Layered Manganese Bismuth Tellurides with GeBi₄Te₇- and GeBi₆Te₁₀-type Structures: Towards Multifunctional Materials

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The crystal structures of new layered manganese bismuth tellurides with the compositions Mn_{0.85(3)}Bi_{4.10(2)}Te₇ and Mn_{0.73(4)}Bi_{6.18(2)}Te₁₀ were determined by single-crystal X-ray diffraction, including the use of microfocused synchrotron radiation. These analyses reveal that the layered structures deviate from the idealized stoichiometry of the 12P-GeBi₄Te₇ (space group P3m1) and 51R-GeBi₆Te₁₀ (space group R3m) structure types they adopt. Modified compositions Mn_{1-x}Bi_{4+2x/3}Te₇ (x = 0.15 – 0.2) and Mn_{1-x}Bi_{6+2x/3}Te₁₀ (x = 0.19 – 0.26) assume cation vacancies and lead to homogenous bulk samples as confirmed by Rietveld refinements. Electron diffraction patterns exhibit no diffuse streaks that would indicate stacking disorder. The alternating quintuple-layer [M₂Te₃] and septuple-layer [M₃Te₄] slabs (M = mixed occupied by Bi and Mn) with 1:1 sequence (12P stacking) in Mn_{0.85}Bi_{4.10}Te₇ and 2:1 sequence (51R stacking) in Mn_{0.81}Bi_{6.13}Te₁₀ were also observed in HRTEM images. Temperature-dependent powder diffraction and differential scanning calorimetry show that the compounds are high temperature phases, which are metastable at ambient temperature. Magnetization measurements are in accordance with a MnII oxidation state and point at predominantly ferromagnetic coupling in both compounds. The thermoelectric figures of merit of n-type conducting Mn_{0.85}Bi_{4.10}Te₇ and Mn_{0.81}Bi_{6.13}Te₁₀ reach $zT = 0.25$ at 375 °C and $zT = 0.28$ at 325 °C, respectively. Although the compounds are metastable, compact ingots exhibit still up to 80% of the main phases after thermoelectric measurements up to 400 °C.

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Layered Manganese Bismuth Tellurides with GeBi_4Te_7 - and $\text{GeBi}_6\text{Te}_{10}$ -type Structures: Towards Multifunctional Materials

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ABSTRACT: The crystal structures of new layered manganese bismuth tellurides with the compositions $\text{Mn}_{0.85(3)}\text{Bi}_{4.10(2)}\text{Te}_7$ and $\text{Mn}_{0.73(4)}\text{Bi}_{6.18(2)}\text{Te}_{10}$ were determined by single-crystal X-ray diffraction, including the use of microfocused synchrotron radiation. These analyses reveal that the layered structures deviate from the idealized stoichiometry of the $12P$ - GeBi_4Te_7 (space group $P\bar{3}m1$) and $51R$ - $\text{GeBi}_6\text{Te}_{10}$ (space group $R\bar{3}m$) structure types they adopt. Modified compositions $\text{Mn}_{1-x}\text{Bi}_{4+2x/3}\text{Te}_7$ ($x = 0.15 - 0.2$) and $\text{Mn}_{1-x}\text{Bi}_{6+2x/3}\text{Te}_{10}$ ($x = 0.19 - 0.26$) assume cation vacancies and lead to homogenous bulk samples as confirmed by Rietveld refinements. Electron diffraction patterns exhibit no diffuse streaks that would indicate stacking disorder. The alternating quintuple-layer $[\text{M}_2\text{Te}_3]$ and septuple-layer $[\text{M}_3\text{Te}_4]$ slabs ($\text{M} = \text{mixed occupied by Bi and Mn}$) with 1:1 sequence ($12P$ stacking) in $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and 2:1 sequence ($51R$ stacking) in $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ were also observed in HRTEM images. Temperature-dependent powder diffraction and differential scanning calorimetry show that the compounds are high-temperature phases, which are metastable at ambient temperature. Magnetization measurements are in accordance with a Mn^{II} oxidation state and point at predominantly ferromagnetic coupling in both compounds. The thermoelectric figures of merit of n -type conducting $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ reach $zT = 0.25$ at 375°C and $zT = 0.28$ at 325°C , respectively. Although the compounds are metastable, compact ingots exhibit still up to 80% of the main phases after thermoelectric measurements up to 400°C .

1 Introduction

Layered chalcogenides have received much attention due to their exceptional properties. These include topologically non-trivial electronic structures, charge-density waves, superconductivity or promising thermoelectric properties.¹⁻⁷ For thermoelectric waste-heat recovery and Peltier cooling near room temperature (RT), the layered semiconductor Bi_2Te_3 and its substitution variants with Sb and Se are used in technical applications.⁸ The thermoelectric performance of Bi_2Te_3 has been optimized e.g. by Se substitution and Cu doping.⁹ In addition to its thermoelectric properties, angle-resolved photoemission spectroscopy (ARPES) has proved that Bi_2Se_3 and Bi_2Te_3 are topological insulators.^{3,12-14} Variants of Bi_2Te_3 or Bi_2Se_3 doped with transition metals such as Cr or Fe exhibit different magnetic interactions caused by the dopants; they may represent a new class of magnetic topological insulators in the field of spintronics.^{15,16} Probably motivated by its natural abundance, Mn, has widely been used as a dopant in Bi_2Te_3 ; and structural, electrical and magnetic properties have been studied.¹⁷⁻²² For example, thin-film topological insulators based on Mn- or Cr-doped Bi_2Te_3 are potential candidates for highly sensitive anomalous Hall effect sensors.^{17,23} In contrast to the

ordinary Hall effect caused by the Lorentz force, the anomalous Hall effect arises from the spin-orbit interaction of spin-polarized charge carriers in conductive ferromagnetic materials and provides an alternative approach for magnetic sensing.

Layered Bi_2Te_3 exhibits a $15R$ stacking sequence of three slabs per unit cell separated by van der Waals gaps (cf. Section 3.3, Fig. 5), each slab composed of double layers of $[\text{BiTe}_6]$ octahedra often called “quintuple layer” as it consists of five atom layers. Many compounds can be derived from Bi_2Te_3 by formally inserting $Tt\text{Te}$ ($Tt = \text{Pb, Ge, Sn}$) units.²⁴ In addition to its thermoelectric behavior, SnBi_2Te_4 shows a pressure-induced electronic topological transition between 3.5 and 5.0 GPa.²⁵ ARPES yields evidence for topological surface states with Dirac dispersion in the indirect bandgap of bulk $\text{Pb}(\text{Bi}_{2-x}\text{Sb}_x)\text{Te}_4$.²⁶ The GeBi_2Te_4 -type structure of these compounds is described by a $21R$ stacking sequence, whose “septuple” layers comprise three triple layers of condensed octahedra as described by ${}^2_\infty[\text{Te}_{3/3}\text{M}(\mu\text{-Te}_{3/6})\text{M}(\mu\text{-Te}_{3/6})\text{MTe}_{3/3}]$ ($\text{M} = \text{Ge, Bi}$; usually disordered), again separated by van der Waals gaps.^{27,28} Formally adding one Bi_2Te_3 -type quintuple layer per GeBi_2Te_4 -type septuple building block results in the GeBi_4Te_7 structure type with a $12P$ stacking sequence.^{27,29}

