Antiferromagnetic Topological Insulator MnBi$_2$Te$_4$:
Synthesis and Magnetic properties

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**ABSTRACT**: Recently, MnBi₂Te₄ has been discovered as the first intrinsic antiferromagnetic topological insulator (AFM TI), and will become a promising material to discover exotic topological quantum phenomena. In this work, we have realized the successful synthesis of high-quality MnBi₂Te₄ single crystals by solid-state reactions. The as-grown MnBi₂Te₄ single crystal exhibits a van der Waals layered structure, which is composed of septuple Te-Bi-Te-Mn-Te-Bi-Te sequences as determined by powder X-ray diffraction (PXRD) and high-resolution high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM). The magnetic order below 25 K as a consequence of A-type antiferromagnetic interaction between Mn layers in the MnBi₂Te₄ crystal suggests the unique interplay between antiferromagnetism and topological quantum states. The transport measurements of MnBi₂Te₄ single crystals further confirm its magnetic transition. Moreover, the unstable surface of MnBi₂Te₄, which is found to be easily oxidized in air, deserves attention for ongoing research on few-layer samples. This study on the first AFM TI of MnBi₂Te₄ will guide the future research on other potential candidates in the MBi₂Te₃ family (M = Ni, V, Ti, etc.).

**INTRODUCTION**

During the last decade, tremendous efforts and breakthroughs in topological quantum states have aroused great enthusiasm in pursuing the correlation between topology and symmetry. The magnetism and crystal symmetry that affect the time reversal and inversion symmetry, respectively, are undoubtedly critical factors for condensed matters and thus have been deeply investigated in both theoretical and experimental aspects, resulting in numerous novel topological quantum phenomena. From the perspective of material science, it is of crucial importance to develop material systems with the coexistence of magnetism and topology that spontaneously breaks the time-reversal symmetry. Most current works tried to introduce magnetism into topological materials extrinsically by doping magnetic impurities. However, the extrinsic magnetic defects are difficult to control experimentally, which hinders the progress in subsequent applications, for instance, dissipationless electric transportation in quantum anomalous Hall device and topological quantum computation. Hence, synthesizing novel intrinsic magnetic topological materials in which magnetism and topology natively coexist, becomes a key research topic to future applications.

Appealingly, recent first-principle predictions and experiments have demonstrated MnBi₂Te₄ an intrinsic magnetic topological material, which belongs to antiferromagnetic (AFM) TIs and hosts unparalleled topological physics in both bulk and thin film. MnBi₂Te₄ crystallizes in the tetradymite-type structure with the $R\bar{3}m$ space group and lattice constants $a = 4.33$ Å, $c = 40.91$ Å. As a member of van der Waals (vdW) layered materials, MnBi₂Te₄ consists of Te-Bi-Te-Mn-Te-Bi-Te septuple layers (SLs) stacking in the ABC sequence along the c-axis (out-of-plane axis), as depicted in Figure 1a. Therefore, it can be viewed as derived from topological insulator, Bi₂Te₃, by inserting a Mn-Te layer into the middle of its Te-Bi-Te-Bi-Te quintuple layer (QL). Each Mn$^{2+}$ in high-spin configuration affords 5 $\mu_B$ magnetic moment according to Hund’s rule. The intralayer exchange coupling between Mn-Mn is ferromagnetic (FM) along an out-of-plane easy axis, while the interlayer exchange coupling between neighboring SLs is antiferromagnetic (AFM), generating a three-dimensional A-type AFM order.

Hence, the synthesis of high-quality MnBi₂Te₄ single crystals with well-defined AFM
order is essential to the research of magnetic topological material, as well as to the potential applications, such as dissipationless transport and low-power electronics. According to previous studies, MnBi2Te4 can be synthesized through a number of approaches, but lacks of the evidence of high purity crystalline samples29. During the preparation of this paper, we noticed that there have been several publications concerning the growth and characterizations of MnBi2Te4 crystals 20, 30, 31. However, the synthetic strategy toward high-quality millimeter-sized MnBi2Te4 single crystals with unambiguous AFM transition was still challenging. More importantly, the oxidation behavior, which is critical to clarify the stability of exfoliated samples, has not been studied yet.

Herein, we report effective synthesis of exclusive MnBi2Te4 single crystals with a clear and complete antiferromagnetic transition at 25 K. This progress could extend a variety of potential AFM TIs in MBi4Te3 (M = Ni, V, Ti, etc.)23. The quality of MnBi2Te4 single crystals is verified by a number of characterizations in detail. The oxidation behavior of MnBi2Te4 suggests that the surface of MnBi2Te4 tends to be oxidized in air while the bulk is stable. Intriguingly, magnetic and transport properties of MnBi2Te4 single crystals corroborate its AFM order and field-induced magnetic transitions, in good consistence with its prospective intrinsic AFM TI nature.

