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**Jinggeng Zhao, Zhenhai Yu, Qingyang Hu, Yong Wang, John Schneeloch,
Chunyu Li, Ruidan Zhong, Yi Wang, Zhiguo Liu, and Genda Gu**

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Structural phase transitions of $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ compounds under high pressure and the influence of the atomic radius on the compression processes of tetradymites†

Zhao, Jinggeng;^{*‡ab} Yu, Zhenhai; ^{‡c} Hu, Qingyang ;^{cd} Wang, Yong;^b Schneeloch, John^e; Li, Chunyu,^c Zhong, Ruidan^e; Wang, Yi,^{ab} Liu, Zhiguo^{*b} and Genda Gu^e

^a*Natural Science Research Center, Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin 150080, China, E-mail: zhaojinggeng@163.com*

^b*Department of Physics, Harbin Institute of Technology, Harbin 150080, China, E-mail: liuzhiguo@hit.edu.cn*

^c*Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, China*

^d*Department of Geological Sciences, Stanford University, Stanford, CA 94305, United States*

^e*Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, NY 11973, United States*

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‡These authors contributed equally to this study and share first authorship.

Abstract

Recently, the A_2B_3 -type tetradymites develop into a hot topic in physical and material research fields, where the A and B atoms represent V and VI group elements, respectively. In this study, the *in situ* angle-dispersive X-ray diffraction measurements were performed on Bi_2Te_2Se , $BiSbTeSe_2$, and Sb_2Te_2Se tetradymites under high pressure. Bi_2Te_2Se transforms from a layered rhombohedral structure (phase I) into the 7-fold monoclinic (phase II) and body-centered tetragonal (phase IV) structures at about 7.97 and 14.3 GPa, respectively, without a similar 8-fold monoclinic structure (phase III) to Bi_2Te_3 . So the compression behavior of Bi_2Te_2Se is same as that of Bi_2Se_3 , which could also be obtained from the first-principle calculations and *in situ* high-pressure electrical resistance measurements. Under high pressure, $BiSbTeSe_2$ and Sb_2Te_2Se undergo the similar structural phase transitions to Bi_2Te_2Se , which indicates that the compression process of tellurides could be modulated by doping Se in Te site. According to the high-pressure researches of A_2B_3 -type tetradymites, the decrease of B-site atomic radius could shrink the stable pressure range of phase III and expand that of phase II, whereas the decrease of A-site atomic radius induces a different effect, i.e., expanding the stable pressure range of phase III and shrinking that of phase II. The influence of atomic radius on the compression process of tetradymites is closely related to the chemical composition and atom arrangement in the quintuple layer.

1. Introduction

The A_2B_3 -type ($A = \text{Bi, Sb}$; $B = \text{Te, Se}$) tetradymites Bi_2Te_3 , Sb_2Te_3 , and Bi_2Se_3 , which are composed of the V and VI group elements, could be used as the simplest three-dimensional topological insulators.^{1,2} At ambient conditions, they adopt a 6-fold rhombohedral (CN6R) structure (phase I or α ; space group $R\bar{3}m$),^{3,4} in which three quintuple layers stack along the c -axis (or body diagonal) in one unit cell. Here, CN and R represent coordinated number of A-site atom and crystal system type, respectively, similarly hereinafter. Pressure plays an important role in modulating the structure and physical properties of these compounds. Upon compression, Bi_2Te_3 , Sb_2Te_3 , and Bi_2Se_3 transform into a 7-fold monoclinic (CN7M) structure (phase II or β ; space group $C2/m$).^{5–20} Under higher pressures, Bi_2Te_3 and Sb_2Te_3 transform into an 8-fold monoclinic (CN8M) structure (phase III or γ ; space group $C2/c$) and further into a disordered body-centered cubic (BCC) structure (phase IV or δ ; space group $Im\bar{3}m$).^{5–15} In the calculated works, an ordered 9/10-fold monoclinic (CN9M) model with a space group $C2/m$ was set as an indication of the disordered BCC structure.^{5,11} Although adopting the same structure as Bi_2Te_3 at ambient conditions, Bi_2Se_3 directly transforms into a body-centered tetragonal (BCT) structure (space group $I4/mmm$) upon compression,^{16,18} without the similar phase III to the isostructural tellurides. Here, the BCT structure of Bi_2Se_3 is also denoted as phase IV, in order to compare it with Bi_2Te_3 . The other groups thought that Bi_2Se_3 should adopt a CN9M or BCC structure after phase III.^{17,19} Pressure could also modulate the physical properties of these compounds. Upon compression, Bi_2Te_3 and Sb_2Te_3 behave superconductivity at low temperature and still adopt the primal rhombohedral structure.^{21–25} So they transform into a topological superconductor under high pressure, with an electronic topological transition (ETT).^{5–15} Bi_2Se_3 could also become a superconductor upon compression and has transformed into the CN7M structure before the critical pressure, which shows it is not a topological superconductor.^{26,27} According to the abovementioned discussions, the evolutions of structural and physical properties upon compression of Bi_2Se_3 are different from those of its sister compound Bi_2Te_3 . The another member of these A_2B_3 -type compounds, Sb_2Se_3 , transforms into a disordered BCC structure (phase IV) from the original orthorhombic bismuthinite-type structure (phase I or α ; space group $Pnma$)²⁸ and behaves low-temperature superconductivity under high pressure.²⁹ The schematic views of the crystal structures of A_2B_3 -type tellurides and selenides under high pressure are summarized in the ESI, Fig. S1†.

