

Pressure-Induced Topological and Structural Phase Transitions in an Antiferromagnetic Topological Insulator *

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Recently, natural van der Waals heterostructures of $(\text{MnBi}_2\text{Te}_4)_m$ have been theoretically predicted and experimentally shown to host tunable magnetic properties and topologically non-trivial surface states. We systematically investigate both the structural and electronic responses of MnBi_2Te_4 and MnBi_4Te_7 to external pressure. In addition to the suppression of antiferromagnetic order, MnBi_2Te_4 is found to undergo a metal–semiconductor–metal transition upon compression. The resistivity of MnBi_4Te_7 changes dramatically under high pressure and a non-monotonic evolution of $\rho(T)$ is observed. The nontrivial topology is proved to persist before the structural phase transition observed in the high-pressure regime. We find that the bulk and surface states respond differently to pressure, which is consistent with the non-monotonic change of the resistivity. Interestingly, a pressure-induced amorphous state is observed in MnBi_2Te_4 , while two high-pressure phase transitions are revealed in MnBi_4Te_7 . Our combined theoretical and experimental research establishes MnBi_2Te_4 and MnBi_4Te_7 as highly tunable magnetic topological insulators, in which phase transitions and new ground states emerge upon compression.

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Magnetic topological insulators (MTIs), possessing both magnetic and topological properties, provide a promising material platform for the realization of exotic topological quantum phenomena, such as the quantum anomalous Hall (QAH) effect, axion insulator states, the proximity effect and Majorana modes.^[1–6] Thereinto the QAH effect has been observed experimentally in magnetically doped topological insulator (TI) thin films,^[7] while the fabrication of homogeneous thin films has long been limited by deposition techniques, hindering extensive studies of the unique material systems. Hence,

intrinsic MTIs with homogeneous magnetic and electronic properties are desired and can provide new opportunities to study novel topological quantum phenomena.

Recently, intrinsic MTIs of $(\text{MnBi}_2\text{Te}_4)_m(\text{Bi}_2\text{Te}_3)_n$ has been theoretically predicted and experimentally synthesized to have tunable magnetic properties and topologically nontrivial surface states.^[11–23] As shown in Fig. 1, $(\text{MnBi}_2\text{Te}_4)_m(\text{Bi}_2\text{Te}_3)_n$ crystallizes in a van der Waals layered structure, sharing a similar crystal structure with Bi_2Te_3 ,^[8] a typical TI under ambient conditions. Crystallizing in a rhombohedral structure with space group $R\bar{3}m$, $\text{MnBi}_2\text{Te}_4(m = 1, n = 0)$ consists of Te-Bi-Te-Mn-Te-Bi-Te septuple layers (SLs) as the building block, each of which can be viewed as a Bi_2Te_3 quintuple layer (QL) intercalated by a MnTe bilayer. $\text{MnBi}_4\text{Te}_7(m = 1, n = 1)$ adopts space group $P\bar{3}m1$ with a hexagonal superlattice crystal structure with alternate stacking of one MnBi_2Te_4 SL and one Bi_2Te_3 QL. MnBi_2Te_4 and MnBi_4Te_7 are both identified to be natural van der Waals heterostructures as evidenced by high-angle annular dark field (HAADF)-STEM measurements.^[12]

Pressure as a conventional thermodynamic parameter is a clean and useful means to tune the interatomic distance and consequently, can be used to engineer the electronic and, subsequently, the macroscopic physical properties of the system. In addition, it is possible to trigger novel structural and/or electronic transitions. Indeed, we recently observed pressure-induced topological phase transitions and even superconductivity in topological materials.^[24–27] In this work, we study the effect of pressure on the electrical transport properties and crystal structures of MnBi_2Te_4 and MnBi_4Te_7 in a diamond anvil cell (DAC) apparatus. The antiferromagnetic (AFM) metallic ground state of MnBi_2Te_4 and MnBi_4Te_7 single crystal is gradually suppressed by pressure, and the conductance as well as the crystal structure change dramatically upon further compression. Through *ab initio* band structure calculations, we find that the application of pressure does not qualitatively change the electronic and topological nature of the two systems until the structural phase transition is

observed in the high-pressure regime. Based on synchrotron XRD and Raman spectroscopy measurements, detailed high-pressure crystal structure and phase transitions are discussed.

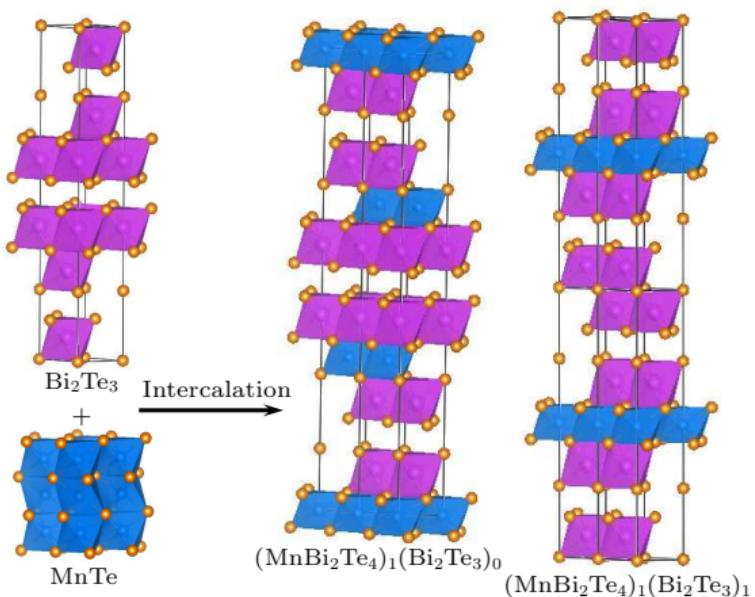


Fig. 1. Crystal structure of Bi_2Te_3 ($R\bar{3}m$, No. 166),^[8] MnTe ($P6_3/mmc$, No. 194),^[9] MnBi_2Te_4 ($((\text{MnBi}_2\text{Te}_4)_1(\text{Bi}_2\text{Te}_3)_0)$, $R\bar{3}m$, No. 166)^[10] and MnBi_4Te_7 ($((\text{MnBi}_2\text{Te}_4)_1(\text{Bi}_2\text{Te}_3)_1)$, $P\bar{3}m1$, No. 164),^[11] respectively. The MnBi_2Te_4 unit cell consists of three septuplet monoatomic layers with a stacking sequence of $\text{Te}(1)\text{-Bi}(1)\text{-Te}(2)\text{-Mn}(1)\text{-Te}(2)\text{-Bi}(1)\text{-Te}(1)$ along the c -axis, and the seven monoatomic layers are centro-symmetrical with respect to Mn. In detail, Mn crystallographic sites are of octahedral coordination and are surrounded by six $\text{Te}(2)$ atoms at the same distance as under ambient conditions. Bi is at the center of a distorted octahedron and is surrounded by three $\text{Te}(2)$ atoms and three $\text{Te}(1)$ atoms as the nearest neighbors. Triple slabs of MnTe_6 and BiTe_6 are octahedral edge-linked with each other, and similarly for the SL of MnBi_4Te_7 . Alternation of QL ($\text{Te}(2)\text{-Bi}(1)\text{-Te}(1)\text{-Bi}(1)\text{-Te}(2)$) and SL ($\text{Te}(3)\text{-Bi}(2)\text{-Te}(4)\text{-Mn}(1)\text{-Te}(4)\text{-Bi}(2)\text{-Te}(3)$) blocks stack along the c -axis and MnBi_4Te_7 is in the trigonal space group $P\bar{3}m1$.