RESULTS AND DISCUSSION

Crystal Growth and Growth Mechanism. The challenge in synthesizing ternary intermetallic compounds via solid-state approaches is how to circumvent the uneven distribution of elements in the reaction. To begin with, high-quality Bi2Te3 and MnTe binary were synthesized as precursors by directly reacting the stoichiometric mixture of high-purity Bi and Te, and Mn and Te, respectively (seen in Method and Figure S1a, b). Afterwards, high-quality single crystal MnBi2Te4 was grown from a 1:1 mixture of Bi2Te3 and MnTe. The sample sealed in an evacuated silica ampoule was firstly heated to 973 K, followed by being slowly cooled to 864 K in 7 days and annealed for at least 14 days. After being air-quenched, shiny crystals were selected by cracking the sample chunk. The coarse part of the crystal was carefully cut-off with a scalpel or cleaned off by a scotch tape with the aid of an optical microscope. The growth method can successfully afford MnBi2Te4 plate-like single crystals up to 3 mm in size with shiny flat surface, indicating its layered structure (cf. inset of Figure 1b).

In fact, attempts by direct reacting of Bi, Mn and Te elements (seen in Method, trial 1) always gave Bi2Te3 and MnTe as impurities (product 1), which is confirmed by powder X-ray diffraction (PXRD) in Figure S1c. It is reasonable to assume that MnBi2Te4 forms by the solid-state intercalation of MnTe into Bi2Te3, which is favored by the long-term annealing. The short-term annealing yields a mixture of MnBi2Te4, Bi2Te3 and MnTe (product 2), which is revealed by PXRD in Figure S1d. Furthermore, to gain insights into the reaction mechanism, the high-resolution high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was performed on the (0 1 0) crystallographic plane of product 2, and directly shows the mixing of quintuple layers (QLs) from Bi2Te3 and SLs from MnBi2Te4 (Figure S2). This demonstrates an uncompleted reaction of Bi2Te3 and MnTe, which supports aforementioned mechanism. In contrast, for crystal obtained from prolonged annealing, the HAADF-STEM image in Figure 2b clearly resolves its (0 1 0) crystallographic plane with pure SLs from MnBi2Te4. Therefore, prolonged annealing is essential to guarantee the thorough intercalation
of MnTe into Bi$_2$Te$_3$. The thermal property of MnBi$_2$Te$_4$ is revealed with differential thermal analysis (DTA). As-grown MnBi$_2$Te$_4$ crystals display an intense exothermic peak at 872 K on the heating trace, indicating its melting point. Two endothermic peaks at 857 K and 849 K on the cooling run correspond to the crystallization of MnBi$_2$Te$_4$ and Bi$_2$Te$_3$ respectively. The lower intensity of endothermic peaks compared to that of the exothermic peak indicates that the crystallization of MnBi$_2$Te$_4$ is slow and difficult and MnBi$_2$Te$_4$ might be partly decomposed to Bi$_2$Te$_3$ above the melting point. The weight loss of MnBi$_2$Te$_4$ in thermogravimetric (TG) curve (Figure 1d) could result from the volatilization of Bi$_2$Te$_3$ with a low melting point. As a result, the annealing temperature requires a strict control to avoid the material loss during the crystallization of MnBi$_2$Te$_4$.

**Characterization.** PXRD was carried out to determine the phase and quality of the as-grown MnBi$_2$Te$_4$ crystal. Figure 1b shows that the diffraction of raw MnBi$_2$Te$_4$ crystals only occurs in the sharp and intense peaks that follow the (0 0 l), l=3n, diffraction rule, verifying the rhombohedral symmetry and preferred orientation along the [0 0 1] direction. The PXRD pattern of finely ground MnBi$_2$Te$_4$ powder in Figure 1b is in good agreement with the calculated PXRD pattern of MnBi$_2$Te$_4$, demonstrating its R3m space group and lattice constants a = 4.33 Å, c = 40.91 Å$^{29,30}$. No impurity peaks are observed, confirming the high purity of the as-grown MnBi$_2$Te$_4$ crystal. Besides, Figure 1d shows the Raman spectrum of MnBi$_2$Te$_4$ crystals with an appreciable blue shift with respect to that of Bi$_2$Te$_3$, which might result from the stronger in-plane bonding of Mn-Te.

The weak vDW interactions in the layered structure suggest that the top surface of MnBi$_2$Te$_4$ can be peeled off with scotch tape to expose fresh surface for the following characterization. Figure 2a displays the scanning electron microscope (SEM) image of an exfoliated MnBi$_2$Te$_4$ crystal with obviously segregated layers, confirming that MnBi$_2$Te$_4$ is a layered material integrated by van der Waals forces. Energy dispersive X-ray spectroscopy (EDX) was also used to analyze the element distribution of MnBi$_2$Te$_4$ crystals. As shown in Figure 2c, no peaks other than Mn, Bi, Te, C and Al are observed in the EDX spectrum of MnBi$_2$Te$_4$. Please note that C and Al is attributed to the conductive tape and sample stage, respectively. The EDX elemental mapping further reveals a uniform element distribution of Bi, Mn and Te (Figure 2d). The element ratio is further confirmed by inductively coupled plasma mass spectrometry (ICP-MS) analysis, which provided that Mn:Bi:Te is 1:2.14:3.96, agreeing with the chemical formula of the title compound. More importantly, the HAADF-STEM image in Figure 2b clearly shows the (0 1 0) crystallographic plane of MnBi$_2$Te$_4$ single crystal with unambiguously resolved SLs. As the contrast is proportional to the atomic number, the relatively dark atomic layer in the middle of SLs can be assigned to Mn, while two brightest layers are from Bi atoms. Thus, the HAADF-STEM study verifies the stacking sequence of Te-Bi-Te-Mn-Te-Bi-Te in a SL, which agrees well with the structure model. The thickness of a Te-Bi-Te-Mn-Te-Bi-Te SL layer is ~ 1.3 nm according to HAADF-STEM analysis, consistent with one third of the lattice constant of c-axis (Figure 2b).