Insertion of a second Bi_2Te_3 -type layer results in the $\text{GeBi}_6\text{Te}_{10}$ structure type, described by a 51R stacking sequence. From another point of view, these structures can be understood as consisting of distorted rocksalt-type slabs similar to those in GeBi_2Te_4 and in Bi_2Te_3 , separated by van der Waals gaps.²⁴ Mn doping and its influence on the thermoelectric properties was also reported for the layered compound $\text{Ge}_4\text{Sb}_2\text{Te}_7$ crystallizing with a $\text{Ge}_3\text{As}_2\text{Te}_6$ -type structure.³⁰ MnBi_2Te_4 has been reported to be the first compound of the series $M\text{Te}(\text{Bi}_2\text{Te}_3)_n$ where M is a transition metal represented by manganese.³¹ Single-crystal data of MnBi_2Te_4 revealed Mn/Bi antisite disorder; the magnetic properties are strongly anisotropic and antiferromagnetic ordering is observed below 24 K.^{32,33} Investigations on the phase diagram of the system Mn/Bi/Te indicated that there are further layered compounds in that system,³⁴ and estimates concerning their structures were suggested. In heterostructured $\text{Bi}_2\text{Se}_3/\text{MnBi}_2\text{Se}_4$ thin films, which were grown by means of molecular beam epitaxy, MnBi_2Se_4 crystallizes in the same structure type as bulk MnBi_2Te_4 .³⁵ We have now synthesized further members of the homologous series $(\text{MnTe})(\text{Bi}_2\text{Te}_3)_n$ with GeBi_4Te_7 -type^{27,29} or $\text{GeBi}_6\text{Te}_{10}$ -type²⁴ structures. According to single-crystal X-ray data, single-phase syntheses and chemical analyses, their chemical compositions significantly deviate from the idealized formulae. Measurements of transport properties with respect to thermoelectric behavior represent one step towards characterizing these potential multifunctional materials.

2 Experimental

Synthesis: Bulk samples were obtained from the elements Mn (chunks, Onyxmet, 99.9%), Bi (Alfa Aesar, 99.999%) and Te ingots (Haines & Maassen, 99.9%). Mn was heated under vacuum with small silica glass powder at 1000 °C for 1 day to completely remove brownish MnO_2 from the surface. After this cleaning procedure, Mn was stored under argon to avoid oxidation. Stoichiometric mixtures (approximately 2 g) of the elements according to the various sum formulae mentioned in the following sections were sealed in graphitized flat-bottomed silica glass ampules (inner diameter: 12 mm, wall thickness: 1.5 mm) under argon atmosphere, placed in tube furnaces and heated from RT to 950 °C. The samples were kept at these conditions for 1 d and subsequently cooled to RT by quenching at air. The resulting ingots were then annealed at 575 °C for 1 week, again followed by quenching at air. Disc-shaped ingots used for thermal conductivity measurements were obtained by using flat-bottomed silica-glass ampules. The samples were polished to a plane-parallel thickness of 1.07 mm ($\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$) or 1.29 mm ($\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$), by using SiC grinding powder. Cuboid-shaped samples for measurements of the electrical conductivity and the Seebeck coefficient were fabricated using a diamond wire saw and polished with SiC grinding powder. The samples are dark gray with metallic luster. Upon exposure to air over months, no hydrolysis, oxidation or decomposition were observed, even for powder samples.

Powder diffraction: For powder X-ray diffraction (PXRD) at RT, the samples were crushed and spread on Mylar foil. Data were

recorded on a Huber G670 diffractometer (Guinier geometry with imaging-plate detector and integrated read-out system) using $\text{Cu-K}\alpha_1$ radiation [$\text{Ge}(111)$ monochromator, $\lambda = 1.54051 \text{ \AA}$]. WINXPOW³⁶ was used for data evaluation and TOPAS³⁷ for Rietveld refinements. Reflection profiles were described with fundamental parameters using a direct convolution approach. Crystallite strain was described using a Voigt function, and preferred orientation was refined with spherical harmonics of the 4th order. The background of each diffraction pattern was modelled by a set of 18 parameters (shifted Chebychev polynomial). Structure models with their equivalent isotropic displacement parameters were taken from the single-crystal data. Temperature-dependent measurements in rotating silica glass capillaries under dry Ar atmosphere were obtained with synchrotron radiation (beamline ID11, ESRF, Grenoble) on a Huber diffractometer ($\lambda = 0.18972 \text{ \AA}$) with a FReLoN 2K CCD detector.⁴⁴ A hot-gas blower (GSB 1300, FMB Oxford) with a maximal heating rate of 20 K min^{-1} was used. For temperature calibration, hexagonal BN was used since its c lattice parameter increases with temperature almost linearly.³⁸ In order to adjust the measured temperatures of the heating and cooling curves according to the calibration, a second-order polynomial fit was used for interpolation.

Single-crystal X-ray diffraction: X-ray diffraction data of a $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ single-crystal were obtained on a STOE STADIVARI diffractometer ($\text{Ag-K}\alpha_1$ radiation, $\lambda = 0.56086 \text{ \AA}$) with a Dectris Pilatus 300k detector. Integration was done with X-Area³⁹ and numerical absorption correction using X-RED⁴⁰ and X-SHAPE.^{41,42} Single-crystal diffraction data of $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ were obtained using microfocused synchrotron radiation (beamline ID11, ESRF, Grenoble)⁴³ on a Huber diffractometer ($\lambda = 0.30996 \text{ \AA}$) with a FReLoN 2K CCD detector.⁴⁴ Integration was done using CrysAlis Pro⁴⁵ and semiempirical absorption correction was applied with SADABS.⁴⁶ Incomplete absorption in the CCD phosphor as a function of beam incidence was taken into account.⁴⁷ Solution and refinement of both structures was done with SHELX-2014.⁴⁸ Further details on the crystal structure analyses can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers 1891486 ($\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$) and 1891488 ($\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$). Crystal structures were visualized with Diamond.⁴⁹

Thermal analysis: $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ powders were analyzed by means of differential scanning calorimetry (DSC) using a Setaram Labsys ATD-DSC device with k-probe (Ni-Cr/Ni-Al; $T_{\text{max}} = 800 \text{ °C}$) thermocouples and Al_2O_3 as a reference compound. Weighted amounts of each specimen (ca. 50 mg) were sealed in small evacuated silica ampules and exposed to two consecutive heating and cooling cycles from RT up to 800 °C at the rate of 2 K min^{-1} .