The MnBi_2Te_4 and MnBi_4Te_7 single crystals in this work were grown using a flux-assisted method.^[12] High-pressure resistivity measurements were performed in a nonmagnetic DAC. A cubic BN/epoxy mixture layer was inserted between BeCu gaskets and electrical leads. Four Pt foils were arranged in a van der Pauw four-probe configuration to contact the

sample in the chamber for resistivity measurements. NaCl was used as the pressure transmitting medium (PTM) and pressure was determined by the ruby luminescence method.^[28]

An *in situ* high-pressure Raman spectroscopy investigation of MnBi₂Te₄ and MnBi₄Te₇ was performed using a Raman spectrometer (Renishaw inVia, UK) with a laser excitation wavelength of 532 nm and low-wavenumber filter. A symmetric DAC with anvil culet sizes of 400 μm was used, with silicon oil as the PTM. The *in situ* high-pressure XRD measurements were performed at beamline 13-BM-C of the Advanced Photon Source (APS) (x-ray wavelength $\lambda = 0.4340 \text{ \AA}$) and beamline BL15U of Shanghai Synchrotron Radiation Facility (x-ray wavelength $\lambda = 0.6199 \text{ \AA}$). Symmetric DACs with anvil culet sizes of 400 μm and 300 μm and T301 gaskets were used. Neon was used as the PTM and pressure was determined by the ruby luminescence method.^[28] The two-dimensional diffraction images were integrated into angle-resolved diffraction intensity profiles using the software DIOPTAS.^[29] Rietveld refinements on crystal structures under high pressure were performed using the General Structure Analysis System (GSAS) and the graphical user interface EXPGUI.^[30]

The *ab initio* calculations were performed within the framework of density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP),^[31] with the exchange-correlation functional considered in the generalized gradient approximation potential.^[32] A k-mesh of $9 \times 9 \times 1$ for MnBi₂Te₄ and $9 \times 9 \times 3$ for MnBi₄Te₇ was applied. The experimental lattice constants were adopted under different pressures with atomic positions optimized for a total energy tolerance of 10^{-5} eV . To account for the correlation effect of the transition metal element Mn in both MnBi₂Te₄ and MnBi₄Te₇, the GGA+U functional with $U = 3 \text{ eV}$ for the *d*-orbitals of Mn is adopted. The spin-orbital coupling was considered self-consistently in this work. The topological surface states were calculated by applying the iterative Green's function approach^[33] as implemented in WannierTools^[34] based on the maximally localized Wannier functions^[35] as obtained through the VASP2WANNIER90^[36]

interfaces in a non-self-consistent calculation.

As a typical layered material, the electrical transport and magnetic properties of MnBi_2Te_4 and MnBi_4Te_7 are expected to be sensitive to the competition between interlayer and intralayer interactions, which can be effectively tuned by applying external pressure. We performed resistivity measurements on several single crystals at various pressures. Figures 2(a), 2(b), and 2(c) show the typical $\rho(T)$ curves of MnBi_2Te_4 for pressures up to 34.0 GPa. As shown in Fig. 2(a), the resistivity–temperature slope $d\rho/dT$ of MnBi_2Te_4 clearly shows a positive value, indicating metal-like conduction in the low-pressure range. With an increase of pressure, $\rho(T)$ curves show an upturn behavior at low temperatures. Upon further compression, a metal–semiconductor transition is observed and $\rho(T)$ displays a semiconductor-like behavior for $P > 12$ GPa. Interestingly, the resistivity ultimately undergoes a metallization at a pressure above 16.3 GPa and does not change significantly in response to further increases in the pressure. No superconductivity was observed down to 1.8 K in this pressure range.

It should be noted that $\rho(T)$ of MnBi_2Te_4 displays a kink at the AFM transition $T_N = 24.5$ K at 0.4 GPa (Fig. 2(d)), which is consistent with the magnetic measurements shown in Fig. S1 (see the Supplemental Material) and those in other reports.^[20] The rapid drop of resistivity below T_N is attributed to the reduction of spin scattering after the formation of long-range AFM order.^[37] As indicated by the arrow in Fig. 2(d), T_N determined from the resistivity kink shifts to lower temperatures with increasing pressure. Over 4.9 GPa, the upturn resistivity trend at lower temperature becomes much stronger and the kink merges into the $\rho(T)$ curve. The fitting results demonstrate that T_N approaches zero at approximately 9.3 GPa. Since the interlayer distance deceases under high pressure, it is speculated that the pressure-induced enhancement of antiferromagnetic/ferromagnetic competition and the partial delocalization of Mn-3d electrons not only destroys long-range AFM order, but also promotes charge-

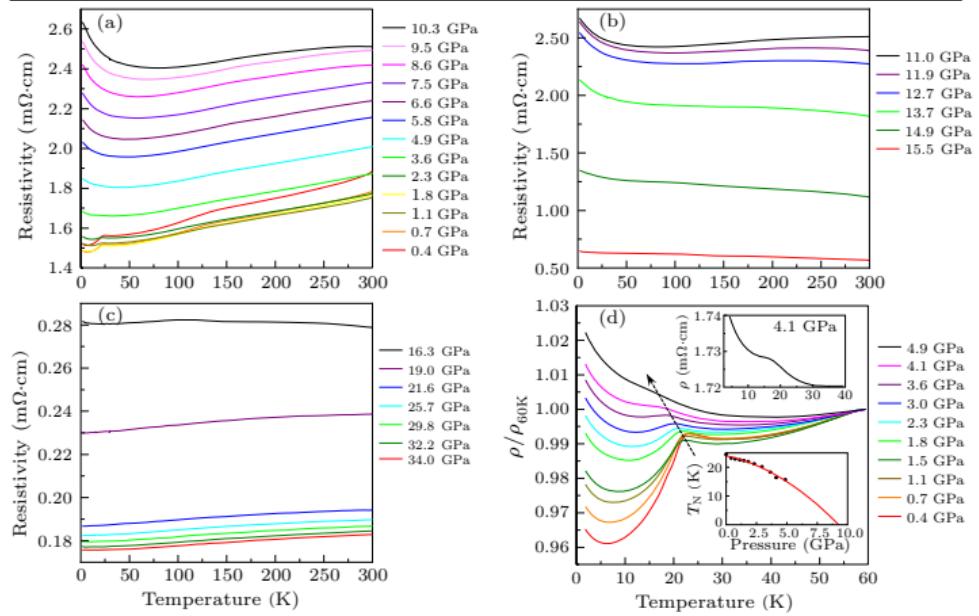


Fig. 2. Electrical resistivity of MnBi₂Te₄ as a function of temperature for pressures up to 10.3 GPa (a), 15.5 GPa (b) and 34.0 GPa (c); (d) detail of the normalized resistivity of MnBi₂Te₄ as a function of temperature at various pressures to monitor the shift of the AFM transition kink. The inset shows the enlarged resistivity–temperature curve at 4.1 GPa and fitting of the AFM transition temperature as a function of pressure.

carrier localization through enhanced spin fluctuations and/or the formation of a hybridization gap at high pressure.

The high-pressure experiments have been repeated on different samples with good reproducibility of the observed transition temperatures. Based on the above resistivity measurements, we summarize a T – P phase diagram for MnBi₂Te₄ single crystals in Fig. 3(a). The resistivity of MnBi₂Te₄ shows non-monotonic evolution with increasing pressure. Over the entire temperature range, the resistivity is first suppressed with applied pressure and reaches a minimum value at about 2 GPa. As the pressure further increases, the resistivity increases with a maximum occurring at 11.0 GPa and the AFM order shifted to a lower temperature. Accompanying the suppression of the AFM transition, the electrical transport properties also change qualitatively from metal-like $d\rho/dT > 0$ to semimetal- or semiconducting-like behavior $d\rho/dT < 0$. For $P > 12$ GPa, the resistivity abruptly decreases and a transi-

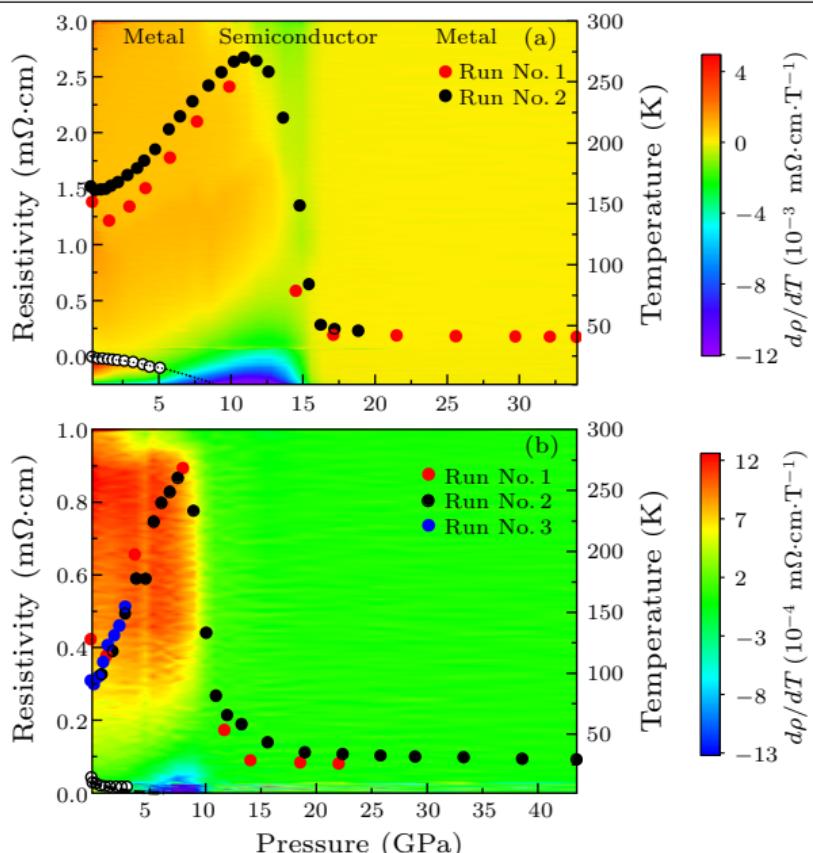


Fig. 3. Electronic phase diagrams of MnBi₂Te₄ (a) and MnBi₄Te₇ (b). The black, blue and red solid circles represent different runs of electrical resistivity measurements at 1.8 K. The black open circles indicate AFM transition temperatures due to the transport measurements.

