pronounced residual density (blue isosurfaces) between the quintuple layers, indicating partially occupied van der Waals sites and weak interlayer bonding typical of rhombohedral $R\bar{3}m$ chalcogenides [30,31]. As pressure rises to 2.0(1) GPa, the interstitial density becomes more localized and contracts toward the Te^I anions, signaling the initial closure of the vdW gap.

Concomitantly, the lobes around Bi grow more isotropic, reflecting enhanced p - p overlap with the neighboring chalcogen layers. Between 2.9(1) GPa and 3.9(1) GPa, close to the ETT identified in transport and Raman measurements [16–18,32,33], the maps undergo a qualitative change: interlayer residuals largely vanish while the red positive contours around Te^I and $\text{Se}_{0.9}$ intensify, consistent with scenario of charge transfer from Bi 6p states into antibonding Te/Se orbitals. This

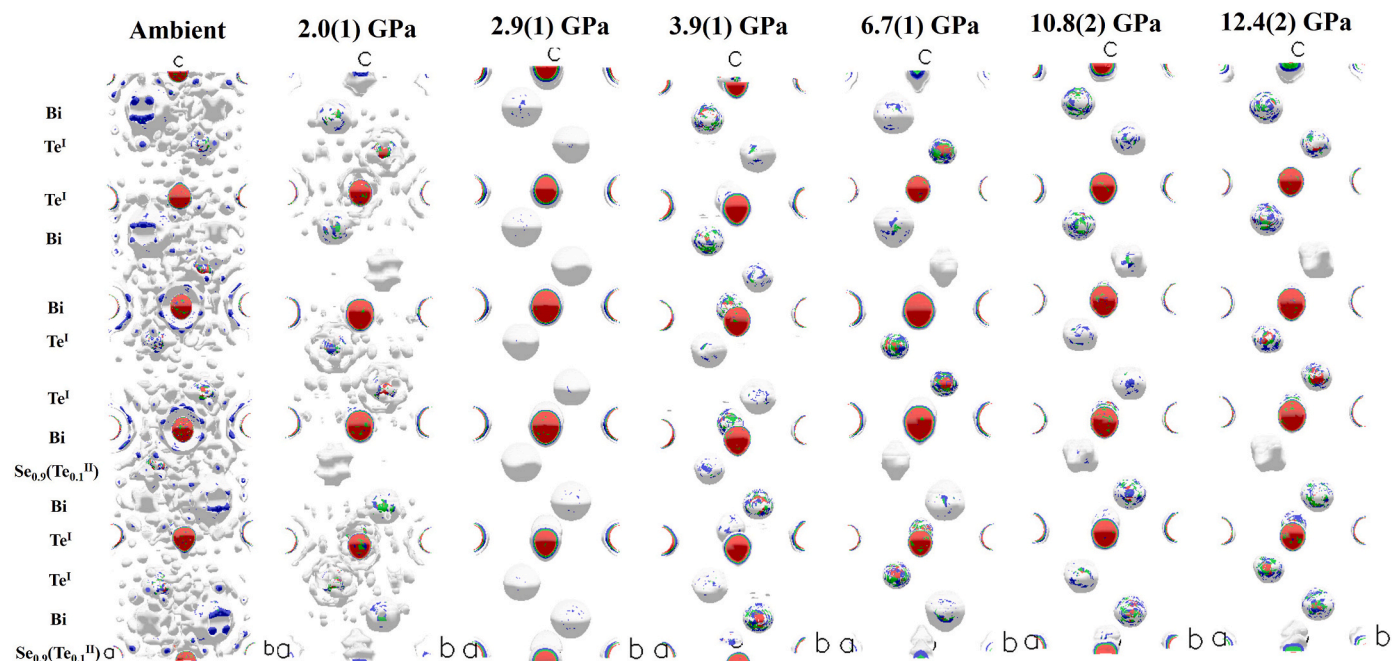


Fig. 3. Difference-Fourier maps ($\pm 0.2 \text{ e } \text{\AA}^{-3}$, view vertical $[110]$ face) show a clear pressure-driven charge migration: diffuse interlayer density at ambient pressure collapses by $\approx 2.9 \text{ GPa}$ (Lifshitz point); electrons concentrate on Te/Se, van-der-Waals gaps empty, and spherical shells emerge around the chalcogens—early warning of the $R\bar{3}m \rightarrow C2/m$ tilt and the cation re-ordering that ultimately feeds the cubic phase.