Electron microscopy: Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were done using a Zeiss LEO 1530 instrument (acceleration voltage 20 kV) equipped with an EDX detector (INCA software,⁵⁰ Oxford Instruments). Selected-area electron diffraction (SAED), high-

resolution transmission electron microscopy (HRTEM) and further EDX were executed on a Philips CM-200 STEM (LaB₆ cathode, 200 kV, super-twin lens, point resolution 0.23 nm) equipped with RTEM 136-5 EDX detector (EDAX, Genesis software⁵¹). A double-tilt low-background sample holder (Gatan) was used. For TEM investigations, the bulk material was manually cut with a diamond saw, glued on a copper ring, mechanically ground to a thickness of approximately 30 µm, polished using a dimple grinder (Gatan) and finally Ar-ion-thinned (Duo-Mill, Gatan). Evaluation of SAED data was done using the AnalySIS software.⁵² For HRTEM and SAED simulations, jEMS⁵³ was used. Micrographs and diffraction patterns were evaluated using Digital Micrograph.⁵⁴

Thermoelectric characterization: Thermal diffusivity (κ) was measured under He atmosphere using a Linseis LFA1000 apparatus equipped with an InSb detector (aperture diameter 3 mm). Simultaneous heat loss and finite pulse corrections were applied using Dusza's model.⁵⁵ Values were averaged from five measurement points at each temperature. For κ calculation, they were multiplied with the Dulong-Petit heat capacity (Mn_{0.85}Bi_{4.10}Te₇: $C_p = 0.1659 \text{ J g}^{-1} \text{ K}^{-1}$; Mn_{0.81}Bi_{6.13}Te₁₀: $C_p = 0.1624 \text{ J g}^{-1} \text{ K}^{-1}$) and the density as derived by the weight and the volume determined by Archimedes' principle with a precision of 0.03 g cm^{-3} (Mn_{0.85}Bi_{4.10}Te₇: 7.53 g cm^{-3} ; Mn_{0.81}Bi_{6.13}Te₁₀: 7.65 g cm^{-3}). Densities were at least 98.5% of the corresponding X-ray densities. DSC measurements (cf. Fig. S1 – S denotes items in the *Electronic Supplementary Information*, ESI[†]) confirm that C_p corresponds to the Dulong-Petit value within experimental error although DSC measurements of Bi₂Te₃⁵⁶ indicate that C_p near RT is still below the Dulong-Petit value. However, other related compounds such as (Sn_{1-x}Pb_x)Bi₂Te₄⁵⁷ or GeBi₄Te₇⁵⁸ reach this value near RT. The Seebeck coefficient S (in $\mu\text{V K}^{-1}$) and the electrical conductivity σ (in S cm^{-1}) were measured on cuboid samples (Mn_{0.81}Bi_{6.13}Te₁₀: $8.13 \text{ mm} \times 1.25 \text{ mm} \times 1.76 \text{ mm}$, Mn_{0.85}Bi_{4.10}Te₇: $6.92 \text{ mm} \times 1.09 \text{ mm} \times 1.91 \text{ mm}$) simultaneously under He atmosphere using a Linseis LSR-3 instrument with NiCr/Ni and Ni contacts and a continuous reversal of the polarity of the thermocouples (bipolar setup). Measurements comprised three heating/cooling cycles 50–400–50 °C with 25 °C steps at 10 K min^{-1} heating rate and three data points per temperature. The errors of S and σ are smaller than 10%; for κ , they are ca. 5%. The combined uncertainty may amount to $\sim 15\%$ for the zT value.

Magnetic measurements: Temperature- and field-dependent magnetic measurements were performed on pressed powder samples (ca. 10 mg) using a Superconducting Quantum Interference Device (SQUID) magnetometer (MPMS[®]3) from Quantum Design. Temperature-dependent zero-field-cooled (ZFC) and field-cooled (FC) warming magnetization measurements were performed at magnetic fields of 0.02 T and 1 T in the temperature range from 2–320 K and field-dependent magnetization measurements were done at 2 K and at 300 K.

3 Results and discussion

3.1 Phase composition and homogeneity

Compounds with nominal compositions MnTe(Bi₂Te₃)_n with $n = 2$ or 3 may be expected to crystallize in the GeBi₄Te₇^{27,29} or GeBi₆Te₁₀²⁴ structure types. Corresponding reactions, however, did not lead to single-phase samples. Samples with the nominal composition MnBi₄Te₇ contain two phases, i.e. a mixture of GeSb₂Te₄-type and GeBi₄Te₇-type compounds (Fig. S2, ESI[†]). The nominal composition MnBi₆Te₁₀ yields a mixture GeBi₄Te₇-type and GeBi₆Te₁₀-type phases (Fig. S3, ESI[†]). In contrast, nominal compositions such as Mn_{0.85}Bi_{4.10}Te₇ (derived from single-crystal data, cf. section 3.3) and Mn_{0.81}Bi_{6.13}Te₁₀ (which was suggested by preliminary single-crystal data) lead to samples that appear to be single-phase according to Rietveld refinements based on PXRD data (Fig. 1 and Tables S1, S2, and S3 in the ESI[†]). In both cases, the refined parameters of the single-crystal structure analyses were used for the Rietveld refinement and only lattice parameters were refined. For GeBi₆Te₁₀-type samples, they agreed with those of the single-crystal. For Mn_{0.85}Bi_{4.10}Te₇, lattice parameters from PXRD differ slightly from those of the single crystal but correspond to those of the GeBi₄Te₇-type phase in heterogeneous samples with the nominal composition MnBi₆Te₁₀, from which the single crystal was isolated (Table S4, ESI[†]). The deviations from the stoichiometric compositions GeBi₄Te₇ and GeBi₆Te₁₀ are consistent with the EDX data obtained from Mn_{0.85}Bi_{4.10}Te₇ and Mn_{0.81}Bi_{6.13}Te₁₀ bulk samples (Table S5, ESI[†]). The measured Mn concentrations match the nominal compositions significantly better than those expected for stoichiometric MnBi₄Te₇ and MnBi₆Te₁₀. Very small amounts of a manganese telluride side phase were detected in the bulk sample Mn_{0.85}Bi_{4.10}Te₇ by SEM-EDX; in Mn_{0.81}Bi_{6.13}Te₁₀, however, appeared to be phase-pure (Fig. S4, ESI[†]). Note that nominal compositions Mn_{0.92}Bi_{4.08}Te₇ and Mn_{0.85}Bi_{6.15}Te₁₀ derived from refinements not assuming charge neutrality (section 3.3) but full occupation of all Wyckoff positions yield no single phases according to Rietveld refinements, at least not with the synthesis route described above (Fig. S5, ESI[†]).