tion from semiconducting to metallic behavior takes place at further increased pressure. Similarly, pressure-induced non-monotonic evolution was also observed in MnBi₄Te₇, as shown in Fig. 3(b). Although resistivity changes significantly under high pressure, $\rho(T)$ exhibits a metallic behavior over the whole temperature range (Fig. S2). No transition from metallic to semiconducting behavior was observed within the studied pressure range. The AFM order of MnBi₄Te₇ shifted to a lower temperature with increasing pressure, which is similar to that of MnBi₂Te₄ (Fig. S3).

The angular dispersive XRD patterns of MnBi₂Te₄ at various pressures are shown in Fig. 4(a). Under ambient conditions and in the low-pressure range ($P \leq 14.6$ GPa), all

the diffraction peaks of MnBi_2Te_4 could be indexed to the rhombohedral $R\bar{3}m$ (No. 166) structure by Rietveld refinement (Fig. 4(b)). High-pressure XRD experiments in pressure steps of 1–2 GPa were performed on MnBi_2Te_4 via a DAC. At pressures exceeding 14.6 GPa, structural disorder becomes apparent. Above 17.4 GPa, diffraction peaks from crystalline phase disappear, and a new broad peak appears at approximately 2.65 Å in *d*-spacing. This indicates that the sample has completely transformed into an amorphous state.

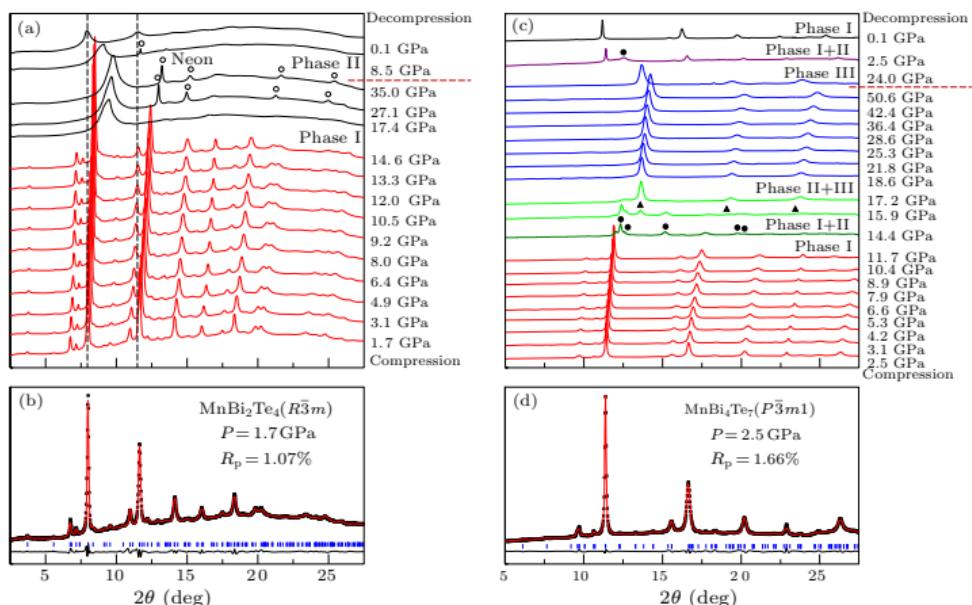


Fig. 4. XRD patterns collected at various pressures for MnBi_2Te_4 with an x-ray wavelength of $\lambda = 0.4340 \text{ \AA}$ (a) and MnBi_4Te_7 with an x-ray wavelength of $\lambda = 0.6199 \text{ \AA}$ (c); the black open circles are from PTM neon; typical Rietveld refinement of phase I of MnBi_2Te_4 (b) and MnBi_4Te_7 (d), respectively. The experimental and simulated data are indicated by black stars and red lines, respectively. The solid lines shown at the bottom of the figures are the residual intensities. The vertical bars indicate peak positions.

In contrast, a different structure evolution for MnBi_4Te_7 is observed under high pressure (Fig. 4(c)). In the low-pressure range, phase I of MnBi_4Te_7 crystallizes in a trigonal space group $P\bar{3}m1$ (No. 164), as shown in Fig. 4(d). At 14.4 GPa, a high-pressure phase, phase II, was observed. This phase is only stable in a narrow pressure range and coexists with the phase I or the phase III upon compression. Above 18.6 GPa, only

phase III exists and no further transitions are observed up to 50.6 GPa. Upon decompression, phase III persists to 24.0 GPa. When the pressure is decreased to 2.5 GPa, phase II and phase I recover and coexist. After a full pressure release, MnBi₄Te₇ recovers the ambient-pressure structure.

To verify our speculation on the crystallographic structural phase transition sequence under high pressure, Raman scattering spectroscopy was employed to characterize the pressure-induced phase transition (Fig. 5(a)). According to group theory analysis and the results in the literature,^[38] there are four Raman-active modes ($2E_g + 2A_{1g}$) for MnBi₂Te₄. The E_g and A_{1g} modes are related to the in-plane A(VI)–B(V) and out-of-plane lattice vibrations, respectively (Fig. 5(b)). At 0.3 GPa, four peaks are assigned as follows: $47.4\text{ cm}^{-1}(E_g)$, $67.4\text{ cm}^{-1}(A_{1g})$, $104.2\text{ cm}^{-1}(E_g)$, and $139.8\text{ cm}^{-1}(A_{1g})$.^[38] As the pressure increases, all four modes exhibit blue shift due to the increase in the strength of the Bi–Te covalent interaction (Fig. 5(c)). Upon further compression exceeding a pressure of 17.8 GPa, all the peaks disappear. The pressure-induced amorphization occurs at 17.8 GPa, which coincides with the XRD result at 17.4 GPa. In addition, a reversible phase transition associated with a compressed lattice (where the lattice constants are decreased) is verified by the Raman spectrum of the sample after recovery to 1 atm. The Raman spectra of MnBi₄Te₇ were also measured using a DAC and a similar phenomenon was observed under high pressure (Fig. S4). It should be noted that no new Raman modes were observed under higher pressure, although a structural phase transition is observed by synchrotron XRD measurements. One can expect that pressure-induced metallization or vibration modes become weaker under high pressure, which may account for the absence of Raman modes.