redistribution weakens the $\text{Te}^{\text{I}}\text{--Bi}$ bond asymmetry and promotes the shear instability that precipitates the $R\bar{3}m \rightarrow C2/m$ transformation at $\sim 14.5(2) \text{ GPa}$ (see Fig. 1). Indeed, at $6.7(1) \text{ GPa}$ the residual density reappears as faint arcs centered on the pseudo-mirror plane that becomes the unique axis of the monoclinic cell, implying the onset of layer sliding prior to the diffraction-visible phase transition. Above $10.8(2) \text{ GPa}$, where monoclinic symmetry dominates, the electron density surrounding Te^{I} evolves into nearly spherical shells, while the Bi contours elongate along the c -axis. This behavior points to a progressive equalization of Te--Bi bond lengths, in agreement with the refined interatomic distances that converge to $3.02 \text{ \AA}$ at $12.4(2) \text{ GPa}$. Simultaneously, weak density pockets emerge at the octahedral voids located midway between adjacent quintuple layers, foreshadowing the cation rearrangement that culminates in the cubic $Im\bar{3}m$ phase above $31.4(4) \text{ GPa}$. A comparable build-up of interstitial charge preceding the layered-to-cubic conversion

has been reported for Bi_2Se_3 and Bi_2Te_3 , but at lower pressures, emphasizing the role of Se substitution in delaying the complete collapse of the vdW gap [11,15]. The pressure-dependent maps therefore provide a real-space picture of how chemical and external pressure cooperate to modify bonding. Initially, compression enhances Bi–Te covalency within the quintuple block, triggering an ETT that redistributes carriers and softens shear modes. Continued pressure transfers charge into interlayer voids, stabilizing a more isotropic coordination that ultimately favors the high-symmetry cubic network. These observations corroborate the sequence inferred from diffraction (Fig. 1) and highlight the importance of charge redistribution, instead of merely steric packing, in governing the polymorphic landscape of Bi-chalcogenides [34]. As mentioned above, since thermoelectric performance of the materials is strongly influenced by carrier concentration and scattering at the Fermi level, the ability to visualize pressure-driven charge transfer, thus,

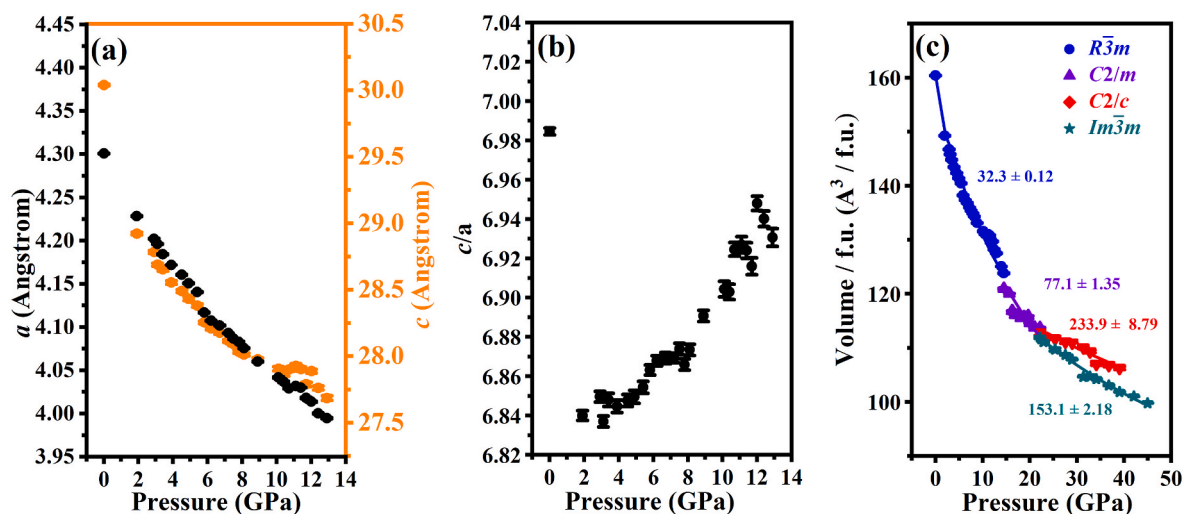


Fig. 4. High-pressure compressibility of $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ extracted from synchrotron ADXRD. (a) Axial lattice parameters a (black) and c (orange) within the rhombohedral phase as a function of pressure; (b) Evolution of the axial parameter ratio c/a ; (c) The Birch-Murnaghan fits give bulk moduli.

offers valuable guidance for engineering Bi₂Te₃-based alloys through combined chemical and mechanical tuning [35–37].