**Oxidation Behavior and Stability.** We conducted X-ray photoelectron spectroscopy (XPS) measurement to gain insights into oxidation states of MnBi$_2$Te$_4$. The XPS measurement was firstly carried out on the fresh surface of the MnBi$_2$Te$_4$ crystal. The XPS survey spectrum verifies the elemental composition (Figure S3a). A low O 1s peak indicates slight surface oxidation of MnBi$_2$Te$_4$ due to the short exposure to atmosphere during sample transferring.
Furthermore, the oxidation states for each element can be assigned in the corresponding high-resolution spectra in Figure 3a-c. Two peaks in Bi 4f spectrum at 157.8 eV and 163.1 eV are ascribed to Bi 4f\(_{7/2}\) and Bi 4f\(_{5/2}\) of Bi\(^{3+}\) in Bi-Te bonds (Figure 3a)\(^{32-34}\). As shown in Figure 3b, Te 3d spectrum contains two major peaks at 572.2 eV (Te 3d\(_{5/2}\)) and 582.6 eV (Te 3d\(_{3/2}\)), corresponding to Te\(^{2-}\) in Bi-Te bonds and Mn-Te bonds\(^{35,36}\). In addition, two minor peaks at 576.0 eV and 586.3 eV can be observed in Te 3d spectrum, which is attributed to Te-O bonds and indicates slight oxidation of MnBi\(_2\)Te\(_4\) surface\(^{32}\). Figure 3c displays the Mn 2p spectrum, which can be deconvoluted into two sets of four sub peaks (Mn1\(^{2+}\), Mn2\(^{2+}\), Mn3\(^{3+}\), Mn4\(^{4+}\)). Mn1 and Mn1’ peaks are located at 640.1 eV and 651.8 eV, which arises from broken Mn-Te bonds caused by oxidation. The strongest Mn2 and Mn2’ peaks at 641.1 and 653.4 eV are contributed by Mn\(^{2+}\) in Mn-Te bonds, indicating the major oxidation state of Mn is 2+. Mn3 and Mn3’ at 642.5 and 655.5 eV, and Mn4 and Mn4’ at 645.8 and 658.6 eV are satellite peaks of Mn1 and Mn1’, and Mn2 and Mn2’, respectively, which results from the charge transfer between the outer shell of Te and the unfilled 3d shell of Mn in the photoelectron process.\(^{35-38}\) To reveal the oxidation stability, we exposed MnBi\(_2\)Te\(_4\) crystals to air over a week, and then investigated the oxidation states with XPS. The survey spectrum in Figure S3b shows an evidently higher O 1s peak, indicating the severer oxidation owing to longer exposure to air. It is also approved by high-resolution XPS spectra. The Bi 4f spectrum in Figure 3d exhibits two strong peaks at 159.2 and 164.4 eV that can be assigned to the Bi-O bonds\(^{32}\). Similarly, Te 3d (Figure 3e) and Mn 2p (Figure 3f) spectra of oxidized MnBi\(_2\)Te\(_4\) surface displays more pronounced oxidation peaks (Te-O) and peaks arising from oxidation (Mn1 and Mn1’) than those of fresh MnBi\(_2\)Te\(_4\) surface. Interestingly, EDX and Raman results of oxidized MnBi\(_2\)Te\(_4\) in Figure S4 show no obvious difference from those of fresh MnBi\(_2\)Te\(_4\), implying that the oxidation is a surface behavior of MnBi\(_2\)Te\(_4\). Therefore, we can conclude that the surface of MnBi\(_2\)Te\(_4\) is likely to be oxidized and it is critical to keep samples in inert atmosphere especially when handling exfoliated few-layer MnBi\(_2\)Te\(_4\) samples.