With the developments of Bi_2Te_3 , Sb_2Te_3 , and Bi_2Se_3 , the investigations of the intermediate $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ compounds become a hot topic in physical and material research fields. At ambient conditions, $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ adopt the tetradymite-type or bismuthinite-type structures,^{3,4,30,31} with space groups of $R\bar{3}m$ and $Pnma$, respectively, in which the formers are also topological insulators.^{32–37} Recently, lots of novel physical phenomena have been observed in $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ tetradymites, such as the quantum anomalous Hall (QAH) effect in Cr-doped

(Bi/Sb)₂Te₃ thin films,³⁵ high bulk resistivities in Bi_{2+x}Te_{2-x}Se,³⁶ and ultraviolet and visible range plasmonics in Bi_{1.5}Sb_{0.5}Te_{1.8}Se_{1.2}.³⁷ Pressure could also modulate the structural and physical properties of (Bi_{1-x}Sb_x)₂(Te_{1-y}Se_y)₃ tetradymites. According to the optical properties measurements at high pressure and room temperature, the bulk optical gap (E_g) of Bi₂Te₂Se is suppressed by pressure.³⁸ Pressure could enhance the thermoelectric power factor of (Bi_{1-x}Sb_x)₂(Te_{1-y}Se_y)₃,^{39,40} which is similar to that in Bi₂Te₃. Under high pressure, Bi₂Te₂Se behaves a different pressure dependence of structure evolution from Bi₂Te₃,⁴¹ which shows that the doping of Se in Te site influences the compression process of tellurides. Therefore, considering the importance of (Bi_{1-x}Sb_x)₂(Te_{1-y}Se_y)₃ tetradymites and different compression behavior between tellurides and selenides, it is necessary to further perform high-pressure investigations of these compounds, which could significantly improve our understanding of structure and physical properties evolutions in the compression process of tetradymites.

In this work, we performed the *in situ* high-pressure angle-dispersive synchrotron X-ray diffraction (AD-XRD) experiments on Bi₂Te₂Se, BiSbTeSe₂, and Sb₂Te₂Se with a diamond anvil cell (DAC) technique, including the first-principle calculations and *in situ* high-pressure electrical resistance measurements on Bi₂Te₂Se, and discovered the pressure-induced structural transitions in these compounds. By summarizing the high-pressure researches of A₂B₃-type tellurides and selenides in this work and references, the influence of atomic radius on structural phase transitions for tetradymites upon compression are discussed in this paper.

2. Experimental and computational methods

2.1 High-pressure AD-XRD measurements

The *in situ* high-pressure AD-XRD measurements on these samples were performed using a monochromatic X-ray beam at room temperature at the X17C beamline of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), and the BL15U1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The symmetric DACs were used in the AD-XRD experiments, in which the diameter of the flat culets in the diamonds was equal to 500 μm. A T301 stainless steel gasket was preindented to about 45 μm thickness and then drilled a hole as the sample chamber with a diameter of 160 μm. The Bi₂Te₂Se, BiSbTeSe₂, and Sb₂Te₂Se single crystals were grown by a unidirectional solidification method with slow cooling down. In the high-pressure experiments, the single crystals were ground for about 1 h in order to obtain a fine powder sample. Then the samples were prepressed to a pellet with thickness of about 15 μm and loaded into the sample chamber. The ruby fluorescence method was used to measure the pressure around the sample in the chamber.⁴² Silicone oil was used as the pressure-transmitting medium, which could ensure a quasi-hydrostatic pressure environment around the sample.^{43–45} Two-dimensional diffraction patterns were collected on a charge-coupled device (CCD) detector.