Fig. 4 summarizes the compressibility and elasticity of Bi₂Te_{2.1}Se_{0.9} derived from ADXRD up to 45.0(5) GPa. Fig. 4(a) and (b) track the evolution of the lattice parameters within the ambient-pressure rhombohedral $R\bar{3}m$ phase. The *a*-axis contracts monotonically from 4.44 Å to 3.99 Å, whereas the *c*-axis shrinks more slowly, giving rise to a noticeable rise in the *c/a* ratio below 2.9 GPa. Such anisotropic compression is a unique characteristic of vdW layered chalcogenides and reflects the relative softness of the inter-quintuple gap compared with the covalent Bi–Se(Te) bonds inside each block [15]. The ratio *c/a* shown in Fig. 4(b) is a dimensionless parameter and is used here to highlight anisotropic lattice compression. The pressure dependence of the volume per formula unit (Fig. 4(c)) was fitted with second-order Birch-Murnaghan equations of state (BM-EoS) for each crystallographic regime [38]. The minimum in *c/a* locating at 2.9 GPa coincides with an inflection in the axial moduli (Fig. 4(b)) and matches the pressure at which an ETT was previously inferred from transport and Raman anomalies in Se-rich Bi–Te alloys [16–18,32,33]. Table S3 list the bulk modulus of Bi₂Te_{2.1}Se_{0.9} and other alloy of the same family. The bulk modulus *B*₀ rises from 32.3 ± 0.1 GPa in $R\bar{3}m$ to 77.1 ± 1.4 GPa in the first monoclinic phase *C2/m*, in good agreement with values reported for Bi₂Se_{1.19}Te_{1.75} [11]. A further stiffening to 233.9 ± 8.8 GPa accompanies the monoclinic *C2/m*-to-monoclinic *C2/c* conversion, which is more difficult pressed than Bi₂Te_{0.9}Se_{2.1}. While the high-pressure cubic $Im\bar{3}m$ polymorph softens slightly to 153.1 ± 2.2 GPa, echoing the behavior of cubic Bi₂Se_{1.19}Te_{1.75} above 20 GPa [39]. These stepwise increases reflect the progressive elimination of the vdW gap and the concomitant growth of the three-dimensional Bi-chalcogen connectivity. The apparent decrease in bulk modulus from 233.9 ± 8.8 GPa for the monoclinic *C2/c* phase to 153.1 ± 2.2 GPa for the subsequent cubic $Im\bar{3}m$ polymorph may appear to be counter-intuitive at first sight, yet it can be rationalized when the fitting protocols, the stress state of the sample and the bonding topology of the two lattices are considered. First, the BM-EoS of *C2/c* was extracted from a narrow pressure window ($\Delta P \approx 8.9(1)$ GPa) that lies immediately above the *C2/m*→*C2/c* transition. In this interval the volume contracts by less than 3 %, so the third-order Birch-Murnaghan fit is dictated mainly by the first derivative $K' = \frac{\partial B_0}{\partial P}$, which is fixed to the canonical value of 4 as a common practice, any residual non-hydrostatic stress will steepen the apparent *P*(*V*) slope and inflate *B*₀ [40]. Diamond-anvil studies on layered chalcogenides have repeatedly shown that deviatoric stresses can reach 1–2 GPa above 20.5(2) GPa even when soft pressure media are used, leading to overestimates of *B*₀ for low-symmetry phases such as monoclinic or orthorhombic ZnS-type lattices [41]. By contrast, the cubic data were collected over a broader range (31.4(4)–45.0(5) GPa) and the higher symmetry of $Im\bar{3}m$ averages out shear components, yielding a more reliable, and lower, modulus. Second, the bonding topology changes qualitatively at the *C2/c*→ $Im\bar{3}m$ reconstruction. The orthorhombic cell retains distorted octahedra in which Bi–Ch (Ch = Se, Te) distances are short and second-neighbor repulsion is strong, producing a steep *dP/dV*. In the cubic phase Bi atoms occupy body-centered positions and the Ch framework adopts a near-bcc packing with larger mean Bi–Ch separations. Density-functional calculations for Bi₂Se₃ show that this re-entrant expansion of the first coordination shell reduces the curvature of the energy-volume curve and hence the bulk modulus [15,20]. A similar softening upon turning cubic-structured has been reported for Sb₂Te₃ [42] and for several post-quartz oxides, emphasizing that higher crystallographic symmetry does not necessarily imply a stiffer lattice, especially when the local bond geometry is altered. Finally, it should be noted that the quoted errors for the orthorhombic fit are an order of magnitude larger than those for the cubic BM-EoS, reflecting the limited data span and possible phase coexistence. We therefore attribute the seemingly anomalous stiffening of the orthorhombic segment primarily to a combination of stress anisotropy and BM-EoS-fitting artefacts rather

than to an intrinsic increase in bond rigidity. It should be noted that the bulk moduli derived from BM-EoS fitting should be interpreted with caution, particularly for low-symmetry phases stabilized over limited pressure intervals. In the present case, the monoclinic *C2/c* phase only spans over a comparatively narrow pressure range, which increases the sensitivity of the fitted bulk modulus to the selected fitting window, as well as to the parameter covariance between *B*₀ and its pressure derivative *K'*. When the pressure interval is restricted, fixing or constraining *K'* can artificially enhance the fitted *B*₀ value, leading to an apparent stiffening that may not solely reflect intrinsic lattice compressibility. In addition, despite the use of a soft pressure-transmitting medium, deviatoric stress is expected to increase at elevated pressures and can steepen the apparent *P*–*V* slope, especially in low-symmetry monoclinic structures. Consequently, the unusually large bulk modulus obtained for the *C2/c* phase should not be over-interpreted as a direct indication of intrinsic bond stiffening. Instead, the BM-derived elastic parameters reported here should be regarded as effective moduli under quasi-hydrostatic conditions, providing quantitative experimental benchmarks for comparison across phases and compositions. By contrast, the high-symmetry cubic $Im\bar{3}m$ phase is fitted over a broader pressure range and is comparatively less sensitive to stress anisotropy, as symmetry averaging reduces the impact of deviatoric components. Accordingly, the elastic parameters obtained for the cubic phase are expected to more properly reflect the intrinsic compressibility of the dense three-dimensional framework. Taken together, the lattice-parameter evolution, BM-EoS fits, and strain analyses delineate a coherent picture in which electronic reorganization near the Lifshitz-type transition facilitates the collapse of the van der Waals gap, followed by reconstructive transitions that progressively densify the lattice. The Eulerian strain versus normalized stress plots in Fig. 5(a)–(c) provide additional insight into the elastic response. In the rhombohedral region the linear fit to *H* versus strain yields an axial modulus *H*₀ of 24.1 GPa and a positive pressure derivative, consistent with the steep rise in *B*₀. A clear kink at around 2.9 GPa marks the ETT and precedes the structural transition at 14.5(2) GPa, underscoring the role of electronic instabilities in priming the lattice for shear-driven layer sliding [19]. For the monoclinic phases, separate fits along the *a*- and *c*-axes (Fig. 5(b) and (c)) reveal that compression is initially accommodated by soft shear along *b*, but stiffens markedly once octahedral tilting locks in above ~25.3(3) GPa. The axial moduli extracted here are within 5 % of those reported for Bi₂Se_{2.1}Te_{0.9}, indicating that the mechanical hardening accompanying Se → Te substitution is modest compared with the dramatic increase produced by the symmetry change itself [12]. The lattice-parameter trends, BM-EoS fits, and strain analyses thus delineate a coherent picture in which electronic re-ordering at ~2.9 GPa facilitates a first-order collapse of the vdW gap at 14–15 GPa, followed by two higher-pressure reconstructive transitions that progressively densify the framework. The quantitative moduli obtained here will be valuable for modeling phonon transport and evaluating the pressure dependence of the thermoelectric figure of merit in Bi–Se–Te solid solutions.