The composition has been varied in order to check whether the compounds form solid solutions. Charge neutrality assuming Mn^{II}, Bi^{III}, Te^{-II} and cation vacancies was taken into account as these compounds exhibit small bandgaps (section 3.6). The composition can be varied in the range of $x = 0.15 - 0.20$ for Mn_{1-x□_{x/3}}Bi_{4+2x/3}Te₇ and in the range of $x = 0.19 - 0.26$ for Mn_{1-x□_{x/3}}Bi_{6+2x/3}Te₁₀. The homogeneity of the corresponding bulk samples has been confirmed by Rietveld refinements and EDX measurements (see Fig. S6, and Table S6, ESI[†]). Lattice parameters do not change significantly (Tables S4, and S7, ESI[†]). This might be due to vacancies compensating the effect of different atom radii.

Fig. 1 PXRD patterns of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (left) and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ (right); Rietveld refinements taking into account structure models based on SCXRD refinements (section 3.3) for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (GeBi_4Te_7 -type structure), $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ ($\text{GeBi}_6\text{Te}_{10}$ -type structure, the slightly different Mn content has no influence on the Rietveld refinement); experimental data (black points), fitted curves (gray) and difference plots (black, below); reflection markers correspond to the GeBi_4Te_7 structure type (left) and the $\text{GeBi}_6\text{Te}_{10}$ structure type (right), respectively.

3.2 Stability of manganese bismuth tellurides with GeBi_4Te_7 or $\text{GeBi}_6\text{Te}_{10}$ structure type as a function of particle size

Annealing at 585 °C and subsequent quenching affords phase-pure samples of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ with GeBi_4Te_7 -type structure and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ with $\text{GeBi}_6\text{Te}_{10}$ -type structure according to PXRD patterns. Temperature-programmed PXRD data show no changes except thermal expansion up to ca. 210 °C (Fig. 2). At this temperature, both compounds start decomposing into phases with Bi_2Te_3 structure type and a Mn-rich phase as visible in samples after thermoelectric measurements (section 3.6, Fig. S7, ESI[†]). The decomposition of fine powdered samples is complete at 270 °C for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and at 295 °C for $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$. Fig. 2 shows the disappearance of characteristic low-angle reflections of the long-periodic structures and the emergence of typical reflections of the Bi_2Te_3 structure type upon decomposition (Fig S8, ESI[†]). Temperature-programmed PXRD data of MnBi_2Te_4 show similar decomposition.^{31,32} Reference 34 does not report this decomposition as temperature-dependent PXRD was not used but is crucial to detect the metastability. In addition, the decomposition of bulk samples is much slower as discussed later in this chapter. As this decomposition extends over a wide temperature range, it cannot be detected in DSC measurements (Fig. 3 and Fig. 4), which has been discussed in detail for MnBi_2Te_4 .³² However, there are characteristic DSC signals for other effects, whose tentative assignment is listed for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ in Table S8 and Fig. S9 (ESI[†]) and for $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ in Table S9 and Fig. S10 (ESI[†]). Upon heating of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$, two endothermic signals are observed (Fig. 3). We attribute the first signal to the melting of Bi_2Te_3 (a shoulder on the low-temperature side of the first signal) and of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$, since the starting material was partially decomposed (Fig. S11, ESI[†]). It is followed by the melting of another compound, possibly MnBi_2Te_4 , whose slow

exothermic formation is unlikely to be detected.^{32,33} The first cooling curve shows three exothermic signals, which can be assigned to the solidification of Bi_2Te_3 , $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and MnBi_2Te_4 , respectively, as tentatively confirmed by PXRD (Fig. S12, ESI[†]). The second heating cycle is similar.

Fig. 2 Temperature-programmed PXRD starting from phase-pure samples with the compositions (a) $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and (b) $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$, synchrotron radiation ($\lambda = 0.18972$ Å), heating rate 20 K min⁻¹.

Fig. 3 DSC of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$: first heating (top) and cooling (bottom) curves.

Fig. 4 DSC of $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$: first heating (top) and cooling (bottom) curves.

The DSC curve upon heating of $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ shows four endothermic signals (Fig. 4). The first one might indicate small amounts of a Bi-rich bismuth telluride, which could form next to MnTe_2 by redox decomposition (compare Fig. S13, ESI†). In analogy with the above interpretation for the $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ sample, the following signals probably correspond to the almost simultaneous melting of Bi_2Te_3 and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$, then of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$, and of MnBi_2Te_4 . The cooling curve hosts a broad unstructured signal that may indicate glassy behavior or partial crystallization of disordered compounds (Fig. 4). We speculate that just above the melting point of Bi_2Te_3 , the Mn-containing ternaries undergo a series of stepwise structure transformations. The DSC experiment was probably too fast to resolve these transitions. PXRD after the DSC measurement indicates a Bi_2Te_3 -type structure mixed with GeBi_4Te_7 - and $\text{GeBi}_6\text{Te}_{10}$ - and possibly GeBi_2Te_4 -type structures (Fig. S14, ESI†). The second DSC heating cycle is similar but shows fewer signals during heating (Table S9 and Fig. S10, ESI†).

Due to these complex phase relationships, manganese bismuth tellurides with GeBi_4Te_7 -type or $\text{GeBi}_6\text{Te}_{10}$ -type structure cannot be obtained by quenching or slowly cooling the melt. Annealing in the existence range of the compounds is essential. As they constitute high-temperature phases that decompose at lower temperatures, quenching after the annealing step is beneficial.

However, *ex situ* SEM images and EDX measurements after three heating cycles up to 400 °C, which were performed for thermoelectric characterization (section 3.6), show that the decomposition is much slower in compact ingots; the samples still consist mainly of the initial phase (Fig. S15 and Table S10, ESI†). Corresponding Rietveld refinements reveal ca. 80% of the main phase along with possibly Mn-doped Bi_2Te_3 ⁵⁹ (space group $R\bar{3}m$) and MnTe_2 ⁶⁰ with pyrite-type structure (space group $Pa\bar{3}$) (Fig. S7, ESI†). Thus, the metastability with respect to decomposition is best shown using very fine powders.

As mentioned above, this metastability was also observed for MnBi_2Te_4 , where the decomposition products should be non-stoichiometric Bi-rich bismuth tellurides^{61–63} “ $\text{Bi}_2\text{Te}_{3-x}$ ” and MnTe_{2-y} .^{31,32} According to temperature-programmed PXRD, GeBi_4Te_7 - and $\text{GeBi}_6\text{Te}_{10}$ -type compounds are not formed from decomposed samples during cooling (Fig. S16 and S17, ESI†). This could mean that the reaction is too slow at 500 °C and below, or that the decomposition products are spatially segregated, resulting in strongly inhibited solid-state reactivity. A possible reason for the increased stability of the bulk material compared to the finely ground samples could be that the metastable compounds decompose faster after many defects were brought into the crystal structure by crushing and that stresses in compact samples may hinder decomposition. In order to exclude alternative explanations such as reactions with the silica-glass capillary or impurities, crushed samples of $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ and $\text{Mn}_{0.85}\text{Bi}_{4.15}\text{Te}_7$ were annealed in silica-glass ampoules at 300 °C for 1 day, so that most of the single phases decomposed to a Bi-rich Bi_2Te_3 -like phase and MnTe_2 (pyrite type, $Pa\bar{3}$) (Fig. S18, ESI†). After this treatment, the samples were used as starting material for our synthesis route, i.e. they were melted again, followed by annealing and quenching. This again leads to phase-pure samples according to PXRD (Fig. S19, ESI†).