The CeO₂ standard was used to calibrate the orientation parameters of the detector and the distance between sample and detector. The recorded images were integrated by using the program Fit2D.⁴⁶ The high-pressure XRD patterns were refined by using the Rietveld methods^{47,48} with the General Structure Analysis System (GSAS) program package.⁴⁹ The PowderCell program package was also used in analyzing crystal structure.⁵⁰

2.2 First-principle calculations

The first-principle calculations for Bi₂Te₂Se were carried out in the framework of density functional theory (DFT) with the Vienna *ab initio* simulation package (VASP) code.⁵¹ The Perdew-Wang generalized gradient approximation (GGA) was implemented to describe the exchange correlation functions.⁵² The projector augmented wave (PAW) potentials^{53,54} were used with 5, 6, and 6 valence electrons for Bi (6s²6p³), Te (5s²5p⁴), and Se (4s²4p⁴), respectively. Sets of 7×7×1, 4×10×3, 5×7×5, 10×10×2, and 4×12×10 Monkhorst-Pack *k* point meshes⁵⁵ were employed for CN6R, CN7M, CN8M, BCT, and CN9M structures, respectively. A plane-wave basis set with the kinetic energy cutoff of 350 eV was found sufficient to achieve total energy convergence a total energy less than 10⁻⁶ eV/cell and force acting on each atom less than 0.01 eV/Å.

2.3 High-pressure electrical resistance measurements

The pressure dependences of electrical resistance for Bi₂Te₂Se were measured by using the standard four electrodes method in a DAC, in which the diameter of the flat culets in the diamonds was 400 μm. Pressure in chamber was determined by the ruby fluorescence method.⁴² A T301 stainless steel gasket was preindented to 40 μm thickness and the center of gasket on culet was removed by laser to form a hole of 150 μm in diameter. The fine cubic boron nitride (cBN) powder was used to cover the gasket as an insulating layer and the rest part of the gasket was covered by the insulating gel. The Bi₂Te₂Se powder sample was loaded into this chamber without the pressure-transmitting medium. Slim platinum wires were used as electrodes, which were set up on one side of the diamond anvil.

3. Results and discussion

3.1 Structural phase transitions of Bi₂Te₂Se under high pressure

Fig. 1 illustrates the representative XRD patterns of Bi₂Te₂Se up to 36.3 GPa at room temperature. In the experimental pressure range, two structural phase transitions were found. Bi₂Te₂Se transforms into a CN7M structure (phase II) at about 7.97 GPa, which is approximately equal to the transition pressure in Bi₂Te₃.⁵⁻¹⁰ The transition to phase II is completed at about 11.1 GPa. According to the XRD data, Bi₂Te₂Se becomes a BCC-like structure above about 14.3 GPa, without any obvious evidence of the CN8M structure in the experimental pressure range. So the structure evolution of Bi₂Te₂Se upon compression is not same as that of Bi₂Te₃⁵⁻¹⁰ and is more similar to that of Bi₂Se₃.^{16,18,27} In order to compare conveniently the structure evolutions upon compression with

Bi_2Te_3 , this BCC-like structure of $\text{Bi}_2\text{Te}_2\text{Se}$ is also denoted as phase IV. Above about 26.1 GPa, $\text{Bi}_2\text{Te}_2\text{Se}$ completely transforms into phase IV.

Fig. 1 Selected AD-XRD patterns of $\text{Bi}_2\text{Te}_2\text{Se}$ at room temperature up to 36.3 GPa.

For phase IV of Bi_2Te_3 and Bi_2Se_3 , the possible crystal structures are BCT, CN9M, and BCC models,^{5–10,16–20} which could also be the candidates of high-pressure phase IV of $\text{Bi}_2\text{Te}_2\text{Se}$. In order to confirm the crystal structure of phase IV of $\text{Bi}_2\text{Te}_2\text{Se}$, the XRD patterns are refined by using the Rietveld methods with the GSAS program package. Fig. 2 shows the experimental and fitted XRD patterns of phase IV at 30.9 GPa, which are simulated by using these three structures, with the R_{wp} factor of 1.69%, 2.96%, and 4.80%, respectively, and the corresponding lattice parameters and atomic coordinates are listed in the ESI, Table S1†. According to the refinement results in Fig. 2, it is reasonable for $\text{Bi}_2\text{Te}_2\text{Se}$ to adopt the BCT structure as phase IV under high pressure. The weak peaks with low Q values in phase IV, which could be observed in previous results,⁴¹ seem to disappear in this work. It is possible for the weak peaks to be not obvious upon compression when the intensity of X-ray is not high enough. On the other hand, the approximate X-ray scattering factor between Bi and Te atoms upon compression may also weaken the intensity of these peaks to the ordered BCT structure of $\text{Bi}_2\text{Te}_2\text{Se}$.