Fig. 6(a) presents representative high-pressure Raman spectra of Bi₂Te_{2.1}Se_{0.9}, while Fig. 6(b) compiles the complete data set as a false-color contour plot. At ambient pressure the spectrum is dominated by the in-plane *E*_g² shear vibration at 103 cm^{−1} and the out-of-plane *A*_g² breathing mode at 136 cm^{−1}, in agreement with the factor-group analysis for the rhombohedral $R\bar{3}m$ phase [15]. Compression to 1.4(1) GPa hardens both modes, but the breathing mode exhibits a noticeably larger pressure coefficient (3.8 cm^{−1} GPa^{−1}) than the shear mode (2.9 cm^{−1} GPa^{−1}), underscoring the greater compliance of the vdW gap relative to the covalent Bi-chalcogen bonds. This anisotropic stiffening is consistent with the axial compressibility extracted from X-ray diffraction (Fig. 4 (a)). The frequency ratio $\omega_{A_g^2}/\omega_{E_g^2}$ decreases steadily and reaches a minimum near 2.9 GPa, coincident with the ETT inferred from X-ray strain analysis (Fig. 4). A pronounced anomaly occurs near 2.9 GPa: the *A*_g² mode softens by ~2 cm^{−1} and its intensity diminish, while the *E*_g²

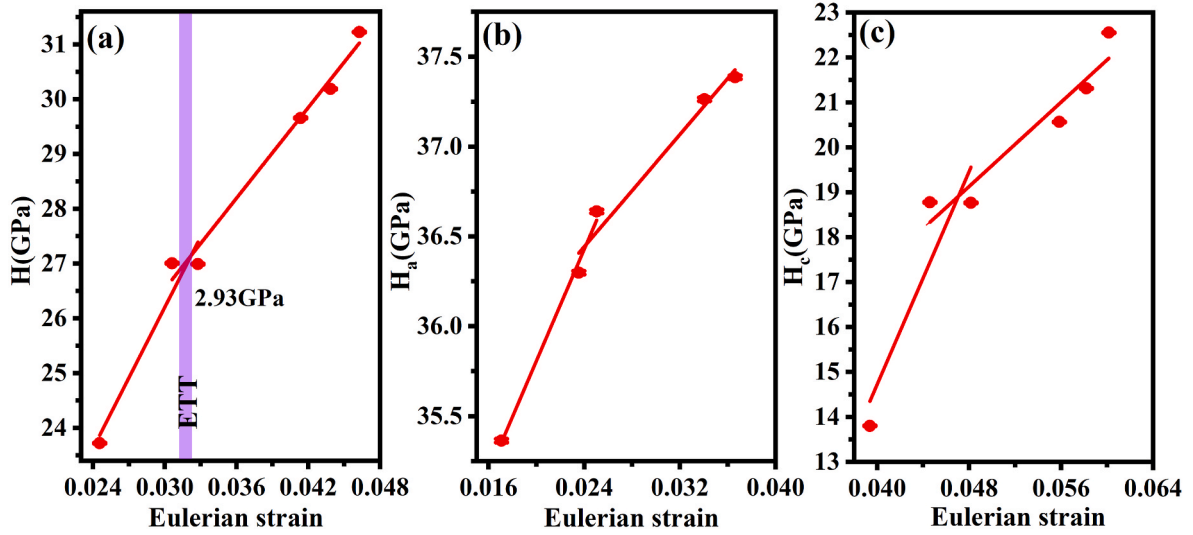


Fig. 5. High-pressure elasticity of $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ extracted from synchrotron ADXRD. Panels (a)-(c) plot H vs Eulerian-strain reveal a 2.93 GPa kink (shaded violet)-the Lifshitz trigger that foreshadows the van der Waals gap collapse.