3.3 Crystal structures of $\text{Mn}_{0.85(3)}\text{Bi}_{4.10(2)}\text{Te}_7$ and $\text{Mn}_{0.73(4)}\text{Bi}_{6.18(2)}\text{Te}_{10}$

The crystal structures of representative crystals of manganese bismuth tellurides with GeBi_4Te_7 -type and $\text{GeBi}_6\text{Te}_{10}$ -type structures were elucidated from X-ray diffraction data. In the structure refinements, charge neutrality was used as a constraint assuming oxidation states of II for Mn and III for Bi. The presence of Mn^{II} is also in accordance with the magnetization measurements, i.e., the effective moment μ_{eff} is in agreement with the value expected for Mn^{II} for both compounds (cf. section 3.5). Furthermore, other oxidation states seem unlikely as the oxidation potential of Te is not expected to enable higher oxidation states of the cations. Lower oxidation states of Bi are typically characterized by

homoatomic bonds.⁶⁴ In the related compound MnBi_2Te_4 , the exclusive presence of Mn^{2+} was shown by X-ray absorption spectroscopy and confirmed by magnetic susceptibility measurements.^{32,33} Mixed occupancies of Mn and Bi on all cation sites were refined as indicated by the scattering density present and the resulting R -values. Cation vacancies were assumed to be located only on the Wyckoff positions $1b$ for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $3a$ for $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$, which represent the center of the GeBi_2Te_4 -type building blocks, since vacancies close to the van der Waals gaps are very unfavorable due to a resulting very low coordination number 2 for Te atoms at the van der Waals gap.

Fig. 5 Crystal structures of a) $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ with $\text{GeBi}_6\text{Te}_{10}$ -type structure; b) $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ with GeBi_4Te_7 -type structure; c) $\text{Mn}_{0.85}\text{Bi}_{2.1}\text{Te}_4$ ³² with GeBi_2Te_4 -type structure; d) Bi_2Te_3 ²⁴ – for cation distribution, including mixed sites, cf. Tables 2 and 4 (M1 is the Mn-rich site).

Mn_{0.85(3)}Bi_{4.10(2)}Te₇

Crystallographic data and details of the structure refinement for a crystal with the refined composition Mn_{0.85(3)}Bi_{4.10(2)}Te₇ isolated from a heterogeneous sample with the nominal composition MnBi₆Te₁₀ are listed in Table 1, atomic positions and displacement parameters are given in Table 2. In contrast to Mn/Bi intermixing on the cation sites, the vacancy concentration of 5.1(17) % on the 1*b* site seems not very significant; the assumption of an idealized composition MnBi₄Te₇ results in almost the same residuals ($R1 = 0.0332$ for $I > 2\sigma(I)$). However, such an idealized composition yields no single-phase samples (cf. section 3.1). The EDX analysis of the investigated crystal (Fig. S20, ESI[†]) yields the composition Mn_{5.8(5)}Bi_{35.9(5)}Te_{58.3(3)}, which confirms a deficiency of Mn in good agreement with the nominal composition of Mn_{0.85}Bi_{4.10}Te₇ = Mn_{7.1}Bi_{34.3}Te_{58.6} (Table S11, ESI[†]).

A refinement without assuming charge neutrality but full site occupancies (i.e., no vacancies) also results in similar *R*-values and a composition Mn_{0.92}Bi_{4.08}Te₇; however, corresponding reactions also yield no single-phase products (cf. section 3.1). Mn_{0.85}Bi_{4.10}Te₇ crystallizes in the space group $P\bar{3}m1$ and can be described by a 12*P* stacking sequence with two different building blocks (Fig. 5b): double layers of edge-sharing [BiTe_{3/3}Te_{3/6}] octahedra similar to those in Bi₂Te₃²⁴ (Fig. 5d) and GeBi₂Te₄-type (Fig. 5c) septuple layers of condensed octahedra described by $^2_{\infty}[\text{Te}_{3/3}M(\mu\text{-Te}_{3/6})M(\mu\text{-Te}_{3/6})M\text{Te}_{3/3}]$. The atomic interaction within each layer is much stronger than the interlayer van-der-Waals-like bonding. Similar lattice parameters were reported for Mn-doped BiTe (space group $P\bar{3}m1$; $a = 4.3783(1)$ Å, $c = 23.8107(8)$ Å),⁶⁵ whose BiSe-type structure consists of Bi₂Te₃-like layers separated by double layers of Bi atoms resembling those in elemental Bi. However, such a structure model cannot reproduce our diffraction data.

Mn_{0.73(4)}Bi_{6.18(2)}Te₁₀

Crystallographic data and details of the structure refinement for a crystal with the refined composition Mn_{0.73(4)}Bi_{6.18(2)}Te₁₀ isolated from a heterogeneous sample with the nominal composition MnBi₆Te₁₀ are given in Table 1; atomic positions and displacement parameters are listed in Table 3. Based on the above mentioned constraints, the refinement yields a significant vacancy concentration of 9(2) % on the site 1*b*. Constraining to the stoichiometric composition MnBi₆Te₁₀ leads to higher residuals ($R1 = 0.0315$ for $I > 2\sigma(I)$) and such an idealized composition does not lead to single-phase samples (cf. section 3.1). Assuming full occupancies without constraining to charge neutrality yields a composition of Mn_{0.85}Bi_{6.15}Te₁₀, again not suitable for the synthesis of single-phase samples. The EDX analysis of the crystal used for data collection (Fig. S21 and Table S12, ESI[†]) confirms a Mn Mn_{0.73}Bi_{6.18}Te₁₀ obtained in the structure refinement. In space group $R\bar{3}m$, the asymmetric unit consists of distorted NaCl-type septuple building blocks similar to those in GeBi₄Te₇, which are separated by two Bi₂Te₃-like layers, resulting in a deficiency and is in good agreement with the composition 51*R* stacking sequence (Fig. 5a). Again, Mn/Bi intermixing,

especially on the 3*a*, is a characteristic feature of this structure.