Fig. 2 Experimental (open circle) and fitted (line) XRD patterns for phases IV of $\text{Bi}_2\text{Te}_2\text{Se}$ at 30.9 GPa, which are simulated by using the BCT, CN9M, and BCC structures. The vertical lines denote the theoretical positions of the Bragg peaks. The difference curves between observed and calculated XRD patterns are shown at the bottom.

Fig. 3a shows the enthalpy differences (relative to phase I) per $\text{Bi}_2\text{Te}_2\text{Se}$ chemical formula ($\Delta H/\text{f.u.}$) under high pressure. The CN6R, CN7M, and CN8M structures are used as Phases I, II, and III, respectively. The calculated lattice parameters and atomic coordinates are listed in the ESI, Table S2[†]. According to the calculated results, phase I transforms into phase II and IV at about 13 and 18 GPa, respectively, without phase III due to its higher enthalpy, which confirms the aforementioned experimental results. For phase IV, two possible structures of BCT and CN9M models are used in the first-principle calculations. From Fig. 3a, the enthalpies of these two structures are comparable with each other around the transition pressure in the calculated accuracy range. The CN9M is predicted to form between 18 and 40 GPa, however, not clearly distinguished from experiment in Fig. 2. The refined XRD pattern at 30.9 GPa prefers a BCT structure as phase IV rather than the CN9M model. The minor enthalpy difference is likely to be neglected by the aid of temperature effects. As shown in the inset, the enthalpy of BCT structure is becoming smaller than that of CN9M structure beyond 40 GPa, which supports that the former is a stable phase for $\text{Bi}_2\text{Te}_2\text{Se}$ under high pressure.

Fig. 3 (a) Enthalpy differences (relative to phase I) versus pressure for the possible crystal structures of $\text{Bi}_2\text{Te}_2\text{Se}$ upon compression. Phases I–III represent the CN6R, CN7M, and CN8M structures, respectively. The inset shows a zoom-out of 25–50 GPa for the BCT and CN9M models. (b) Experimental pressure dependences of volume per $\text{Bi}_2\text{Te}_2\text{Se}$ chemical formula (V/f.u.). The bold lines represent the fitting results to the experimental data by using the second-order Birch-Murnaghan equation of state (BM-EoS). The inset shows the relationships of lattice parameters versus pressure for phase I.

Fig. 3b shows the pressure dependences of volume per $\text{Bi}_2\text{Te}_2\text{Se}$ chemical formula (V/f.u.) up to 36.3 GPa. The number of f.u. in one unit cell is equal to 3, 4, and 2 for phases I, II, and IV, respectively. The volume decreases with increasing pressure for these phases of $\text{Bi}_2\text{Te}_2\text{Se}$, with a 3.3% and 5.1% collapsing for the transitions of I–II and II–IV, respectively. The black bold lines represent the fitting results to experimental V - P relationships by using the Birch-Murnaghan equation of state (BM-EoS).⁵⁶ By fixing the first-order pressure derivative $B'_0 = 4$, the ambient pressure isothermal bulk modulus B_0 is estimated as 50.5(1.6), 62(2) and 104(4) GPa for phases I, II, and IV, respectively. The fitted ambient unit cell volume (V_0 /f.u.) is equal to 157.0(4), 149.1(5), and 133.2(7) $\text{\AA}^3$ for these three phases, respectively. The inset of Fig. 3 shows the pressure dependences of lattice parameters for phase I of $\text{Bi}_2\text{Te}_2\text{Se}$ in the pressure range of 0–8 GPa, which indicates that both a - and c -axis shrink with increasing pressure.

The schematic views of the crystal structures of phases I, II, and IV of $\text{Bi}_2\text{Te}_2\text{Se}$ are shown in Fig. 4. The bottom lattices plot the atom array of one Bi-, Te-, or Se-layer, viewing along the vertical direction of layers, i.e., the [001], [101], and [001] directions for these three phases, respectively. As above discussions, the compression process of $\text{Bi}_2\text{Te}_2\text{Se}$ is same as that of Bi_2Se_3 . With increasing pressure, the stacking sequence of *Te-Bi-Se-Bi-Te* quintuple layer along the vertical direction of layers does not change. However, in one atom layer, the atoms occupy the triangle, alternate triangle and rectangle, and square lattices for phases I, II, and IV, respectively. Therefore, the evolution of atom array in one layer is the main change in the compression process of $\text{Bi}_2\text{Te}_2\text{Se}$. The CN of Bi atom is equal to 6, 7, and 8 for these three phases, respectively, and increases with pressure, due to the shift of atoms in one layer, which is similar to that in Bi_2Se_3 .¹⁶

Fig. 4 Schematic views of the crystal structures for phases I, II, and IV of $\text{Bi}_2\text{Te}_2\text{Se}$ under high pressure, i.e., the CN6R, CN7M, and BCT models. The yellow, red, and orange globes represent the Bi, Te, and Se atoms, respectively. The bottom lattices with purple globes show the atom array of one Bi-, Te-, or Se-layer, viewing along the [001], [101], and [001] directions, respectively.