To understand the non-monotonic change of the measured resistivity under different pressures, we performed detailed *ab initio* calculations and examined both the bulk and surface electronic structures of MnBi₂Te₄ (Figs. 6 and S5). Electron transportation is mainly determined by the states around the

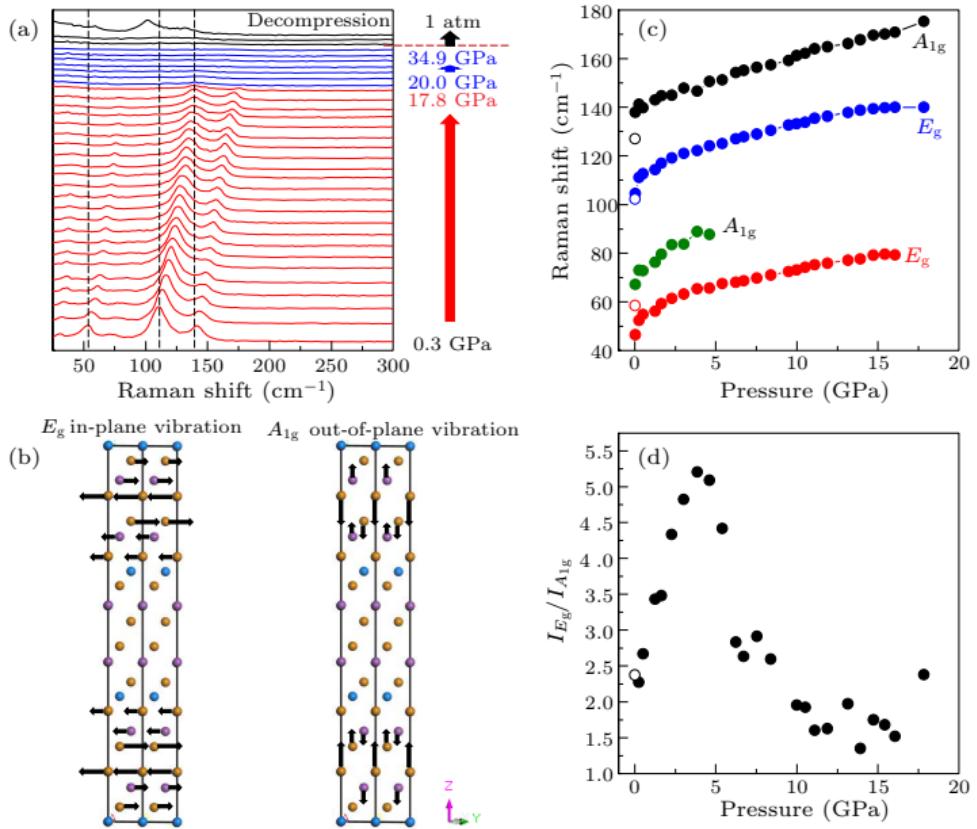


Fig. 5. (a) Raman spectra at various pressures for MnBi₂Te₄; (b) phonon mode symmetry and direction of vibration for MnBi₂Te₄; (c) Raman mode frequencies for MnBi₂Te₄ in compression (solid circle) and decompression (open circle); (d) pressure dependence of $I_{E_g}/I_{A_{1g}}$ intensity ratio for MnBi₂Te₄. For accurate peak intensity comparison, the strong E_g and A_{1g} modes with respective Raman shifts of 104.2 cm^{-1} and 139.8 cm^{-1} at 1 atm are chosen. Peak intensity and peak position are obtained by Gaussian and Lorentzian mixed line shape fitting. Open circles represent data recovered for 1 atm.

Fermi level which can be effectively tuned by external pressure. Concerning a topological system, these states contain both the bulk and the topological surface/edge contributions. It is widely known that the topology of a topological system is fully determined by the symmetry and the associated Berry curvature of the bulk bands. As long as they are qualitatively unchanged, the topology persists (Fig. S5). However, external perturbations, such as the pressure, can modify the dispersions of both the bulk and surface bands, resulting in different transport responses. In Fig. 6(a) the electronic structures of

MnBi_2Te_4 are displayed for different pressures. MnBi_2Te_4 is a semiconductor with a gap of 243.4 meV at atmospheric pressure. Once external pressure is applied, the conduction band bottom changes from Z to Γ and the gap size gradually decreases with increasing pressure. At the highest pressure applied which maintains the crystal symmetry of MnBi_2Te_4 , a global gap remains but it is significantly reduced to 16.3 meV.

Due to the topological nature of this system, the total conductance/resistance experimentally measured is subjected to contributions from both the bulk and surface electrons. We, thus, further determined the surface electronic structure of the experimentally cleaved (001) surface (Fig. 6(b)). In sharp contrast to the bulk electronic structure, an overall reentrant behavior of the gapped surface states is observed upon the increase of pressure. Below 4.9 GPa, the magnetic surface states move from below to above the Fermi level, leading to a metal–semiconductor transition solely caused by the surface electrons. The surface states, with a clear separation from the bulk bands at pressures below 4.9 GPa, completely merge into the bulk bands at pressures above 10.5 GPa. Above this pressure, the contribution to the resistivity is mainly determined by the bulk gap and electrons. Thus, the decrease in the bulk gap results in a decrease of the resistivity as shown in Fig. 3(a) above 10.5 GPa. However, below 10.5 GPa, the bulk and surface electrons behave differently, i.e., the surface electrons are gradually localized, and the bulk electrons become more mobile with increasing pressure. Thus, the competition between the two types of electrons results in the decrease–increase behavior of the resistivity observed in Fig. 3(a). More precisely, we suspect that the decrease in the resistivity below 3.1 GPa is mainly induced by the delocalization of the bulk electrons as the surface electrons remain metallic; while the increase in the resistivity is mainly a consequence of the localization of the surface electrons, as the surface states are no longer metallic and have not yet merged into the bulk states.

A similar analysis can be applied to MnBi_4Te_7 (Figs. S5

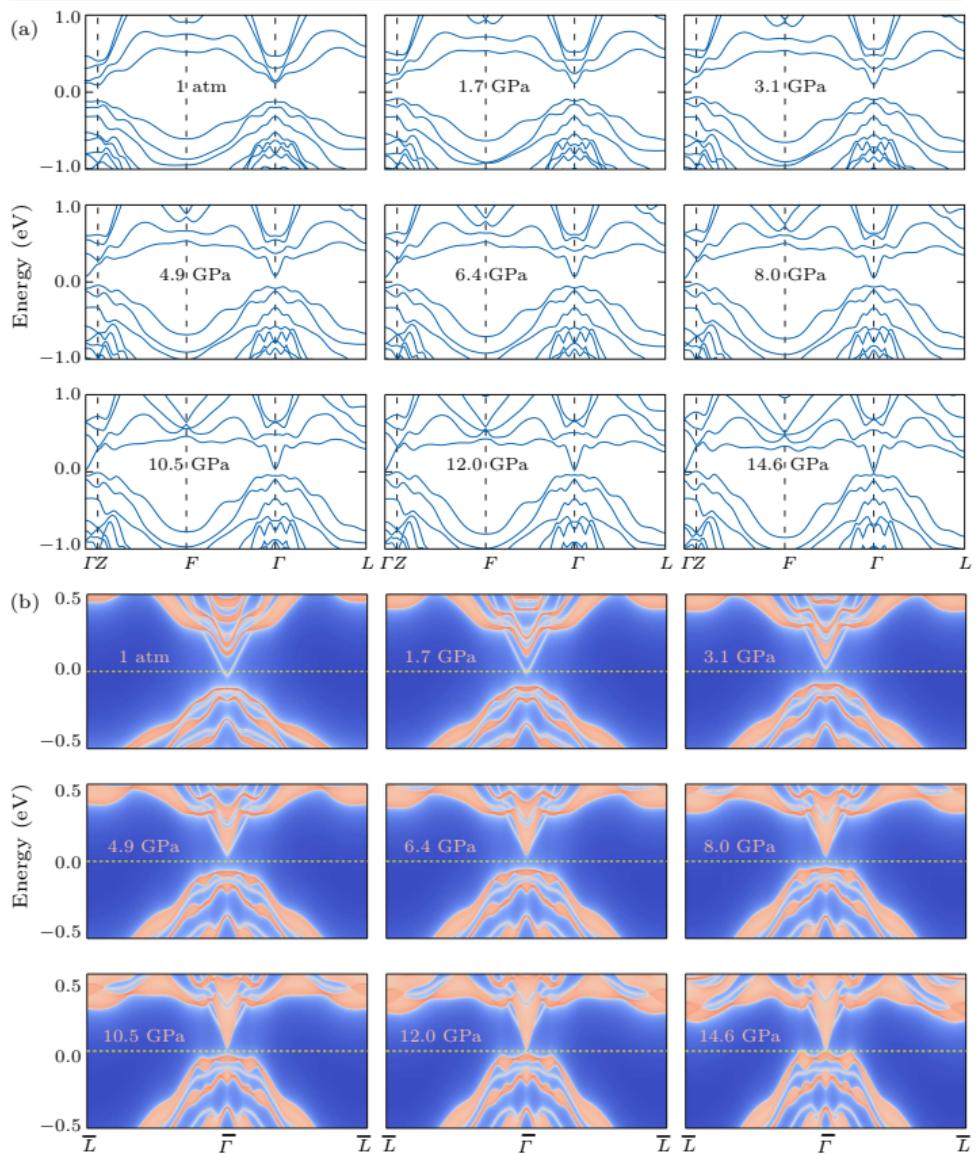


Fig. 6. Bulk and surface electronic structures of MnBi_2Te_4 at different pressures. (a) The bulk electronic structure remains gapped under all applied pressures with roughly monotonic decrease of gap size. (b) The topological surface states on (001) display a reentrant behavior upon the increase of pressure.