Table 1 Crystallographic data for the single-crystal structure determination of Mn_{0.85(3)}Bi_{4.10(2)}Te₇ with GeBi₄Te₇-type structure and Mn_{0.73(4)}Bi_{6.18(2)}Te₁₀ with GeBi₆Te₁₀-type structure.

chemical formula	Mn _{0.85(3)} □ _{0.05(2)} Bi _{4.10(2)} Te ₇	Mn _{0.73(4)} □ _{0.09(2)} Bi _{6.18(2)} Te ₁₀
<i>M</i> (in g mol ⁻¹)	1796.72	2608.1
<i>F</i> (000)	726	3154
crystal system / space group	trigonal / $P\bar{3}m1$ (no. 164)	trigonal / $R\bar{3}m$ (no. 166)
lattice parameters (in Å)	$a = 4.3591(3)$, $c = 23.769(2)$	$a = 4.3698(3)$, $c = 101.829(8)$
<i>V</i> (in Å ³)	391.41(6)	1683.9(3)
<i>Z</i>	1	3
ρ (in g cm ⁻³)	7.63	7.72
μ (in mm ⁻¹)	32.26	13.45
absorption correction	numerical	semiempirical ⁴⁶
radiation	Ag-K α , $\lambda = 0.56086$ Å	synchrotron, $\lambda = 0.30996$ Å
independent reflections	594	723
<i>d</i> _{min} (in Å)	0.68	0.72
refined	27 / 3	36 / 4
parameter / restraints		
$\theta_{\min} / \theta_{\max}$ (in °)	2.03 / 24.30	1.83 / 12.43
extinction coefficient	-	0.0045(3)
<i>R</i> _σ / <i>R</i> _{int}	0.0322 / 0.0649	0.0549 / 0.0706
<i>R</i> indices	$R1 = 0.0331$, $wR2 = 0.0874$	$R1 = 0.0303$, $wR2 = 0.0703$
[<i>I</i> > 2σ(<i>I</i>)]		
<i>R</i> indices (all data)	$R1 = 0.0357$, $wR2 = 0.0895$	$R1 = 0.0312$, $wR2 = 0.0712$
<i>GoF</i> (all)	1.08	1.20
$\Delta\rho_{\min} / \Delta\rho_{\max}$ (in e Å ⁻³)	-1.52 / 1.53	-3.19 / 2.10

Table 2 Wyckoff positions, atomic coordinates, site occupancies and coefficients of the anisotropic as well as equivalent isotropic displacement parameters (in Å²) of Mn_{0.85}Bi_{4.10}Te₇ ($U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$).

Atom	W. p.	x	y	z	occ.
Mn1/ Bi1/ □	1b	0	0	1/2	0.694(11)/ 0.255(6)/ 0.051(17)
Mn2/ Bi2	2d	1/3	2/3	0.3423	0.0414(4)/ 0.959(3)
Mn3/ Bi3	2d	1/3	2/3	0.0860	0.035(3)/ 0.965(3)
Te1	2d	1/3	2/3	0.5680	1
Te2	2c	0	0	0.2703	1
Te3	2d	1/3	2/3	0.8413	1
Te4	1a	0	0	0	1
Atom	$U_{11}=U_{22}=2U_{12}$	U_{33}	$U_{23}=U_{13}$	U_{eq}	
Mn1/ Bi1/□	0.0334(7)	0.0314(10)	0	0.0328(6)	
Mn2/ Bi2	0.0315(2)	0.0368(4)	0	0.0333(2)	
Mn3/ Bi3	0.0300(3)	0.0352(3)	0	0.0318(2)	
Te1	0.0336(3)	0.0291(5)	0	0.0321(3)	
Te2	0.0295(3)	0.0315(5)	0	0.0302(3)	
Te3	0.0290(3)	0.0308(5)	0	0.0296(3)	
Te4	0.0269(4)	0.0269(6)	0	0.0269(3)	

Comparison of selected interatomic distances with Bi₂Te₃ and Mn_{0.85}Bi_{2.1}Te₄³²

Selected interatomic distances are listed in Table S13 (ESI⁺). Bond lengths in the Bi₂Te₃-like quintuple layers in Mn_{0.85}Bi_{4.10}Te₇, i.e. $d(M3-Te) = 3.0543(7)$ Å and $d(M3-Te4) = 3.2410(4)$ Å (labelling cf. Fig. 5), deviate by only 0.4% from interatomic distances in Bi₂Te₃⁶⁶ itself [$d(Bi-Te2) = 3.067$ Å, $d(Bi-Te1) = 3.254$ Å]; they are slightly shorter by ~0.01 Å as the cation position contains 3% – 4% of Mn²⁺, whose radius (0.81 Å for CN 6), which is smaller than that of Bi³⁺ (1.17 Å for CN 6).⁶⁷ The quintuple layers in Mn_{0.73(4)}Bi_{6.18(2)}Te₁₀ [$d(M3-Bi3) = 3.0628(5)$ Å, $d(M3-Te4) = 3.2395(5)$ Å, $d(M4-Te4) = 3.2536(5)$ Å, $d(M4-Te5) = 3.0594(5)$ Å] exhibit the same tendency and deviate only up to 0.4% from the interatomic distances in Bi₂Te₃. All cation-anion bond lengths in the septuple slab of Mn_{0.85}Bi_{4.10}Te₇ [$d(M2-Te2) = 3.0436(7)$ Å, $d(M2-Te1) = 3.2987(9)$ Å, $d(M1-Te1) = 2.9909(7)$ Å] and Mn_{0.73}Bi_{6.18}Te₁₀ [$d(M2-Te2) = 3.0473(5)$ Å, $d(M2-Te1) = 3.3055(6)$ Å, $d(M1-Te1) = 2.9969(4)$ Å] host more bismuth are thus slightly longer than the corresponding bond lengths in Mn_{0.85}Bi_{2.1}Te₄ [$d(M1-Te2) = 3.027(1)$ Å, $d(M1-Te1) = 3.291(1)$ Å, $d(M2-Te1) = 2.977(1)$ Å].³² On the other hand, the distances across the van der Waals gaps between the quintuple and the septuple slab in Mn_{0.85}Bi_{4.10}Te₇ [$d(Te2-Te3) = 3.6559(7)$ Å] and Mn_{0.73}Bi_{6.18}Te₁₀ [$d(Te2-Te3) = 3.6516(5)$ Å] decrease slightly with higher bismuth concentration.

Table 3 Wyckoff positions, atomic coordinates, site occupancies and coefficients of the anisotropic as well as equivalent isotropic displacement parameters (in Å²) for Mn_{0.73}Bi_{6.18}Te₁₀ ($U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$).