**Magnetic and Transport properties.** Magnetic properties of the as-grown MnBi\(_2\)Te\(_4\) single crystal were inspected in a superconducting quantum interference device (SQUID) under zero-field-cooled (ZFC) process. Figure 4a and Figure 4b display the temperature dependence of magnetic susceptibility (\(\chi\)) for the MnBi\(_2\)Te\(_4\) single crystal in out-of-plane (\(H/\parallel c\)) and in-plane (\(H/\parallel ab\)) magnetic fields, respectively. As displayed in Figure 4a, the magnetic susceptibility of MnBi\(_2\)Te\(_4\) in \(H/\parallel c\) increases as temperature decreases and reaches a maximum at 25 K, and then begins to decrease dramatically. This antiferromagnetic transition corresponds to antiferromagnetic order originated from exchange coupling between Mn\(^{2+}\) in the neighboring SLs and displays a Neel temperature (\(T_N\)) of 25 K, which is in good consistence with previous reports\(^{20,30,31}\). Noticeably, the magnetic susceptibility approaches zero as the MnBi\(_2\)Te\(_4\) crystal is cooled down to 2 K, implying an ideal antiferromagnetic state with an out-of-plane easy axis. However, the Neel transition tends to become weaker and finally disappears as the applied out-of-plane magnetic field increases, due to the suppression and spin-flop of interlayer antiferromagnetic coupling caused by an external out-of-plane magnetic field\(^{31}\). The decrease of \(T_N\) with increasing applied magnetic field in Figure S5 also manifests the suppression of magnetic order. The inverse magnetic susceptibility above \(T_N\) shows a linear dependence of temperature above \(T_N\), which follows the Curie-Weiss (CW) law \(\chi = C / (T + \theta_{CW})\). The linear
fitting of $\chi^I$ versus $T$ provides a positive CW temperature $\theta_{CW} \approx 10$ K, and an effective magnetic moment as $\mu_{eff}^C \sim 6.2 \mu_B$ by taking the relationship $C = N_\mu \mu_{eff}^C / 3k_B$ into account. This value agrees the spin-only $\mu_{eff}$ of 5.92 $\mu_B$ for high-spin Mn$^{2+}$ ions with 3d$^5$ configuration, where $\mu_{eff} = 2 \sqrt{J(J+1)} \mu_B$, $J = 5/2$. Comparing with recently published results, it excels the previously reported magnetic moment of 4.04(13) $\mu_B$ per Mn from neutron diffraction$^{27}$, and similar to $\mu_{eff} = 5.9(1) \mu_B$ from magnetic measurements$^{30}$. The consistency between measured and calculated $\mu_{eff}$ could originate from the complete intercalation of Mn-Te bilayers into the Bi$_2$Te$_3$ QLs in this long-term synthesis strategy. We also note that the deviation from the CW law near $T_N$ possibly arises from strong spin fluctuations induced by magnetic phase transition.

As to the measurement in $H \parallel ab$, the inverse magnetic susceptibility (Figure 4b) also follows the CW law and provides an effective magnetic moment as $\mu_{eff}^{ab} \approx 5.4 \mu_B$, which is close to the spin-only $\mu_{eff} \approx 5.92 \mu_B$ for a free Mn$^{2+}$ ion. In addition, we can extract a negative Curie-Weiss temperature $\theta_{CW} \approx -8$ K, implying ferromagnetic interactions among the Mn$^{2+}$, consistent with the predicted A-type AFM feature of MnBi$_2$Te$_4$. While the magnetic susceptibility decreases dramatically below $T_N$ in $H \parallel c$, it only declines slightly below $T_N$ in $H \parallel ab$. The obvious difference of the magnetic susceptibility between in-plane and out-of-plane directions suggests an anisotropy of the AFM order. The anisotropic AFM order of MnBi$_2$Te$_4$ is further revealed in the field dependence of magnetization in Figure 4c and Figure 4d, where the field dependence of magnetization in $H \parallel c$ and $H \parallel ab$ is displayed. The magnetization displays a linear dependence and has no hint for saturation for $T > T_N$, indicating the paramagnetic state. In contrast, for $H \parallel c$ and $T < T_N$, $M$-$H$ curves increase slowly as the field is increased from zero, and exhibit a sharp increase across a critical field $\mu_0 H_{c1} \approx 3.35$ T, and turn to be linear for $\mu_0 H > \mu_0 H_{c1}$, suggesting a metamagnetic phase transition into a canted AFM state caused by field-induced suppression of magnetic order$^{20}$, in good agreement with $\chi$-$T$ curves. Lastly, the absence of hysteresis in $M$-$H$ curves is consistent with the AFM state.

Electrical transport measurements were carried out on a MnBi$_2$Te$_4$ single crystal with a thickness of $\sim 10$ $\mu$m. Figure 5a displays the metallic temperature dependence of longitudinal resistivity $\rho_x$ from 1.5 K to room temperature. A sharp transition at $\sim 25$ K corresponding to the AFM transition is consistent with $T_N$ from the magnetic property measurement. The magneto-resistivity (MR) curves measured in $H \parallel c$ at different temperatures are shown in Figure 5b. As the magnetic field is increased from zero, a sharp decrease of $\rho_x$ takes place over the critical magnetic field ($H_{c1}$) below $T_N$, which indicates the metamagnetic phase transition consistent with forenamed magnetic properties. When further increasing the magnetic field, a kink followed by a gradual decrease in $\rho_x$ emerges, suggesting that the fully polarized spin in Mn$^{2+}$ occurs at a higher critical magnetic field ($H_{c2}$). The similar electric transport behavior with both critical magnetic fields $H_{c1}$, $H_{c2}$ were also observed and reported in recent publications$^{20, 24, 27}$. Figure 5c shows the field dependence of Hall resistivity $\rho_y$, at the same temperatures. The negative slopes indicate that electron is the dominating charge carrier, possibly caused by defects such as Te deficiency or antisite disordering$^{30}$. From the linear region of Hall curves ($H < H_{c1}$), the electron density is extracted to be $2.3 \times 10^{20}$ cm$^{-3}$, and the mobility is calculated to be $\sim 630$ cm$^2$·V$^{-1}$·s$^{-1}$ at 1.5 K. Similarly, Hall curves exhibit a sharp change in the slope across $H_{c1}$ and a twist across $H_{c2}$ below $T_N$, which conforms to the sharp decrease and
kink at \( H_{c1} \) and \( H_{c2} \) in \( \rho_{xx} \) (Figure 5b), respectively.