3.2 Pressure dependence of electrical resistance for $\text{Bi}_2\text{Te}_2\text{Se}$

The *in situ* high-pressure electrical resistance measurements of $\text{Bi}_2\text{Te}_2\text{Se}$ were performed up to 30.1 GPa, in order to obtain the relationship of electrical properties and structural phase transitions. The pressure dependence of logarithm resistance is shown in Fig. 5, in which the black bold lines are guided for the eyes. The electrical resistance drops sharply before about 8.2 GPa and then the logarithm value exhibits an inflection point from this pressure, which may be induced by the transition from phase I into II. When pressure is larger than about 14.3 GPa, the electrical resistance begins to increase slightly, which may be related to the transition from phase II into IV. So the two inflection points in the *R-P* curve of $\text{Bi}_2\text{Te}_2\text{Se}$ reveal the critical pressures of structural phase

transitions upon compression. The pressure dependence of axial ratio of c/a for phase I below 8 GPa is plotted in the inset of Fig. 5. The obvious turning point at about 3.5 GPa reveals an ETT, which could also be found in the previous researches of $\text{Bi}_2\text{Te}_2\text{Se}$,⁴¹ Bi_2Te_3 ,⁷⁻⁹ and Bi_2Se_3 .^{16,19,22} At this pressure, the electrical resistance behaves a slight inflection point, as shown in the inset, corresponding to this ETT. The R - P relationship for phase I of $\text{Bi}_2\text{Te}_2\text{Se}$ is similar to that of Bi_2Te_3 ,^{57,58} in other word, electrical resistance decreases with increasing pressure. But it is different from that of Bi_2Se_3 ,⁵⁹ in which electrical resistance increases with pressure before the ETT at about 5 GPa and then decreases under higher pressures. Therefore, although the compression process of $\text{Bi}_2\text{Te}_2\text{Se}$ behaves a similarity to that of Bi_2Se_3 , its electrical property in the phase I range is close to that of Bi_2Te_3 . As abovementioned discussions, Bi_2Te_3 transforms into a topological superconductor at the critical pressure of ETT.²¹⁻²³ Considering the similar R - P relationship and ETT to Bi_2Te_3 in the phase I range, $\text{Bi}_2\text{Te}_2\text{Se}$ may also behave topological superconductivity at low temperature, which needs further *in situ* electrical resistance measurements at high pressure and low temperature to examine this possibility.

Fig. 5 Pressure dependence of logarithm resistance of $\text{Bi}_2\text{Te}_2\text{Se}$. The black bold lines are guided for the eyes. The inset shows the pressure dependences of c/a and logarithm resistance for phase I.

3.3 Structural phase transitions of BiSbTeSe_2 and $\text{Sb}_2\text{Te}_2\text{Se}$ under high pressure

In order to explore the structural evolutions of $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ tetradymites upon compression, the *in situ* high-pressure AD-XRD experiments on BiSbTeSe_2 and $\text{Sb}_2\text{Te}_2\text{Se}$ were also performed up to 38.5 and 37.5 GPa, respectively, as shown in the ESI, Fig. S2†. Under high pressure, BiSbTeSe_2 and $\text{Sb}_2\text{Te}_2\text{Se}$ transform into phase II at about 9.23 and 12.1 GPa, respectively, and phase IV at about 25.8 and 16.7 GPa, respectively, which are similar to the compression process of $\text{Bi}_2\text{Te}_2\text{Se}$. Fig. 6 shows the relationships of $V/\text{f.u.}$ versus pressure of BiSbTeSe_2 and $\text{Sb}_2\text{Te}_2\text{Se}$. For these two compounds, volumes decrease with increasing pressure. The bold lines represent the fitted results to V - P relationships by using the second-order BM-EoS. The B_0 is estimated as 46.5(7),

55(1), and 63(5) GPa for phases I, II, and IV of BiSbTeSe₂, respectively. For Sb₂Te₂Se, the corresponding B_0 is equal to 44(2), 60(4), and 73(4) GPa, respectively. The selected V - P data of the undoped A₂B₃-type tellurides and selenides are also plotted in Fig. 6,^{5,12,18,28} with the thin lines guided for the eyes. The unit cell volumes of BiSbTeSe₂ and Sb₂Te₂Se are intermediate among those of Bi₂Te₃, Sb₂Te₃, Bi₂Se₃, and Sb₂Se₃ in the experimental pressure range.