Atom	W. p.	x	y	z	occ.
Mn1/ Bi1/ □	3a	0	0	0	0.634(16)/ 0.275(6)/ 0.09(2)
Mn2/ Bi2	6c	0	0	0.29647(2)	0.017(4)/ 0.983(3)
Mn3/ Bi3	6c	0	0	0.23671(2)	0.015(4)/ 0.985(3)
Mn4/ Bi4	6c	0	0	0.47010(2)	0.014(4)/ 0.986(3)
Te1	6c	0	0	0.34922(2)	1
Te2	6c	0	0	0.05365(2)	1
Te3	6c	0	0	0.41290(2)	1
Te4	6c	0	0	0.11658(2)	1
Te5	6c	0	0	0.17957(2)	1
Atom	$U_{11}=U_{22}=2U_{12}$	U_{33}	$U_{23}=U_{13}$	U_{eq}	
Mn1/ Bi1/□	0.0221(5)	0.0238(8)	0	0.0227(4)	
Mn2/ Bi2	0.02252(17)	0.0278(3)	0	0.02428(16)	
Mn3/ Bi3	0.0208(2)	0.0269(3)	0	0.02283(19)	
Mn4/ Bi4	0.0208(2)	0.0265(3)	0	0.02269(19)	
Te1	0.0233(2)	0.0207(4)	0	0.0224(2)	
Te2	0.0191(2)	0.0229(4)	0	0.0204(2)	
Te3	0.0192(2)	0.0204(4)	0	0.0196(2)	
Te4	0.0174(2)	0.0176(4)	0	0.0175(2)	
Te5	0.0190(3)	0.0205(4)	0	0.0195(2)	

3.4 TEM investigations

Structured diffuse scattering was not detected in single-crystal X-ray diffraction patterns of the manganese bismuth tellurides with GeBi₄Te₇ or GeBi₆Te₁₀ structure type (Fig. S22), thus stacking disorder is not pronounced in these compounds. In order to further analyze possible stacking faults or superstructures along [001], selected area electron diffraction patterns (SAED) were recorded. Fig. 6 and Fig. 7 show experimental diffraction patterns and simulated ones based on the results of the crystal structure analyses (section 3.3). The absence of diffuse streaks along [001]* indicates that there is no significant amount of stacking faults. Indexing of the patterns corresponds to the lattice symmetry and unit cell parameters found in the X-ray diffraction experiments. In order to visualize the long-range ordered stacking of the different slabs, HRTEM images were acquired (Fig. 8 and Fig. S23 and S24, ESI⁺). The structural entities of quintuple slabs as in Bi₂Te₃ and septuple slabs as in MnBi₂Te₄ can be clearly identified. Simulated HRTEM images based on the results of the crystal structure analyses fit the experimental ones quite well and thus confirm the structure models (Fig. 8 and Fig. 9). Note that single vacancies have very little influence on the contrasts of atom columns that consist of several atoms and can thus not be detected in such images.

Fig. 6 SAED patterns of a manganese bismuth telluride (from a sample with the nominal composition $\text{MnBi}_6\text{Te}_{10}$) with the GeBi_4Te_7 -type structure and corresponding simulated patterns (kinematical approximation based on the model for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ from the single-crystal structure analysis) with experimental and calculated tilt angles.

Fig. 7 SAED patterns of a manganese bismuth telluride (from a sample with the nominal composition $\text{Mn}_{0.77}\text{Bi}_{6.15}\text{Te}_{10}$) with the $\text{GeBi}_6\text{Te}_{10}$ -type structure and corresponding simulated diffraction patterns (kinematical approximation, based on the model for $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ from the single crystal structure analysis) with experimental and calculated tilt angles.

Fig. 8 HRTEM images (zone axis [100], Fourier filtered) of manganese bismuth tellurides with the GeBi_4Te_7 (bottom) and $\text{GeBi}_6\text{Te}_{10}$ (top) structure types, each with a corresponding SAED pattern; inset: simulation based on the single-crystal data of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ ($\Delta f = -85$ nm, $t = 8.36$ nm; beam semiconvergence 1.2 mrad, defocus spread 15 nm) and $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ ($\Delta f = -67$ nm, $t = 0.88$ nm; beam semiconvergence 1.2 mrad, defocus spread 15 nm); white bars symbolize quintuple Bi_2Te_3 -like slab and black lines symbolize septuple layers characteristic of MnBi_2Te_4 .

Fig. 9 HRTEM defocus series (zone axis [100], Fourier filtered) from a manganese bismuth telluride with the $\text{GeBi}_6\text{Te}_{10}$ -type structure, insets: $\text{GeBi}_6\text{Te}_{10}$ -type structure (green = Te; yellow = Bi-rich; red = Mn-rich: for the exact cation distribution, including mixed sites cf. Tables 2 and 4) and simulated images based on the single-crystal data of $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$, $t = 0.88$ nm; beam semiconvergence 1.2 mrad, defocus spread 15 nm), defocus values Δf are given in the images.

3.5 Magnetic properties

Temperature- and field-dependent magnetization was measured on pellets from single-phase powders with the compositions $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$. In low magnetic fields of $\mu_0 H = 0.02$ T, both compounds demonstrate a temperature-driven phase transition from the paramagnetic into magnetically ordered phases. For $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$, an antiferromagnetic transition can clearly be discerned at $T_N = 13$ K in low fields (see peak in the inset of Fig. 10a at 13 K), which is followed by a subsequent rearrangement of the microscopic spin alignment at lower temperatures, as indicated by an upturn of the magnetization curve. Given the ferromagnetic hysteresis at $T = 2$ K in Fig. 11a, a predominantly ferromagnetic alignment with a large ferromagnetic component of the spins can be envisaged at lowest temperatures. The microscopic spin arrangement and the origin of these two transitions for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ should, however, be elucidated in more detail in the future using single crystals. In comparison, for $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ a very strong upturn of the magnetization below $T_C = 12$ K together with the splitting of the zero-field-cooled and field-cooled magnetization data indicate a transition into a ferromagnetic phase in this compound.

Fig. 10 Magnetization M/H and reciprocal susceptibility of (a) $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and (b) $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ as a function of temperature measured at various applied magnetic fields. The extrapolated line on the right axis is a Curie-Weiss fit to the high-temperature data indicating a value θ_{CW} of 14(2) and 17(2) K for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$, respectively. A small offset $\chi_0 \sim -0.0007(3)$ emu mol $^{-1}$ Oe $^{-1}$ was added to the data to account for the contribution of closed diamagnetic electronic shells.

The effective paramagnetic moment per formula unit can be estimated from the Curie-Weiss fit of the high-temperature data (Fig. 10) and constitutes $5.7(1) \mu_B$ for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $5.8(1) \mu_B$ for $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$, consistent with the high-spin d^5 configuration of Mn^{2+} ($S = 5/2$). Positive values of $\theta_{\text{CW}} = 14(2)$ and $17(2)$ K for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$, respectively, indicate predominantly ferromagnetic coupling. Magnetization curves as function of the magnetic field (Fig. 11)

confirm dominating ferromagnetic interactions in both compounds with pronounced magnetic hysteresis at $T = 2$ K up to about $\mu_0 H = 0.2$ T and an almost saturated magnetization close to the expected value for Mn(II) for fields above ~ 2 T. The remanent magnetization and the coercive field are slightly larger for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ ($\mu_0 H_c = 0.08$ T).

Fig. 11 Magnetic hysteresis curves of (a) $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and (b) $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ at 300 and 2 K. The samples were cooled in zero field from 320 K.