**CONCLUSIONS**

In summary, we have developed a facile strategy to synthesize high-quality MnBi\(_2\)Te\(_4\) single crystal by prolonged annealing across a narrow temperature window. The crystal structure and quality of MnBi\(_2\)Te\(_4\), especially its septuple Te-Bi-Te-Mn-Te-Bi-Sequences and oxidation behavior, have been revealed via various characterizations. The as-grown MnBi\(_2\)Te\(_4\) single crystal exhibits an evident AFM transition at 25 K and field-induced magnetic transitions in both magnetic and transport properties, manifesting its intrinsic AFM nature. This study on the first AFM TI of MnBi\(_2\)Te\(_4\) could open an avenue on novel quantum states and topological phenomena and further inspire research on other potential AFM TIs of MBi\(_x\)Te\(_y\) (M = Cr, V, Ti, etc.)\(^{23}\).

**EXPERIMENTAL SECTION**

**Materials.** Bi (99.99%, Adamas), Mn (99.95%, Alfa Aesar), Te (99.999%, Aladdin) used as received.

**Method.** (a) Synthesis of MnTe. Polycrystalline MnTe was synthesized by directly heating the stoichiometric mixture of high-purity Mn and Te at 1273 K in a vacuum-sealed silica ampoule for 3 days. (b) Synthesis of Bi\(_2\)Te\(_3\). Bi\(_2\)Te\(_3\) crystal was synthesized by a direct solid-state reaction of the stoichiometric mixture of high-purity Bi and Te. The reaction mixture was vacuum-sealed in a silica ampoule, and heated to 1083 K and held for 24 h. After being slowly cooled to 833 K at a rate of 0.1 K min\(^{-1}\), the ampoule was quenched in air to obtain Bi\(_2\)Te\(_3\) crystal. (c) Trail 1. The product 1 was synthesized by direct heating of the stoichiometric mixture of high-purity Mn, Bi and Te at 973 K in a vacuum-sealed silica ampoule for 24 h.

**Characterization.** The powder XRD patterns were collected on a PANalytical Empyrean X-ray diffractometer using Cu Ka radiation. Raman spectra were collected on a Horiba Jobin Yvon LabRam-HR/VV Spectrometer with a 514 nm laser and an 1800 mm\(^{-1}\) grating. DTA and TG analysis (TG) were carried out on a NETZSCH STA449 F3 simultaneous thermal analyzer under N\(_2\) atmosphere, and the sample was enclosed in an Al\(_2\)O\(_3\) crucible. The heating rate was 10 K min\(^{-1}\) from room temperature to 953 K, and then cooled to 573 K at a rate of 3 K min\(^{-1}\). The SEM images and EDX spectra were collected on a FEI NOVA SEM450 scanning electron microscope. The ICP-MS analysis was carried out on a Thermo Fisher iCP QC inductively coupled plasma mass spectrometer. The HAADF-STEM images were collected on a Titan Cubed Themis G2 300 Double Aberration-Corrected Transmission Electron Microscope, while the sample for cross-sectional observation was prepared via a Zeiss Auriga focused ion beam (FIB) instrument. The XPS spectra were collected on a ULVAC PHI Quantera II X-ray Photoelectron Spectrometer.

**Magnetic Property Measurement.** Magnetic Property Measurement were carried out on a Quantum Design Superconducting Quantum Interference Device using a vibrating sample magnetometer.

**Transport measurement.** Electrical transport measurements were carried out in an cryostat (Oxford Instruments) with a base temperature of \( \sim 1.5 \) K and a magnetic field up to 9 T. The longitudinal and Hall voltages were detected simultaneously by using Stanford Research Instrument SR830 lock-in amplifiers with an AC current generated with a Keithley 6221 current
Figure 1. (a) Schematic of crystal structure of the (1 1 0) crystallographic plane of MnBi$_2$Te$_4$ (left) and Bi$_2$Te$_3$ (right). (b) PXRD pattern of MnBi$_2$Te$_4$ single crystal (top) and powder (down). Inset: an optical image of the as-grown MnBi$_2$Te$_4$ single crystal. (c) Raman spectra of MnBi$_2$Te$_4$ and Bi$_2$Te$_3$. (d) Differential thermal analysis (DTA) and thermogravimetric (TG) curves for crystalline MnBi$_2$Te$_4$. 

source.
Figure 2. (a) SEM image of exfoliated MnBi$_2$Te$_4$ single crystal. (b) HAADF-STEM image for the (0 1 0) crystallographic plane of MnBi$_2$Te$_4$, in which SLs can be clearly resolved. Inset: enlarged HAADF-STEM image superimposed with the schematic structure of the (0 1 0) crystallographic plane of MnBi$_2$Te$_4$. (c) EDX spectrum of MnBi$_2$Te$_4$ in (a). (d) SEM image and the corresponding EDX elemental mapping (Bi, Mn and Te).

Figure 3. High-resolution XPS spectra of fresh (a, b, c) and oxidized (d, e, f) surface of MnBi$_2$Te$_4$, respectively. (a, d) Bi 4f, (b, e) Te 3d and (c, f) Mn 2p spectra.
Figure 4. Magnetic properties of MnBi$_2$Te$_4$ single crystal. (a, b) Temperature dependence of magnetic susceptibility for the MnBi$_2$Te$_4$ single crystal measured under ZFC process and inverse magnetic susceptibility as a function of temperature (top x axis and right y axis). The symbol and dash line represent the experimental data and Curie-Weiss fit. Magnetic field is out-of-plane (a) and in-plane (b), respectively. (c, d) Field dependence of magnetization for the MnBi$_2$Te$_4$ crystal measured at different temperatures. Magnetic field is out-of-plane (c) and in-plane (d), respectively.