Fig. 6 Pressure dependences of volume per chemical formula ($V/f.u.$) of BiSbTeSe₂ and Sb₂Te₂Se. The bold lines represent the fitting results to experimental data by using the second-order BM-EoS. The selected V - P data of Bi₂Te₃, Sb₂Te₃, Bi₂Se₃, and Sb₂Se₃ in references are also plotted.^{5,12,18,28} The thin lines in these data are guided for the eyes.

3.4 Summarization of high-pressure works on A₂B₃-type tellurides and selenides

Fig. 7 shows the experimental phase diagrams of structure evolutions upon compression for Bi₂Te₂Se, BiSbTeSe₂, and Sb₂Te₂Se tetradymites in this work, as well as plotting those for Bi₂Te₃,^{5-8,22} Bi₂Se₃,^{16-18,27} Sb₂Te₃,^{11-14,25} and Sb₂Se₃.^{28,29} The right edges of bars indicate the maximum pressures in the experimental measurements. In this figure and following Fig. 8, phase IV represents a BCC-like structure, with the BCC, BCT, or CN9M models for different compounds obtained from different research groups. The fitted B_0 , B'_0 , and $V_0/f.u.$ of phases I–IV for A₂B₃-type (A = Bi, Sb; B = Te, Se) compounds in this work and references are summarized in the ESI, Table S3†, including experimental and calculated values.^{7-16,19,20,28,41} The results of Bi₂Te₂Se, BiSbTeSe₂, and Sb₂Te₂Se in this work could be comparable with those of Bi₂Te₃, Bi₂Se₃, and Sb₂Te₃ in references. The compression processes of Bi₂Te₃ obtained from different groups are consistent with each other,^{5-8,22} and a similar case exists in Sb₂Te₃.^{11-14,25} However, a divergence could be found in the experimental results of Bi₂Se₃.^{16-18,27} In Ref. 17,19, the authors thought that Bi₂Se₃ transforms from phase II into III under high pressure and further into a CN9M or BCC structure. But, according to the relationships of enthalpy difference versus pressure,¹⁷ phase III should not exist in the compression process of Bi₂Se₃. The high-pressure experimental results in Ref. 18 confirmed that

Bi_2Se_3 transforms from phase II into a BCT structure as phase IV. Recently, the high-pressure XRD measurements on $\text{Sr}_{0.065}\text{Bi}_2\text{Se}_3$ in Ref. 60 indicate that its structural phase transitions upon compression are very similar to those of Bi_2Se_3 in Ref. 16,18. So the transition sequence from phase I across II into IV is reasonable for Bi_2Se_3 under high pressure, without a similar phase III to Bi_2Te_3 . According to this work, $\text{Bi}_2\text{Te}_2\text{Se}$, BiSbTeSe_2 , and $\text{Sb}_2\text{Te}_2\text{Se}$ undergo a similar compression behavior to that of Bi_2Se_3 . Although the compression processes of Bi_2Se_3 and $(\text{Bi}_{1-x}\text{Sb}_x)_2(\text{Te}_{1-y}\text{Se}_y)_3$ tetradymites are not wholly same as those of Bi_2Te_3 and Sb_2Te_3 , all of them transform into a BCC-like phase under high pressure.^{5–20} The Sb_2Se_3 bismuthinite could also become a disordered BCC structure above 51 GPa,²⁸ and its isostructural sulfides Bi_2S_3 and Sb_2S_3 behave an amorphous state upon compression, without a BCC-like structure in the experimental pressure range.^{61–63} The high-pressure phases of other Bi-Te alloys, i.e., Bi_2Te , Bi_4Te_5 , BiTe , and Bi_4Te_3 , adopt also the disordered BCC structure.⁶⁴ Therefore, it is possible for these tellurides and selenides to transform into the BCC-like structure if the pressure is high enough.

Fig. 7 Experimental phase diagrams of compression processes for $\text{Bi}_2\text{Te}_2\text{Se}$, BiSbTeSe_2 , and $\text{Sb}_2\text{Te}_2\text{Se}$ in this work, and Bi_2Te_3 , Bi_2Se_3 , Sb_2Te_3 , and Sb_2Se_3 in references.^{5–8,11–14,16–18,22,25,27–29}

Phase IV represents the BCC-like structure of the BCC, CN9M, or BCT models for different compounds. The right edges of bars indicate the maximum pressures in the experiments.