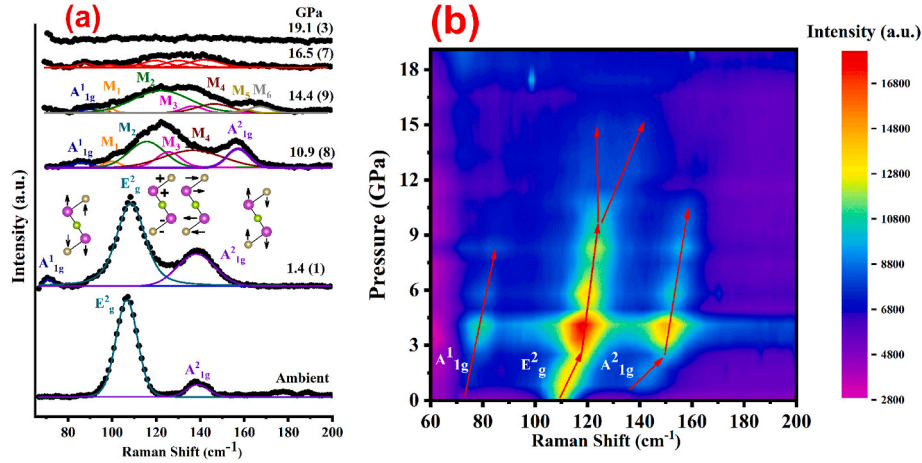


Fig. 6. (a) Raman spectra of $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ from 0 to 19 GPa. Lorentzian fits separate the rhombohedral E_g^2 and A_{1g}^2 modes and new monoclinic bands M_1 - M_6 ; insets depict the atomic displacement patterns of the principal vibrations. (b) False-color contour plot of Raman intensity versus pressure: rhombohedral modes harden linearly, dip at the ~ 2.9 GPa Lifshitz point, the birth and growth as monoclinic modes between 8 and 15 GPa and first-order Raman activity is quenched in the cubic $\text{Im } \bar{3} m$ phase (>16.5 GPa).

mode continues to harden (Fig. 6(b)). Such behavior signals an ETT that modifies electron-phonon coupling by shifting a conduction-band pocket across the Fermi level, as previously reported for Bi_2Te_3 [32, 42] and Se-rich Bi-Te alloys [12]. Beyond the ETT both modes resume a linear blue-shift until ~ 8 GPa, where new peaks M_1 - M_4 emerge between 110 and 150 cm^{-1} (Fig. 6(a)). Their appearance indicates the loss of three-fold rotational symmetry and the activation of zone-edge phonons as the lattice distorts toward the monoclinic $C2/m$ structure identified by X-ray diffraction at 14.5(2) GPa (Fig. 1). Factor-group analysis of the refined $C2/m$ cell predicts six A_g modes below 200 cm^{-1} , matching the number and relative intensities observed at 10.9(8) GPa. The contour map (Fig. 6(b)) highlights the continuous hardening of these monoclinic modes with pressure coefficients of $4\text{--}5 \text{ cm}^{-1}\text{GPa}^{-1}$, markedly larger than those of the parent modes and mirroring the increase in bulk modulus across the $R \bar{3} m \rightarrow C2/m$ transition (Fig. 4(c)). A second reorganization occurs at 14.4(9)–16.5(7) GPa: the original E_g^2 and A_{1g}^2 bands disappear, and two weaker features M_5 and M_6 appear at 148 and 163 cm^{-1} , consistent with the monoclinic $C2/c$ phase predicted by density-functional calculations [15]. Above 16.5(7) GPa all first-order

Raman activity vanishes, indicating the formation of the centrosymmetric cubic $\text{Im } \bar{3} m$ phase whose optical phonons are Raman-silent. The abrupt quenching of intensity confirms that the cubic fraction exceeds 95 %, in excellent accord with the diffraction results. The sequential evolution of phonon frequencies and intensities therefore mirrors the structural pathway $R \bar{3} m \rightarrow C2/m \rightarrow C2/c \rightarrow \text{Im } \bar{3} m$ established crystallographically. Moreover, the softening of the A_{1g}^2 breathing mode at the ETT emphasises the intimate coupling between electronic and lattice instabilities: as the Fermi-surface topology changes, enhanced screening weakens the restoring force of the interlayer vibration, thereby lowering the barrier for the shear distortion that nucleates the monoclinic phase [34,43]. Such interplay between charge redistribution and phonon softening provides a microscopic rationale for the pressure-induced structural sequence in Bi-Te-Se alloys and offers guidance for engineering their thermoelectric and topological properties through combined chemical and external pressure.

Fig. 7 compares the pressure dependences of the principal Raman-active phonons for $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ (teal symbols) with those of the Se-rich analogue $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ (violet symbols, digitized from Tseng et al.