Figure 5. Transport properties of MnBi$_2$Te$_4$ single crystal. (a) Temperature dependence of longitudinal resistivity $\rho_{xx}$ measured from 1.6 K to room temperature. The sharp AFM transition is revealed near $T_N = 25$ K. (b) MR curves in an out-of-plane magnetic field at varied
temperatures. The lower and upper critical fields ($H_{c1}$, $H_{c2}$) are labeled and the temperatures for MR curves are shown by different color from 30 K to 1.5 K. (c) Magnetic field dependence of Hall resistivity traces measured at the same temperatures.

ASSOCIATED CONTENT

Supporting Information

Figure S1. Experimental and reference PXRD patterns of (a) MnTe, (b) Bi$_2$Te$_3$ and (c) Product 1. (d) Product 2.
Figure S2. HAADF-STEM image for the (0 1 0) crystallographic plane of Product 2. Inset: enlarged HAADF-STEM image superimposed with the schematic structure of the (0 1 0) crystallographic plane of MnBi₂Te₄ and Bi₂Te₃.

Figure S3. Survey XPS spectra of (a) fresh and (b) oxidized MnBi₂Te₄ surfaces.
Figure S4. (a) EDX spectrum of oxidized MnBi$_2$Te$_4$. (b) Raman spectrum of oxidized and fresh MnBi$_2$Te$_4$.

Figure S5. Suppression of $T_N$ with increasing applied magnetic fields.

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ACKNOWLEDGMENTS

This work was supported by the Basic Science Center Project of NSFC (Grant No. 51788104), the Ministry of Science and Technology of China (Grants No. 2018YFA0307100, and No. 2018YFA0305603), and the National Natural Science Foundation of China (Grant No. 11674188, U1832218).
REFERENCES

(1) Hasan, M. Z.; Kane, C. L. Colloquium: Topological insulators. Rev. Mod. Phys. 2010, 82, (4), 3045-3067.

(2) Qi, X.-L.; Zhang, S.-C. Topological insulators and superconductors. Rev. Mod. Phys. 2011, 83, (4), 1057-1110.

(3) Armitage, N. P.; Mele, E. J.; Vishwanath, A. Weyl and Dirac semimetals in three-dimensional solids. Rev. Mod. Phys. 2018, 90, (1), 015001.

(4) Haldane, F. D. M. Nobel Lecture: Topological quantum matter. Rev. Mod. Phys. 2017, 89, (4), 040502.

(5) Essin, A. M.; Moore, J. E.; Vanderbilt, D. Magnetoelectric polarizability and axion electrodynamics in crystalline insulators. Phys. Rev. Lett. 2009, 102, (14), 146805.

(6) Fu, L.; Kane, C. L. Superconducting proximity effect and majorana fermions at the surface of a topological insulator. Phys. Rev. Lett. 2008, 100, (9), 096407.

(7) Liu, E.; Sun, Y.; Kumar, N.; Muchler, L.; Sun, A.; Jiao, L.; Yang, S. Y.; Liu, D.; Liang, A.; Xu, Q.; Kroder, J.; Suss, V.; Borrmann, H.; Shekhar, C.; Wang, Z.; Xi, C.; Wang, W.; Schnelle, W.; Wirth, S.; Chen, Y.; Goennenwein, S. T. B.; Felser, C. Giant anomalous Hall effect in a ferromagnetic Kagome-lattice semimetal. Nat. Phys. 2018, 14, (11), 1125-1131.

(8) Tang, P.; Zhou, Q.; Xu, G.; Zhang, S.-C. Dirac fermions in an antiferromagnetic semimetal. Nat. Phys. 2016, 12, (12), 1100-1104.

(9) Xu, G.; Weng, H.; Wang, Z.; Dai, X.; Fang, Z. Chern semimetal and the quantized anomalous Hall effect in HgCr₂Se₄. Phys. Rev. Lett. 2011, 107, (18), 186806.

(10) Zhang, H.; Xu, Y.; Wang, J.; Chang, K.; Zhang, S.-C. Quantum Spin Hall and Quantum Anomalous Hall States Realized in Junction Quantum Wells. Phys. Rev. Lett. 2014, 112, (21), 216803.

(11) Tse, W. K.; MacDonald, A. H. Giant magneto-optical Kerr effect and universal Faraday effect in thin-film topological insulators. Phys. Rev. Lett. 2010, 105, (5), 057401.

(12) He, Q. L.; Pan, L.; Stern, A. L.; Burks, E. C.; Che, X.; Yin, G.; Wang, J.; Lian, B.; Zhou, Q.; Choi, E. S.; Murata, K.; Kou, X.; Chen, Z.; Nie, T.; Shao, Q.; Fan, Y.; Zhang, S.-C.; Liu, K.; Xia, J.; Wang, K. L. Chiral Majorana fermion modes in a quantum anomalous Hall insulator-superconductor structure. Science 2017, 357, (6348), 294-299.