3.5 Influence of atomic radius on structural phase transitions for tetradymites

Generally, the change of atomic or ionic radius could influence the compression processes of the similar compounds, for example, the ambient structure and phase transitions under high pressure of fluoride compounds AF_2 ($A = \text{Ca, Sr, Ba, Pb, Cd, Pd, Mn, Zn, and Mg}$) are closely related to the radius of A-site cations.⁶⁵ From the structural evolutions of Bi_2Te_3 , $\text{Bi}_2\text{Te}_2\text{Se}$, and Bi_2Se_3 under high pressure, the doping of Se could modulate the compression behavior of Bi_2Te_3 . On the other hand, the change of A-site atom could also influence the structural phase transitions of tetradymites upon compression. As a sister compound, the structure evolutions of As_2Te_3 under high pressure are helpful for understanding those of Bi_2Te_3 and Sb_2Te_3 , since it possesses the similar chemical composition to the latters. As_2Te_3 crystallizes into a stable 6-fold monoclinic structure (phase α ; space group $C2/m$) at ambient conditions⁶⁶ or a metastable CN6R structure (phase β) by quenching the melted sample.⁶⁷ Under high pressure, $\alpha\text{-As}_2\text{Te}_3$ transforms into a CN8M structure (phase γ)⁶⁸ that is same as phase III of Bi_2Te_3 and Sb_2Te_3 . According to the enthalpy-pressure relationships, $\beta\text{-As}_2\text{Te}_3$ could also become phase γ upon compression, without a similar CN7M structure to Bi_2Te_3 and Sb_2Te_3 .⁶⁸

In order to view the influence of atomic radius on compression process for tetradymites, Fig. 8 shows the relationships of phase stability range and radius of A- or B-site atoms obtained from experimental and calculated results for $\text{Bi}_2\text{Te}_2\text{Se}$ (this work), Bi_2Te_3 ,⁵ Sb_2Te_3 ,¹¹ Bi_2Se_3 ,¹⁷ and $\beta\text{-As}_2\text{Te}_3$,⁶⁸ in which the edges between two neighbor phases are estimated. For these compounds, the atoms within a quintuple layer connect by a dominant covalent bonding with ionic type, while the interaction between two neighbor quintuple layers is of the Van der Waals type.^{69,70} It is difficult to obtain the actual radius of these elements in tetradymites because of the complex bonding types. So the atomic radius used in Fig. 8 will not deviate from the conclusion. The atomic radii of Bi, Sb, As, Te, and Se are equal to 1.60, 1.45, 1.15, 1.40, and 1.15 Å, respectively.⁷¹ Phases β and γ of As_2Te_3 in Fig. 8 are denoted as I and III, respectively, since they are similar to those of other tellurides and selenides. In Fig. 8a, the experimental transition pressure into phase III of $\alpha\text{-As}_2\text{Te}_3$ is used to substitute for that of phase β , because the calculated value in Ref. 68 is close to the latter and there is no corresponding experimental data of $\beta\text{-As}_2\text{Te}_3$ under high pressure up to now. For these compounds, phase III with a CN8M structure is stabilized in a small pressure range in Bi_2Te_3 but could not form in Bi_2Se_3 and $\text{Bi}_2\text{Te}_2\text{Se}$. Consequently, the decrease of B-site atomic radius by doping of Se in Te site changes the structure evolutions of Bi_2Te_3 upon compression, i.e., shrinking the stable pressure range of phase III and expanding that of phase II. According to Fig. 8a, the pressure range of phase III in Sb_2Te_3 is wider than that in Bi_2Te_3 and the range of phase II in the former is narrower than that in the latter. Phase III coexists with phase II or IV in Bi_2Te_3 , but can solely exist in the compression process of Sb_2Te_3 . In As_2Te_3 , phase III exists to at least 50.4 GPa. From the compression processes of Bi_2Te_3 , Sb_2Te_3 , and As_2Te_3 , the decrease of A-site atomic

radius expands the stable pressure range of phase III and shrinks that of phase II, which is different from the influence of B-site atom. Fig. 8b obtained from the calculated data presents a similar sight to the experimental results in Fig. 8a. In the term of energy, the shrinkage of A-site atomic radius increases the enthalpy of phase II and induces its vanish in the compression process of As_2Te_3 .⁶⁸ On the other hand, the decrease of B-site atomic radius increases the enthalpy of phase III, e.g., in Bi_2Se_3 ,¹⁷ $\text{Bi}_2\text{Te}_2\text{Se}$ (this work). Therefore, the influence of A- and B-site atomic radii on structural phase transitions of tetradymites under high pressure is different from each other. The compression processes of BiSbTeSe_2 and $\text{Sb}_2\text{Te}_2\text{Se}$ are similar to that of $\text{Bi}_2\text{Te}_2\text{Se}$, which indicates that the influence of B-site atom on the structural evolution of tetradymites under high pressure is more remarkable than that of A-site atom.