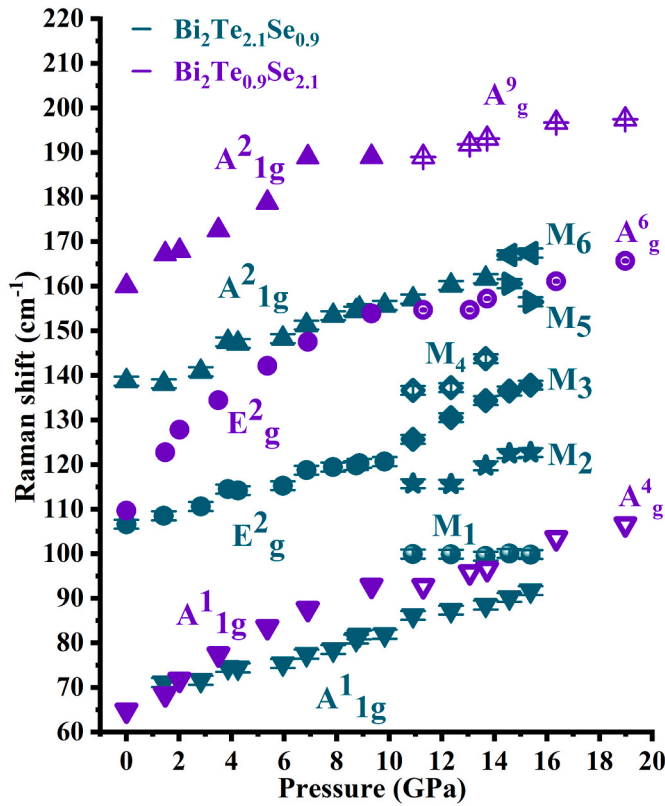


Fig. 7. Pressure evolution of the Raman-active phonons in $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ (teal symbols) compared with the Se-rich analogue $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ (violet symbols from Tseng et al.). Filled symbols trace modes that originate in the rhombohedral $R\bar{3}m$ phase (E_g^2 , A_{1g}^1 , A_{2g}^2), while open or starred symbols denote phonons activated by the monoclinic distortion (M_1 – M_6 and the higher-order A_g^4 , A_g^6 , A_g^9 branches characteristic of nine-/ten-layer stacking variants).

[12]). In both compounds the rhombohedral $R\bar{3}m$ modes, namely E_g^2 , A_{1g}^1 and A_{2g}^2 , harden linearly up to the onset of monoclinic phase, but their pressure coefficients differ markedly. For the Te-rich sample the slopes are 2.9, 3.1 and $3.8 \text{ cm}^{-1} \text{ GPa}^{-1}$, respectively, whereas in $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ the slope exhibits larger values (3.4, 4.0 and $4.6 \text{ cm}^{-1} \text{ GPa}^{-1}$). This systematic increase indicates that replacing Te by the lighter and more electronegative Se stiffens both the interlayer shear (E_g^2) and the out-of-plane breathing (A_{2g}^2) vibrations, in line with the higher bulk modulus reported for Se-rich members of the solid solution [12,39,44]. The divergence between the two data sets becomes pronounced above $\sim 8 \text{ GPa}$. In $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ a family of four monoclinic modes (M_1 – M_4) emerges between 110 and 150 cm^{-1} and persists to around 15 GPa, whereas the Se-rich compound develops six modes that remain Raman-active up to around 18 GPa. The additional modes (A_g^4 , A_g^6 , A_g^9) are fingerprints of the nine- or ten-layer polytype that stabilizes only when the Se fraction exceeds $\sim 50 \%$ [11,12]. Their absence in $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ confirms that this intermediate stacking variant is energetically unfavorable at higher Te content; instead, the lattice proceeds directly from monoclinic $C2/m$ to monoclinic $C2/c$ and finally to cubic $Im\bar{3}m$ as demonstrated by diffraction (Fig. 1).

The lower number of monoclinic modes and their more modest pressure hardening effect ($4\text{--}5 \text{ cm}^{-1} \text{ GPa}^{-1}$ versus $5\text{--}6 \text{ cm}^{-1} \text{ GPa}^{-1}$ in $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$) further indicate that Te-rich layers retain greater shear flexibility, consistent with the delayed appearance of the tetragonal $I4/mmm$ phase observed in Se-rich samples [12]. A second contrast concerns the ETT. The kink in the A_{1g}^1 trajectory that marks the ETT occurs at 2.9 GPa for $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ but is shifted upward to 5.2 GPa in

$\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$, corroborating transport data that show the Lifshitz pressure rises with Se content [15,42]. Because the ETT precedes the structural transition by 6–8 GPa in both alloys, the larger separation in the Se-rich crystal affords a broader window in which electronic tuning can be achieved without altering the lattice symmetry. This feature may partly explain why $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ exhibits a higher pressure-induced enhancement of the Seebeck coefficient than the Te-rich compounds [45]. Briefly, the comparative Raman analysis demonstrates that selenium substitution simultaneously stiffens the lattice, raises the Lifshitz pressure, and favors the formation of complex stacking polytypes, whereas tellurium stabilizes a more compliant framework that collapses directly into dense cubic packing. These insights emphasize the utility of high-pressure phonon spectroscopy for mapping how chemical and external pressure cooperate to shape the structural and electronic landscape of the Bi–Te–Se thermoelectric materials.