(13) Chang, C. Z.; Zhao, W.; Kim, D. Y.; Zhang, H.; Assaf, B. A.; Heiman, D.; Zhang, S. C.; Liu, C.; Chan, M. H.; Moodera, J. S. High-precision realization of robust quantum anomalous Hall state in a hard ferromagnetic topological insulator. Nat. Mater. 2015, 14, (5), 473-7.

(14) Chang, C.-Z.; Zhang, J.; Feng, X.; Shen, J.; Zhang, Z.; Guo, M.; Li, K.; Ou, Y.; Wei, P.; Wang, L.-L.; Ji, Z.-Q.; Feng, Y.; Ji, S.; Chen, X.; Jia, J.; Dai, X.; Fang, Z.; Zhang, S.-C.; He, K.; Wang, Y.; Lu, L.; Ma, X.-C.; Xue, Q.-K. Experimental Observation of the Quantum Anomalous Hall Effect in a Magnetic Topological Insulator. Science 2013, 340, (6129), 167-170.

(15) Katmis, F.; Lauter, V.; Nogueira, F. S.; Assaf, B. A.; Jamer, M. E.; Wei, P.; Satpati, B.; Freeland, J. W.; Eremin, I.; Heiman, D.; Jarillo-Herrero, P.; Moodera, J. S. A high-temperature ferromagnetic topological insulating phase by proximity coupling. Nature 2016, 533, (7604), 513-6.

(16) Mogi, M.; Kawamura, M.; Yoshimi, R.; Tsukazaki, A.; Kozuka, Y.; Shirakawa, N.; Takahashi, K. S.; Kawasaki, M.; Tokura, Y. A magnetic heterostructure of topological insulators
as a candidate for an axion insulator. Nat. Mater. **2017**, *16* (5), 516-521.

(17) Xiao, D.; Jiang, J.; Shin, J. H.; Wang, W.; Wang, F.; Zhao, Y. F.; Liu, C.; Wu, W.; Chan, M. H. W.; Samarth, N.; Chang, C. Z. Realization of the Axion Insulator State in Quantum Anomalous Hall Sandwich Heterostructures. Phys. Rev. Lett. **2018**, *120* (5), 056801.

(18) Mogi, M.; Kawamura, M.; Tsukazaki, A.; Yoshimi, R.; Takahashi, K. S.; Kawasaki, M.; Tokura Y. Tailoring tricolor structure of magnetic topological insulator for robust axion insulator. Sci. Adv. **2017**, *3* (10), eaao1669.

(19) Vidal, R. C.; Bentmann, H.; Peixoto, T. R. F.; Zeugner, A.; Moser, S.; Min, C. H.; Schatz, S.; Kißner, K.; Unzelmann, M.; Fornari, C. I.; Vasili, H. B.; Valvidares, M.; Sakamoto, K.; Fujii, J.; Vobornik, I.; Kim, T. K.; Koch, R. J.; Joziwak, C.; Bostwick, A.; Denlinger, J. D.; Rotenberg, E.; Buck, J.; Hoesch, M.; Diekmann, F.; Rohlf, S.; Kallane, M.; Rossnagel, K.; Otrokov, M. M.; Chulkov, E. V.; Ruck, M.; Isaeva, A.; Reinert F. Massive Dirac Fermion at the Surface of the van der Waals Antiferromagnet MnBi₂Te₄. arXiv:1903.11826v1 Cond-Mat 2019.

(20) Lee S.H.; Zhu Y.; Wang Y.; Miao L.; Pillsbury T.; Kempinger S.; Graf D.; Alem N.; Chang C.-Z.; Samarth N.; Mao Z. Spin scattering and noncollinear spin structure-induced intrinsic anomalous Hall effect in antiferromagnetic topological insulator MnBi₂Te₄. arXiv:1812.00339 Cond-Mat 2018.

(21) Chen, B.; Fei, F.; Zhang, D.; Zhang, B.; Liu, W.; Zhang, S.; Wang, P.; Wei, B.; Zhang, Y.; Guo, J.; Liu, Q.; Wang, Z.; Wu, X.; Zong, J.; Xie, X.; Chen W.; Sun, Z.; Shen, D.; Wang, S.; Zhang, Y.; Zhang, M.; Song, F.; Zhang, H.; BWang, B. Searching the Mn(Sb,Bi)₂Te₄ family of materials for the ideal intrinsic magnetic topological insulator. arXiv:1903.09934 Cond-Mat 2019.

(22) Otrokov, M. M.; Rusinov, I. P.; Blanco-Rey, M.; Hoffmann, M.; Vyazovskaya, A. Y.; Eremeev, S. V.; Ernst, A.; Echenique, P. M.; Arnaud, A.; Chulkov, E. V. Unique Thickness-Dependent Properties of the van der Waals Interlayer Antiferromagnet MnBi₂Te₄ Films. Phys. Rev. Lett. **2019**, *122* (10), 107202.

(23) Li, J.; Li, Y.; Du, S.; Wang, Z.; Gu, B.-L.; Zhang, S.-C.; He, K.; Duan, W.; Xu, Y. Intrinsic magnetic topological insulators in van der Waals layered MnBi₂Te₄-family materials. Sci. Adv. **2019**, *5* (6), eaaw5685-eaaw5685.

(24) Deng, Y.; Yu, Y.; Shi, M. Z.; Wang, J.; Chen, X. H.; Zhang, Y. Magnetic-field-induced quantized anomalous Hall effect in intrinsic magnetic topological insulator MnBi₂Te₄. arXiv:1904.11468 Cond-Mat 2019.