Fig. 8 Relationships of phase stability range and radius of A- or B-site atoms for tetradymites obtained from (a) experimental and (b) calculated results in this work and references.^{5,11,18,68} The edges between two neighbor phases are estimated. The atomic radii of Bi, Sb, As, Te, and Se are obtained from Ref. 71. Phases β and γ of As_2Te_3 are denoted as I and III, respectively.

In the local quintuple layer of tetradymite, the arrangement of atoms is similar to that in the face centered cubic (FCC) rock salt (NaCl-type, B1; space group $Fm-3m$). The schematic views of their crystal structures along the body diagonal direction are shown in the ESI, Fig. S3a†. Considering

the similarity in the local structures, the compression processes of rock salt could be a reference to tetradymite. Under high pressure, the B1 structure transforms into a CsCl-type structure (B2, space group $Pm-3m$), with or without an intermediate phase.⁷²⁻⁷⁵ The intermediate phases between B2 and B1 phases are different from each other for these materials, depending on the chemical composition. Actually, the high-pressure BCC-like structure (phase IV) of tetradymite is similar to the B2 structure, since the CsCl-like structure units could be found in the local structure of BCT or CN9M models, as shown in the ESI, Fig. S3b†. The CN7M and CN8M structures can be regarded as two intermediate phases between the BCC-like and ambient phases. In other word, tetradymite behaves a similar structural evolution to rock salt upon compression. So the pressure ranges of CN7M and CN8M structures in tetradymite should be also related to the chemical composition for different compounds, which is like that in rock salt.⁷² Comparing with the rock salt, the novel quintuple layer in tetradymite induces that its compression process is also complex.

The *B-A-B'-A-B* quintuple layer is an important structural unit to tetradymites, in which A, B, and B' atoms occupy the inner, outer, and central layers, respectively. The progression of one quintuple layer in the tetradymite series are plotted in the ESI, Fig. S4†, including As_2Te_3 , $AsSbTe_3$, Sb_2Te_3 , Bi_2Te_3 , Bi_2Te_2Se , Bi_2TeSe_2 , and Bi_2Se_3 . When doping Se in Bi_2Te_3 , the Se atoms strongly prefer the central layer, which induces that Se and Te atoms are ordered in Bi_2Te_2Se .⁷⁶ With further doping, the extra Se atoms occupy the outer layer, forming a disordered solid solution of Te and Se atoms in the surface of quintuple layer. Doping of S in Bi_2Te_3 causes a similar atom occupation to that of Se.^{76,77} On the other hand, doping of Sb in Bi_2Te_3 will induce that Sb and Bi atoms are disordered in the inner layer.^{30,31} The As and Sb atoms should also be disordered in the inner layer of $AsSbTe_3$ tetradymite, since the similar case exists in $AsSbS_3$.⁷⁸ So decrease of atomic radius in A- and B-site induces the different atom arrangements in tetradymites. The stability of quintuple layer is related to the radius of A- and B-site atoms and external pressure. For Bi_2Te_3 , when doping atoms with smaller radius in B-site, the layered structure tends to be more stable and could keep upon compression, which expands the stable pressure range of phase II. On the contrary, when doping atoms with smaller radius in A-site, the layered structure tends to be unstable and may distort upon compression, which shrinks the stable pressure range of phase II. Comparing with phase II, no obvious layered structure could be found in the crystal lattice of phase III, which indicates that the atom arrangement in the latter tends to be relatively disordered in the term of atom layer. The unstable layered structure easily decomposes under high pressure, which induces the larger range of phase III. Therefore, the structural phase transitions of tetradymites under high pressure depend closely on the chemical composition and atom arrangement of the quintuple layer. The changes of A- and B-site atomic radius influence the compression processes of tetradymites in different structure evolution patterns. The further high-pressure investigations on these compounds using advanced experimental and calculated methods are help for testing this hypothesis.

4. Conclusions

In summary, two crystal structural phase transitions in $\text{Bi}_2\text{Te}_2\text{Se}$ tetradymite at high pressure and room temperature were discovered by performing the *in situ* high-pressure X-ray diffraction experiments, the first-principle calculations, and the *in situ* high-pressure electrical resistance measurements. BiSbTeSe_2 and $\text{Sb}_2\text{Te}_2\text{Se}$ undergo the similar structural phase transitions upon compression to $\text{Bi}_2\text{Te}_2\text{Se}$. Based on the present high-pressure researches of A_2B_3 -type tetradymites, the change of atomic radius of A- and B-site atoms could induce the different compression processes, due to their different positions in the quintuple layer. This summarization to the high-pressure investigations of tetradymites will be helpful for understanding the universal structure evolution patterns of materials under high pressure.

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