and S6). We note that the bulk gap shown in Fig. S6(a) decreases under increasing pressure with the minimum gap decreasing from 196.7 meV to 174.8 meV at Γ , which only renders more substantial contribution to its conductance at higher pressures. At low pressure, the contribution from the surface states becomes dominant. As MnBi_4Te_7 can

be naturally cleaved at MnBi_2Te_4 and Bi_2Te_3 layers, the total surface conductance includes components from both terminations. The topological surface states with MnBi_2Te_4 termination intersect the Fermi level under all examined pressures (Fig. S6(b)), presenting a metallic background in the measured pressure range. Meanwhile, the surface electrons terminated at Bi_2Te_3 become more localized with increasing pressure. The surface band crosses the Fermi level at 2.5 GPa, and gradually moves to higher binding energies with further increase of pressure. The competition between the two types of electrons again results in the decrease-increase behavior of resistivity observed in Fig. 3(b). Below 2.5 GPa, the delocalization of the bulk electrons is attributed to the decrease of resistivity, while the subsequent increase of the resistivity above 2.5 GPa mainly stems from the localization of the surface electrons. At approximately 10.4 GPa, the surface bands merge into the bulk states, after which the resistivity is mainly determined by the bulk electrons, and thus shows a sharp decline as observed in the transport measurements.

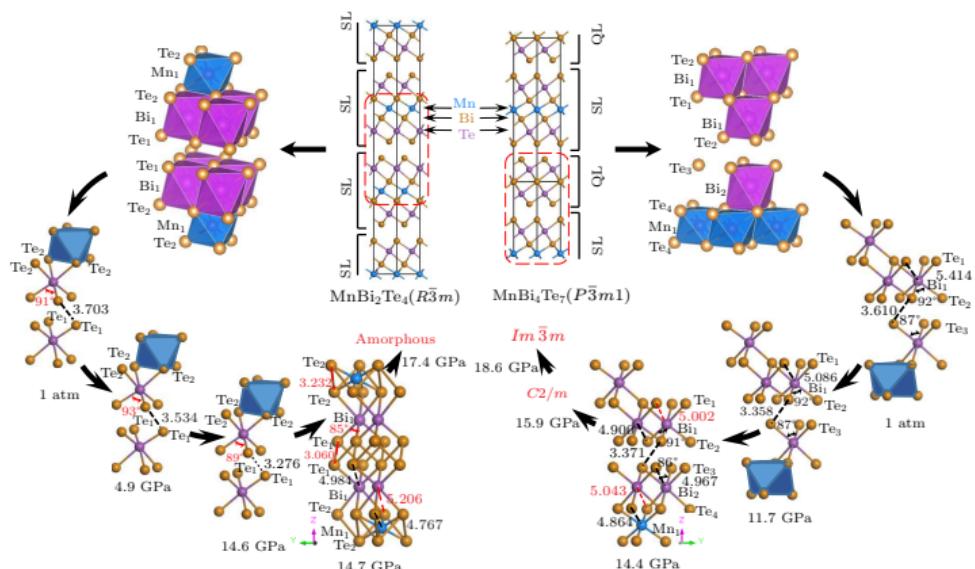


Fig. 7. Schematic representation of the evolution of MnBi_2Te_4 and MnBi_4Te_7 structures under high pressure.

Next, we discuss the high-pressure phase transition. To gain an insight into the structural evolution, pressure-induced

bond length and angle variations in MnTe_6 and BiTe_6 octahedra are derived from the Rietveld refinements (Fig. S7). The Mn–Te bond length decreases with an increase of pressure and the bond angle of $\text{Te}(2)\text{–Mn}(1)\text{–Te}(2)$ changes only slightly (Figs. S7(a) and S7(b)). Below 3.1 GPa, the pressure coefficients of $\text{Bi}(1)\text{–Te}(1)$ and $\text{Bi}(1)\text{–Te}(2)$ bond lengths show the same sign. Also, both the $\text{Te}(1)\text{–Bi}(1)\text{–Te}(1)$ bond angle and the distance between the two $\text{Te}(1)$'s of the near neighbor septuple blocks decrease with increasing pressure (Figs. S7c and S7d). However, $\text{Bi}(1)\text{–Te}(2)$ and $\text{Bi}(1)\text{–Te}(1)$ bond lengths show opposite responses to pressure near 4 GPa, and $\text{Te}(1)\text{–Bi}(1)\text{–Te}(1)$ bond angle also behaves differently from $\text{Te}(1)\text{–Bi}(1)\text{–Te}(2)$ and $\text{Te}(2)\text{–Bi}(1)\text{–Te}(2)$ bond angles (Figs. S7(c) and S7(d)). These results indicate that the distorted octahedral BiTe_6 deforms more significantly above 3.1 GPa and bends towards Mn atoms (Fig. S7(e)). This releases stress along the *c*-axis and weakens the interaction between the nearest neighbor SL. Upon further compression, interlayer interaction enhancement dominates and ultimately the interlayer $\text{Te}(1)\text{–Te}(1)$ bond is formed. The pressure dependence of the *c/a* ratio for the $R\bar{3}m$ phase of MnBi_2Te_4 (plotted in Fig. S8(a)) shows a minimum at approximately 3.1 GPa. This is consistent with the Raman spectroscopy observations. The in-plane Bi–Te vibration was enhanced significantly with pressure. With further compression, the ratio of out-of-plane Bi–Te vibrations is enhanced when the pressure exceeds 3.8 GPa as shown in the evolution of the intensity ratio ($I_{E_g}/I_{A_{1g}}$) in Fig. 5(d). A similar phenomenon was observed in the MnBi_4Te_7 phase (Fig. S4(d)). It is clear that the structural change induced by external pressure will significantly modify the corresponding electronic structure. The reduced interlayer distance will enhance the three-dimensional dispersion of the system. As a result, the electronic states around the Fermi level will be considerably modified, which, ultimately, influences the macroscopic resistivity. Thus, such layered MTIs with large inter-layer distances are ideal for pressure engineered materials.

In compression, there is a quite distinct compression be-

havior between MnBi_2Te_4 and MnBi_4Te_7 . Figure 7 shows the pressure-induced structural evolution of MnBi_2Te_4 and MnBi_4Te_7 , respectively. The former transforms to an amorphous phase at approximately 17.4 GPa, while the latter transforms from a rhombohedral to a mixed high-pressure phase at 14.4 GPa, and finally phase III obtained at 18.6–50.6 GPa. For phase II of MnBi_4Te_7 , Le Bail refinement yielded a monoclinic structure with $a = 14.4192(3)$ Å, $b = 3.9415(9)$ Å, $c = 17.1202(7)$ Å, and $\beta = 148.62(7)^\circ$. The XRD pattern of phase III is simple and can be indexed to an $Im\bar{3}m$ (No. 229) structure with $a = 3.6796(0)$ Å (Fig. S9, Table S1). The different compression behavior is related to the distortion of MnTe_6 and BiTe_6 , which is induced by competition under high pressure. In MnBi_2Te_4 , the Te(2)–Te(2) bond forms besides Te(1)–Te(1) linked in the low-pressure range accompanied by MnTe_6 octahedron flattening. In contrast, the distances of Bi(1)–Te(1) (5.002 Å) and Bi(1)–Te(2) (4.900 Å) are shorter than Bi(2)–Te(4) (5.043 Å) in MnBi_4Te_7 and Bi(1)–Te(2) (5.206 Å) in MnBi_2Te_4 . As a result, the pressure-induced distorted Bi(1) Te_6 octahedron in the Bi_2Te_3 quintuple block tends to form a heptahedrally coordinated BiTe_7 unit and further $\text{Bi}(\text{Te})_n$ ($n > 7$). At 18.6 GPa, the Te–Te and Bi–Te distances in MnBi_4Te_7 are close to each other because of the flatter MnTe_6 octahedron as well as the improved interaction between QL and SL (Fig. S10). An alternating Bi, Te structure with Mn intercalation exists during the formation of an isotropic phase along the layers and perpendicular to the layers. The structural evolution of MnBi_4Te_7 under high pressure resembles the situation in the case of Bi_2Te_3 .^[8,39,40] Recent sister compounds $\text{MnBi}_6\text{Te}_{10}$ ($m = 1$, $n = 2$) and $\text{MnBi}_8\text{Te}_{13}$ ($m = 1$, $n = 3$) have been grown successfully.^[41–44] It will be interesting to characterize the structural evolution of this series $(\text{MnBi}_2\text{Te}_4)_m(\text{Bi}_2\text{Te}_3)_n$ of compounds and summarize pressure-induced phase transition in these layered compounds.