In addition, it has been previously reported that within the compositional system of Bi_2Te_3 – Bi_2Se_3 , selenium atoms preferentially substitute at the central chalcogen layer of the quintuple-layer structure [11, 46]. More recently, Sun et al. [47] demonstrated that in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ thin films, selenium atoms tend to replace tellurium atoms at the middle chalcogen layer when $0 < x < 1$, whereas for $2 < x < 3$, the substitution preferentially occurs at the outer (top and bottom) chalcogen layers of the quintuple unit. Ren et al. [48] indicated that, due to the stronger bonding with Bi, the Se atoms trapped between two Bi atoms are less exposed to evaporation. As a result, the formation of Se vacancies is suppressed. Similarly, the antisite defects between Te and Bi are also expected to be suppressed because of preferable bonding between Se and Bi, in contrast to Se–Te bonding. The ordered nature thus minimizes the additional disorder that could be caused by Se/Te randomness [48]. Fig. 8 demonstrates the pressure dependence of interlayer distances of $\text{Bi}(\text{Se}_{0.9}+\text{Te}_{0.1})^{\text{II}}$, $\text{Bi}-\text{Te}^{\text{I}}$ and $\text{vdW Te}^{\text{I}} \dots \text{Te}^{\text{I}}$, obtained from GSAS Rietveld refinements. When compressed to $P \approx 2 \text{ GPa}$, the $\text{Bi}-\text{Te}^{\text{I}}$ spacing increases slightly, whereas the $\text{vdW Te}^{\text{I}}-\text{Te}^{\text{I}}$ layer contracts, whereas pressure being raised above $\sim 2 \text{ GPa}$ the trends diverge/reverse accordingly. Nevertheless, the same qualitative behavior is reproduced at 6 GPa and 12 GPa, indicating robust pressure sensitivity of the outer-layer separations, while the $\text{Bi}(\text{Se}_{0.9}+\text{Te}_{0.1})^{\text{II}}$ distance remains nearly invariant. The pressure-insensitive of the $\text{Bi}(\text{Se}_{0.9}+\text{Te}_{0.1})^{\text{II}}$ layer might process highest bonding energy with Bi and Se, indicating all of Se atoms are largely located on the center of the quintuple layer and tightly bond with the neighboring Bi atoms. The calculated layer distances

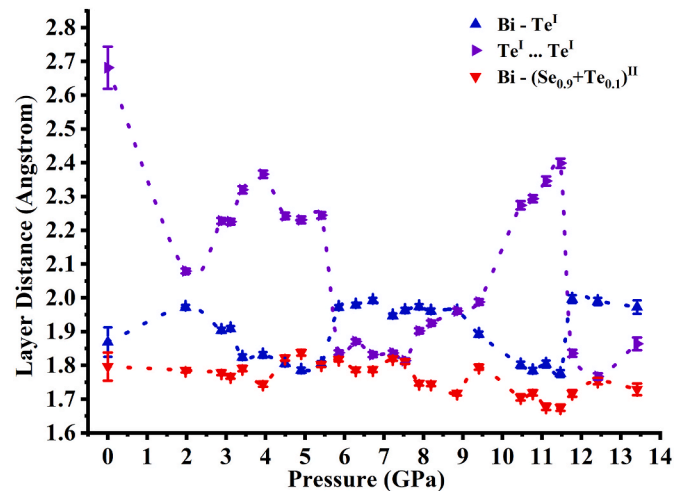


Fig. 8. Pressure dependence of interlayer distances in the quintuple layers and the van der Waals (vdW) gap. Symbols denote distinct interlayer metrics in the quintuple-layer stack: blue right-pointing triangles ($\text{Bi}-\text{Te}^{\text{I}}$), magenta left-pointing triangles with a dashed guide ($\text{vdW Te}^{\text{I}}-\text{Te}^{\text{I}}$), and red downward triangles ($\text{Bi}(\text{Se}_{0.9}+\text{Te}_{0.1})^{\text{II}}$).

versus pressure up to 14 GPa are summarized in Table S4. Consequently, in this study of $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$, this site-selective substitution implies that Se atoms are more likely to occupy the inter layers of the quintuple unit, thereby rendering its local structure and properties more akin to that of pristine Bi_2Te_3 . Alternatively, considering the larger atomic radius of tellurium (1.40 Å) compared to selenium (1.15 Å) [49], the preferential occupation of Se atoms at the central layer may introduce a significant degree of internal chemical pressure. This internal stress can be interpreted as an effective positive external pressure, leading the tensile field around the central chalcogen layers [50], which could elevate the critical pressure required to induce structural phase transitions in the alloyed system. Consistent with previous reports on Bi_2Te_3 – Bi_2Se_3 solid solutions, selenium atoms preferentially occupy the central chalcogen layer of the quintuple unit, whereas tellurium atoms favor the outer layers. This site-selective substitution modifies the internal chemical pressure and bonding hierarchy within the quintuple block, leading to anisotropic stress distribution that affects lattice compressibility and phase stability under external pressure. In the present study, this mechanism provides a natural explanation for the systematically elevated transition pressures observed in $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ relative to Se-rich counterparts, without altering the overall sequence of pressure-driven structural transformations. Accordingly, related interpretations that appeared earlier in the manuscript have been consolidated here to emphasize the essential physical mechanism and to avoid redundancy.