(25) Yan, G.; Jingwen, G.; Jiaheng, L.; Kejing, Z.; Menghan, L.; Xiaozh, L.; Qinhua, Z.; Lin, G.; Lin, T.; Xiao, F.; Ding, Z.; Wei, L.; Canli, S.; Lili, W.; Yu, P.; Xi, C.; Yayaow, W.; Hong, Y.; Wenhui, D.; Yong, X.; Shou-Cheng, Z.; Xucun, M.; Qi-Kun, X.; Ke, H. Experimental Realization of an Intrinsic Magnetic Topological Insulator. Chin. Phys. Lett. **2019**, *36* (7), 076801.

(26) Zhang, D.; Shi, M.; Zhu, T.; Xing, D.; Zhang, H.; Wang, J. Topological Axion States in the Magnetic Insulator MnBi₂Te₄ with the Quantized Magnetoelectric Effect. Phys. Rev. Lett. **2019**, *122* (20), 206401.

(27) Liu, C.; Wang, Y.; Li H.; Wu Y.; Li Y.; Li J.; He, K.; Xu, Y.; Zhang J.; Wang Y. Quantum phase transition from axion insulator to Chern insulator in MnBi₂Te₄. arXiv:1905.00715 Cond-Mat 2019.

(28) Ge, J.; Liu, Y.; Li, J.; Li, H.; Luo, T.; Wu, Y.; Xu, Y.; Wan, J. High-Chern-Number and
High-Temperature Quantum Hall Effect without Landau Levels. *arXiv:1907.09947 Cond-Mat 2019.*

(29) Lee, D. S.; Kim, T.-H.; Park, C.-H.; Chung, C.-Y.; Lim, Y. S.; Seo, W.-S.; Park, H.-H. Crystal structure, properties and nanostructuring of a new layered chalcogenide semiconductor, Bi$_2$MnTe$_4$. *Cryst. Eng. Commun. 2013, 15, (27), 5532-5538.

(30) Zeugner, A.; Nietschke, F.; Wolter, A. U. B.; Gass, S.; Vidal, R. C.; Peixoto, T. R. F.; Pohl, D.; Damm, C.; Lubk, A.; Hentrich, R.; Moser, S. K.; Fornari, C.; Min, C. H.; Schatz, S.; Kissner, K.; Unzelmann, M.; Kaiser, M.; Scaravaggi, F.; Rellinghaus, B.; Nielsch, K.; Hess, C.; Buchner, B.; Reinert, F.; Bentmann, H.; Oeckler, O.; Doert, T.; Ruck, M.; Isaeva, A. Chemical Aspects of the Candidate Antiferromagnetic Topological Insulator MnBi$_2$Te$_4$. *Chem. Mater. 2019, 31, (8), 2795-2806.

(31) Yan, J. Q.; Zhang, Q.; Heitmann, T.; Huang, Z.; Chen, K. Y.; Cheng, J. G.; Wu, W.; Vaknin, D.; Sales, B. C.; McQueeney, R. J. Crystal growth and magnetic structure of MnBi$_2$Te$_4$. *Phys. Rev. Mater. 2019, 3, (6), 064202.

(32) Bando H.; Koizumi K.; Oikawa Y.; Daikohara K.; Kulbachinskii V.A.; Ozaki H. The time-dependent process of oxidation of the surface of Bi$_2$Te$_3$ studied by x-ray photoelectron spectroscopy. *J. Phys.: Condens. Matter 2000, 12, 5607–5616.

(33) Fu, J.; Song, S.; Zhang, X.; Cao, F.; Zhou, L.; Li, X.; Zhang, H., Bi$_2$Te$_3$ nanoplates and nanoflowers: Synthesized by hydrothermal process and their enhanced thermoelectric properties. *Cryst. Eng. Commun. 2012, 14, (6), 2159.

(34) Menke, E. J.; Brown, M. A.; Li, Q.; Hemminger, J. C.; Penner R. M. Bismuth Telluride (Bi$_2$Te$_3$) Nanowires: Synthesis by Cyclic Electrodeposition/Stripping, Thinning by Electrooxidation, and Electrical Power Generation. *Langmuir 2006, 22, (25), 10564-10574.

(35) Iwanowski, R. J.; Heinonen, M. H.; Witkowska, B. X-ray photoelectron study of NiAs-type MnTe. *J. Alloy. Compd. 2010, 491, (1-2), 13-17.

(36) Iwanowski, R. J.; Heinonen, M. H.; Janik, E. X-ray photoelectron spectra of zinc-blende MnTe. *Chem. Phys. Lett. 2004, 387, (1-3), 110-115.

(37) Iwanowski, R. J.; Heinonen, M. H.; Janik, E. Sputter cleaning and annealing of zinc-blende MnTe surface—XPS study. *Appl. Surf. Sci. 2005, 249, (1-4), 222-230.

(38) Woochul, K.; Il Jin, P.; Hyung Joon, K.; Wooyoung, L.; Sam Jin, K.; Chul Sung, K. Room-Temperature Ferromagnetic Property in MnTe Semiconductor Thin Film Grown by Molecular Beam Epitaxy. *IEEE Trans. Magn. 2009, 45, (6), 2424-2427.