In conclusion, we have performed a comprehensive high-pressure study on the electrical transport properties and crystal structures of the MTIs MnBi_2Te_4 and MnBi_4Te_7 in DACs.

The AFM metallic ground state of MnBi_2Te_4 and MnBi_4Te_7 single crystals are gradually suppressed by pressure. The pressure-dependent resistivity over a wide temperature range passes through a minimum at around 3 GPa. Upon further increasing the pressure, resistivity starts to increase rapidly, reaching a maximum at a pressure above 10 GPa. Through *ab initio* calculations, we find that the application of pressure does not destroy the nontrivial topology of the system before structural phase transition. However, the bulk and surface states respond differently to external pressure, resulting in competing contributions to the macroscopic resistivity. Based on synchrotron XRD and Raman spectroscopy measurements, we find that MnBi_2Te_4 transforms to an amorphous phase at around 17.4 GPa, while MnBi_4Te_7 transforms to two new high-pressure phases. Application of pressure effectively tuned the electronic properties and crystal structure of MnBi_2Te_4 and MnBi_4Te_7 . Considering both intriguing magnetism and topology in this layered material, our results call for further experimental and theoretical studies on $(\text{MnBi}_2\text{Te}_4)_m(\text{Bi}_2\text{Te}_3)_n$ and related materials for a better understanding of the interplay between magnetic and topological nature, and its potential application in realizing topological superconductivity.

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Supplementary Material: Pressure-induced Topological and Structural Phase Transitions in an Antiferromagnetic Topological Insulator*

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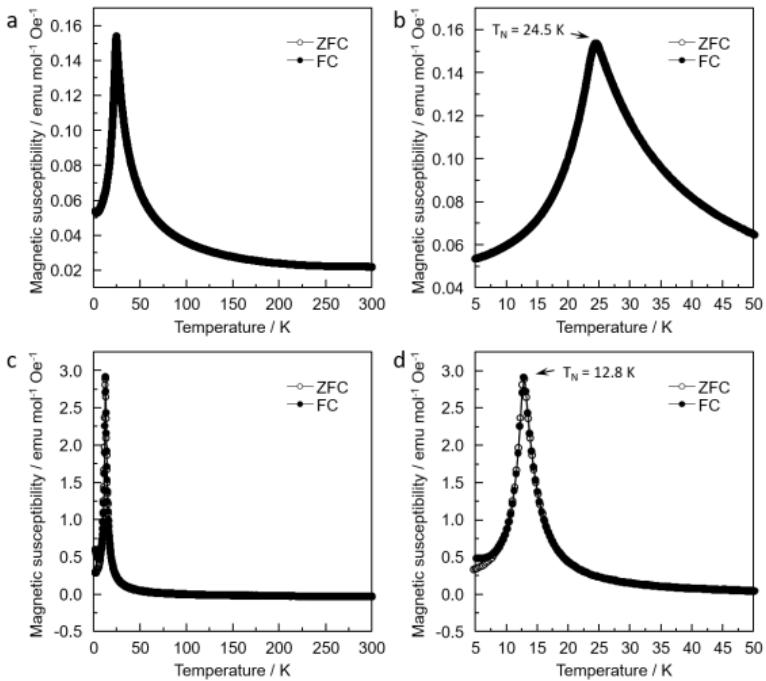


Figure S1. Field cooled (FC) and zero-field cooled (ZFC) temperature dependences of magnetic susceptibility χ measured at 1 T for the MnBi_2Te_4 crystals (a, b) and 50 Oe for MnBi_4Te_7 crystals (c, d) aligned with the magnetic field parallel ($H//c$) to the c -axis. The susceptibility data shows an AFM transition with $T_N = 24.5$ K in MnBi_2Te_4 and $T_N = 12.8$ K in MnBi_4Te_7 .

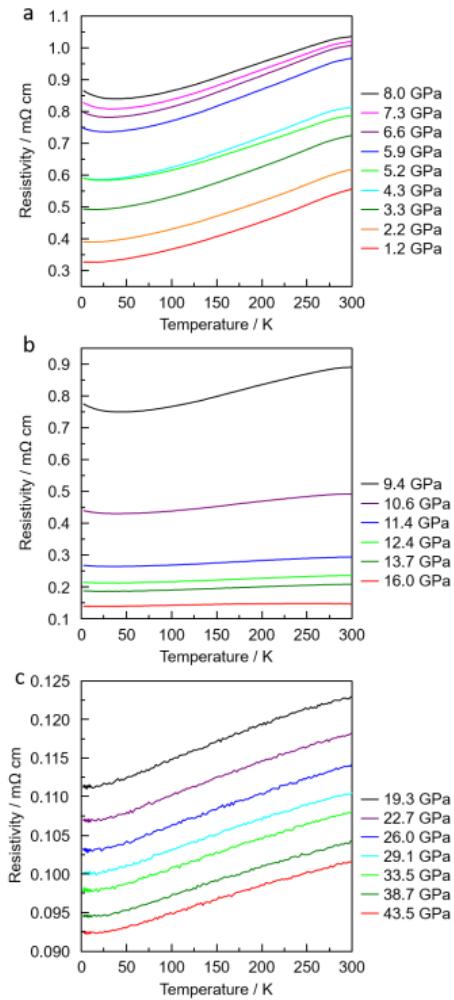


Figure S2. Electrical resistivity of MnBi_4Te_7 as a function of temperature for pressures up to 8.0 GPa (a), 16.0 GPa (b) and 43.5 GPa (c) in run II.

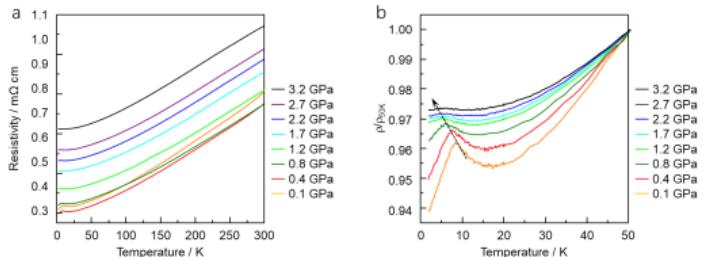


Figure S3. (a) Electrical resistivity of MnBi_4Te_7 as a function of temperature for pressures up to 3.2 GPa in run III; (b) Detail of the normalized resistivity of MnBi_4Te_7 as a function of temperature at various pressures to monitor the shift of the AFM transition kink.