In summary, the pressure-induced structural, electronic, and vibrational evolution of $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ can be followed coherently through the combined synchrotron ADXRD, difference-Fourier mapping, and Raman-scattering data sets presented in Figs. 1–6. Together, they reveal a cascade of polymorphic transformations that is broadly analogous to that of other Bi–Te–Se solid solutions, yet shifted to systematically higher pressures as the Te content increases. $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ exhibits a canonical but chemistry-shifted sequence of pressure-driven transformations, governed by a Lifshitz transition at ~ 2.9 GPa and by progressive charge migration that first destabilizes the layered stacking and later promotes cation re-ordering. The systematic elevation of all transition pressures relative to Se-rich analogues provides a quantitative measure of the competing influences of chemical and external pressure on the stability of monoclinic intermediates. These findings furnish essential input parameters for modelling phonon transport and electronic structure in Bi–Te–Se thermoelectrics, and they illustrate how targeted alloying can be used to decouple electronic and structural instabilities, opening new avenues for high-pressure tuning of topological and thermoelectric performance.

4. Conclusions

In conclusion, the present high-pressure study unambiguously establishes that $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ follows the archetypal rhombohedral $\rightarrow$ monoclinic $\rightarrow$ cubic sequence observed in Bi–Te–Se solid solutions, but with every step shifted upward in pressure by roughly 2–6 GPa when compared with Se-rich counterparts [12]. Synchrotron ADXRD shows that a Lifshitz-type electronic-topological transition at 2.9 GPa softens the inter-layer breathing mode, priming the lattice for a first-order collapse of the van-der-Waals gap that nucleates the $C2/m$ phase at 14.5(2) GPa. Difference-Fourier maps reveal that this collapse is accompanied by charge transfer from Bi-6p to antibonding Te/Se states and, at higher pressures, into interstitial sites –an evolution that ultimately stabilizes the three-dimensionally connected $Im\bar{3}m$ framework above 31.4(4) GPa. Raman spectroscopy traces these events in real time, capturing the disappearance of rhombohedral modes, the birth of zone-edge monoclinic phonons, and the final quenching of first-order activity when centro-symmetry is attained. Comparison with $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ demonstrates that increasing Se content not only stiffens all rhombohedral phonons and raises the Lifshitz pressure but also opens a window for complex nine-/ten-layer stacking polytypes that are absent

in the Te-rich compound. The systematic chemical shift of transition pressures provides a quantitative gauge of how electronegativity and local bonding modulate the delicate balance between shear, tilt, and densification mechanisms in layered chalcogenides. These insights have three broad implications. First, because the rhombohedral $R\bar{3}m$ phase of $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$ remains intact up to $\approx 14.5(2)$ GPa, the elastic and vibrational benchmarks reported here can be fed directly into phonon-transport models to predict how the thermoelectric figure of merit evolves under device-level clamping stresses, confirming that flexible modules laminated below the sub-gigapascal regime will retain structural integrity and deliver reliable energy harvesting in wearable and soft-robotic applications. Second, they show that targeted alloying can be used to decouple electronic and structural instabilities, thereby creating pressure windows in which carrier concentration and band topology can be tuned without triggering irreversible lattice collapse, a prerequisite for device applications that exploit strain or hydrostatic pressure as an active control variable. Finally, we emphasize that the present study focuses on hydrostatic compression of bulk $\text{Bi}_2\text{Te}_{2.1}\text{Se}_{0.9}$, which certainly does not provide direct assessments on device-level performance under operational conditions. Nevertheless, the experimentally established pressure windows for the Lifshitz-type electronic-topological transition and the subsequent polymorphic transformations do provide quantitative constraints on how lattice strain and bonding topology evolve with compression. These benchmarks may motivate future investigations that combine controlled strain platforms (e.g., epitaxial biaxial strain or van der Waals heterostructure engineering) with first-principles calculations to evaluate whether similar electronic reconstructions can be achieved under realistic strain fields without triggering irreversible structural collapse. Accordingly, any implications for strain engineering or device optimization are presented here as a forward-looking perspective rather than a conclusion. The results outline a coherent framework for engineering the functional properties of topological and thermoelectric chalcogenides through the concerted action of chemical substitution and external pressure. Although our study focuses on hydrostatic compression in bulk crystals, the low-pressure ETT near 2.9 GPa suggests that modest lattice strain may be sufficient to tune the Fermi-surface topology in Bi_2Te_3 -derived alloys, motivating future investigations using controlled strain platforms and first-principles calculations.

CRedit authorship contribution statement

Yi-Jia Tsai: Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Sheng-Rui Jian:** Investigation. **Marin M. Gospodinov:** Resources. **Vera Marinova:** Resources. **Dimitre Z. Dimitrov:** Resources. **Dong-Zhou Zhang:** Resources, Methodology, Investigation. **Yu-Chun Chuang:** Resources, Methodology, Investigation. **Yang-Yuan Chen:** Supervision, Funding acquisition. **Min-Nan Ou:** Supervision, Resources, Methodology, Investigation, Funding acquisition. **Jenh-Yih Juang:** Supervision, Resources, Funding acquisition. **Chih-Ming Lin:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Conceptualization.

Potential competing interest

Authors declare no potential competing interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpcs.2026.113604>.

Data availability

Data reported in this research work are available upon request.

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