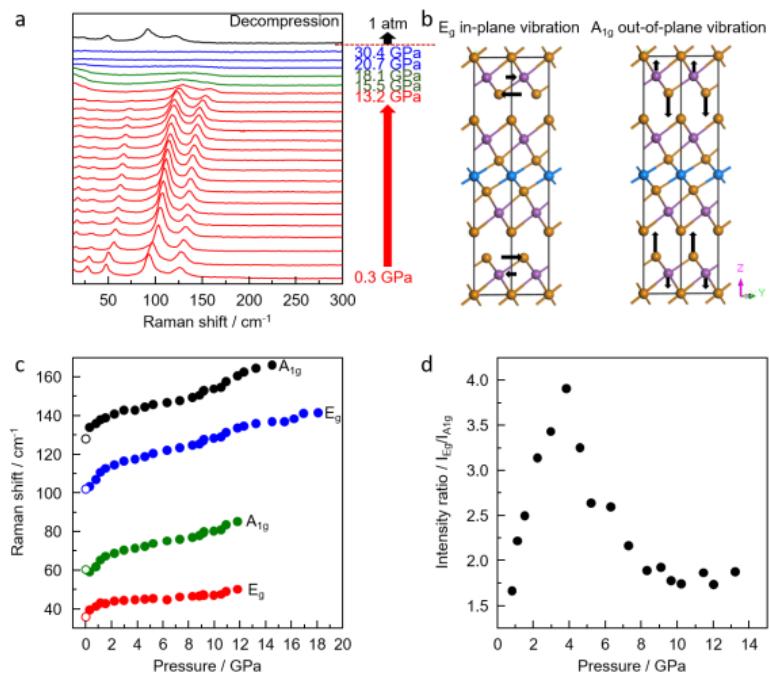
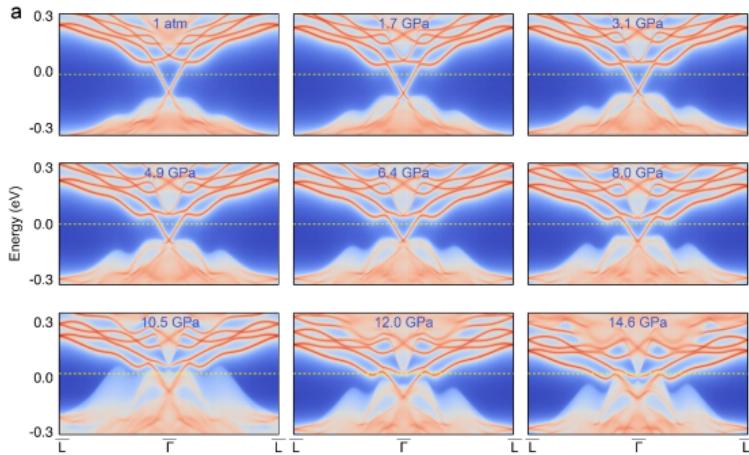


Figure S4. (a) Raman spectra at various pressure for MnBi_4Te_7 ; (b) Phonon mode symmetry and direction of vibration for MnBi_4Te_7 ; (c) Raman mode frequencies for MnBi_4Te_7 in compression (solid circle) and decompression (open circle); (d) Pressure

dependence of $I_{E_g}/I_{A_{1g}}$ intensity ratio for MnBi₄Te₇. For accurate peak intensity comparison, the strong E_g mode and A_{1g} mode which show as 107.8 cm⁻¹ and 137.7 cm⁻¹ at 0.1 GPa, respectively is chosen. Peak intensity and peak position is obtained by Gaussian and Lorentzian mixed line shape fitting.

Raman spectra of MnBi₄Te₇ has been shown in Figure S4, and the vibration modes are in good agreement with previous reports.¹ With the increasing pressure, all the Raman modes shift toward higher frequencies. Lower wavenumber E_g and A_{1g} modes disappear first, accompanied by higher wavenumber E_g and A_{1g} modes become broad obviously over 11.1 GPa. No obvious phase transition is detected below 15.5 GPa, but over it, the high frequency A_{1g} mode disappear and only weak high frequency E_g mode maintains up to 18.1 GPa. It is inconsistent with the XRD results that the pressure of the onset of phase transition occurred at 14.4 GPa and pure phase III appeared at 18.6 GPa. Similar to MnBi₂Te₄, the intensity ratio of in-plane and out-of-plane vibration mode is pressure dependent and the maximum $I_{E_g}/I_{A_{1g}}$ shows at around 3.8 GPa.



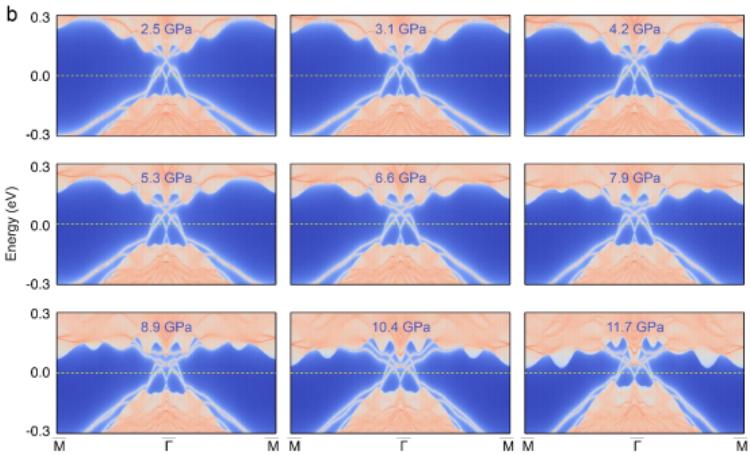
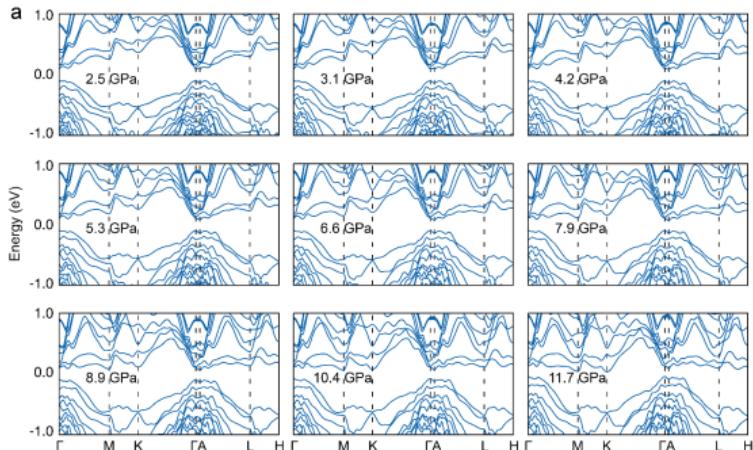


Figure S5. The gapless topological surface states on the effective time-reversal symmetry $\mathcal{S} = T\tau_{1/2}$ preserving surface, indicating stable nontrivial topology in the displayed pressure range. (a) The topological surface states on $(1\bar{1}0)$ of MnBi_2Te_4 . (b) The topological surface states on (100) of MnBi_4Te_7 .



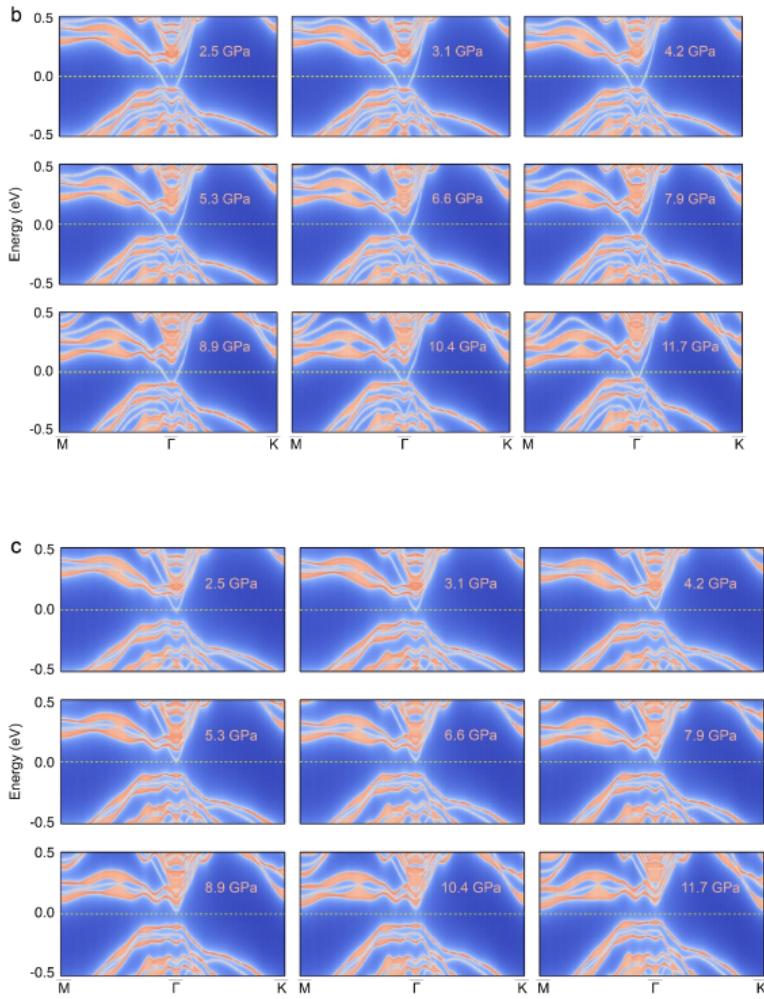


Figure S6. The bulk and surface electronic structures of MnBi_4Te_7 under different pressures. (a) The bulk electronic structure remains gapped under all applied pressures with roughly monotonic decrease of the global gap size in the whole Brillouin zone. (b) The topological surface states of (001) with MnBi_2Te_4 termination intersect the Fermi level under all examined pressures. (c) The topological surface states of (001) with Bi_2Te_3 termination gradually shrink above the Fermi level.

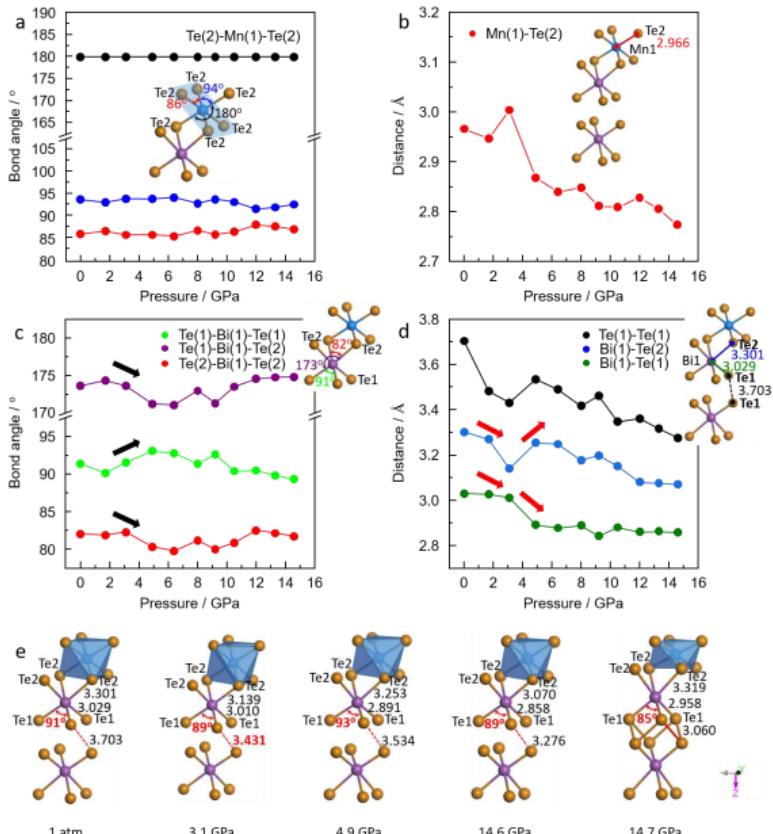


Figure S7. (a) Experimental bond angle of Te(2)-Mn(1)-Te(2) of MnBi₂Te₄ for R-3m under various pressures; (b) bond length of Mn(1)-Te(2) of MnBi₂Te₄ for R-3m under various pressures; (c) bond angle of Te(1)-Bi(1)-Te(1), Te(1)-Bi(1)-Te(2), Te(2)-Bi(1)-Te(2) of MnBi₂Te₄ for R-3m under various pressures; (d) bond length of Te(1)-Te(1), Bi(1)-Te(2), Bi(1)-Te(1) of MnBi₂Te₄ for R-3m under various pressures; (e) Structure evolution in the view of MnTe₆ and BiTe₆ octahedron based on Rietveld refinements of XRD result taken with X-ray wavelength $\lambda = 0.4340 \text{ \AA}$.

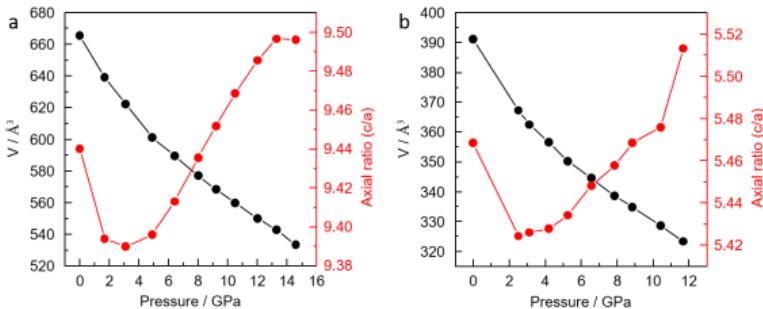


Figure S8. Pressure-dependence of experimental volume and axial ratio (c/a) of MnBi_2Te_4 (a) relative to $R-3m$ phase and MnBi_4Te_7 (b) relative to $P-3m1$ phase, respectively.

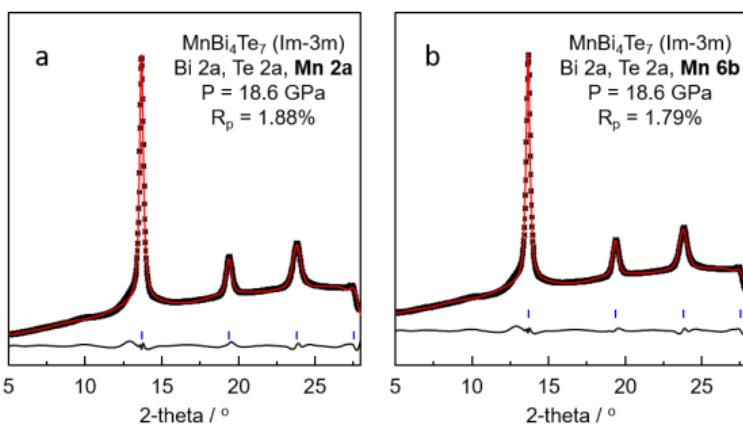


Figure S9. Typical Rietveld refinement of phase III of MnBi_4Te_7 obtained at 18.6 GPa. (a) Bi, Te and Mn atoms assigned on one Wyckoff position 2a in the crystallographic model I; (b) Bi, Te atoms assigned on 2a Wyckoff position and Mn atoms assigned on 6b Wyckoff position in the crystallographic model II. The experimental and simulated data were symbolled with black start and red line. The solid lines at the bottom are the residual intensities. The vertical bars indicate the peak positions.

Considering the close similarities, it is natural to suppose that MnBi_4Te_7 adopts the same structure evolution under high pressure. Nevertheless, an ambiguity in the space group assignment ($Im-3m$) of this new high-pressure phase still exists. The

crystallographic models have two types due to different assignments for the Mn atoms on the Wyckoff positions as shown in Figure S9.

Table S1. Structural parameters of MnBi_4Te_7 at 18.6 GPa at room temperature.

	Model I	Model II
Crystal system	cubic	cubic
Space group	$Im\text{-}3m$ (229)	$Im\text{-}3m$ (229)
a	3.6800(6)	3.6800(2)
atoms position	Wyckoff (x y z)	Wyckoff (x y z)
Mn	2a (0,0,0)	6b (0.5,0,0)
Bi	2a (0,0,0)	2a (0,0,0)
Te	2a (0,0,0)	2a (0,0,0)
Residuals ^a / %	R_{wp} : 1.88% R_p : 1.39%	R_{wp} : 1.79% R_p : 1.31%

^a R_{wp} and R_p as defined in GSAS²

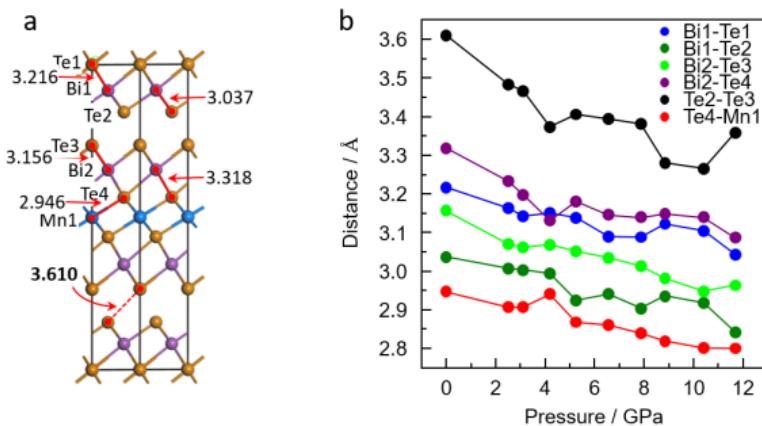


Figure S10. (a) unit cells of MnBi_4Te_7 at 1 atm; (b) Experimental atom distances of Bi1-Te1, Bi1-Te2, Bi2-Te3, Bi2-Te4, Te2-Te3 and Te4-Mn1 of MnBi_4Te_7 for $P\text{-}3m1$ under various pressures.

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