3.6 Thermoelectric properties

Thermoelectric measurements (Fig. 12) were conducted on parts of compact ingots between RT and 400 °C in three consecutive cycles. The temperature evolution of the electrical conductivity σ indicates metallic behavior above RT. Whereas MnBi_2Te_4 has been reported to be a p-type conductor with rather low σ (39 S cm^{-1} at RT),³¹ other investigations on comparable materials indicate n-type conduction, concluding from a negative Seebeck coefficient S and a much higher σ (450 S cm^{-1} at RT).³² Similarly, $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ exhibit negative S and thus are n-type conductors. Despite the shallow minimum in the thermal evolution of S , the bandgap was roughly estimated using the Goldsmid-Sharp relationship,⁶⁸ $E_g = 2eS_{\text{max}}T_{\text{max}}$, with the maximum absolute Seebeck coefficient S_{max} and the corresponding temperature T_{max} . This yields narrow bandgaps of $E_g \approx 0.14$ eV for both $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$. This bandgap corresponds with the high electrical conductivity and with the E_g of other compounds with layered GeBi_4Te_7 - or $\text{GeBi}_6\text{Te}_{10}$ -type structures (Table 4).

Thermal conductivities are rather low and almost constant up to 400 °C with $1.47 \text{ W m}^{-1} \text{ K}^{-1}$ for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $1.63 \text{ W m}^{-1} \text{ K}^{-1}$ for $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$. However, the small value of S limits the maximum zT values up to 0.25 at 375 °C and 0.28 at 325 °C for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$, respectively. The zT values decrease slightly from cycle to cycle, which could be attributed to the metastability of the manganese bismuth

tellurides. The *ex situ* PXRD measurements performed after the thermoelectric measurements (Fig. S7, ESI[†]) show that still up to 80% of the main phase is present in both compounds. SEM investigations (Fig. S15 and Table S10, ESI[†]) confirm that the samples slowly decompose over several measurement cycles (cf. sections 3.1 and 3.2).

Fig. 12 Thermoelectric properties of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (left column) and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ (right column); Seebeck coefficient (first row), electrical conductivity (second row), thermal conductivity and its phononic contribution (third row, calculated according to the Wiedemann-Franz relationship; the decrease of the Lorenz number L has been derived from the increase of the absolute value of S according to $L = 1.5 + e^{-(|S|/116)}$ where L is in $10^{-8} \text{ W } \Omega \text{ K}^{-2}$ and S in $\mu\text{V K}^{-1}$); this equation is accurate within 5% for single parabolic band/acoustic phonon scattering assumption.⁶⁹ and zT values (fourth row); three subsequent heating and cooling cycles.

The quality factor B (eq. 1), the figure of merit $zT = S^2 \sigma T / \kappa$ (eq. 2) and the phononic part of the thermal conductivity κ_{ph} were calculated as a function of the electrons' chemical potential η from the measured transport properties σ , S and κ of the first cycle of the thermoelectric measurement (Fig. 12), which is only very little affected by the decomposition. An effective mass model was used to calculate the optimal carrier concentration zT_{opt} . Details of the calculations are described at the end of the ESI[†] and can also be found in several references.⁷⁰⁻⁷⁵ This approach allows one to calculate the intrinsic electrical conductivity σ_{E0} and κ_{ph} and therefore also the material quality factor B (eq. 1). These intrinsic properties are independent of doping and thus can be separated from

doping and its optimization. The optimal zT values for different temperatures and therefore different B factors are shown in Fig. 13.

$$B = \left(\frac{k_B}{e} \right)^2 \frac{\sigma_{E0}}{\kappa_{\text{ph}}} T \quad (\text{eq. 1})$$

$$zT(\eta) = \frac{S^2(\eta)}{\frac{(k_B/e)^2}{B \ln(1+e^\eta)} + L(\eta)} \quad (\text{eq. 2})$$

The measured zT values of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ indicate that in both compounds the carrier concentrations are higher than optimal as the measured zT values are on the high- η side of the maximal $zT(\eta)$ (note that the carrier concentration is a monotonically increasing function of η). With ideal carrier concentration (i.e. optimal η) the maximum of zT for manganese bismuth tellurides with GeBi_4Te_7 -type structure could increase up to 0.35 at 300 °C and up to 0.47 at 300 °C for the $\text{GeBi}_6\text{Te}_{10}$ -type structure.

Table 4 Electronic properties of MBi_4Te_7 , $\text{MBi}_6\text{Te}_{10}$ ($M = \text{Sn, Pb, Ge}$), $\text{Mn}_{0.85}\text{Bi}_{2.1}\text{Te}_4$, $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$.

Compound	S at RT (in $\mu\text{V K}^{-1}$)	σ at RT (in S cm^{-1})	E_g (in eV)	Ref.
MnBi_2Te_4	168	39	~0.4	31
$\text{Mn}_{0.85}\text{Bi}_{2.1}\text{Te}_4$	-5	475	0.15	32
$\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$	-55	700	0.14	this work
GeBi_4Te_7	-127	435	0.21	76
	-160	230		24
SnBi_4Te_7	-92	250	0.22	76
PbBi_4Te_7	-68	1666	—	76
	-66	1070		24
$\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$	-60	900	0.14	this work
$\text{GeBi}_6\text{Te}_{10}$	-65	920	—	28
$\text{PbBi}_6\text{Te}_{10}$	-47	870	—	24

Fig. 13 Calculated and measured zT values for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (left) and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ (right) as a function of η at 100 °C, 200 °C, 300 °C and 400 °C with $B = 0.047, 0.078, 0.105$ and 0.102 for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $B = 0.076, 0.122, 0.144$ and 0.115 for $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$.

4 Conclusions

The crystal-structure determinations of two new compounds in the manganese–bismuth–telluride system reveal unexpected combinations of chemical composition and structure type. Diffraction data of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and

Mn_{0.73}Bi_{6.18}Te₁₀ indicate that the compounds are isostructural to GeBi₄Te₇^{27,29} and GeBi₆Te₁₀,²⁴ respectively. This is confirmed by a combination of X-ray diffraction, including the application of microfocused synchrotron radiation (for Mn_{0.73}Bi_{6.18}Te₁₀), of TEM imaging and of EDX spectroscopy.⁴³ According to the magnetization measurements, the oxidation state of Mn^{II} is established. This corresponds to the situation in MnBi₂Te₄.^{32,33} The structures contain significant amounts of cation vacancies. Intermixing of Mn and Bi on the cation sites is very pronounced and highly significant. Other layered chalcogenides of the GeBi₂Te₄, GeBi₄Te₇ and GeBi₆Te₁₀ structure types also exhibit very characteristic mixed cation occupancies.^{24,27,28,76–79} This phenomenon is also typical and, in principle, to be expected for manganese bismuth tellurides in these structure types. The non-stoichiometry of Mn_{1-x}□_{x/3}Bi_{4+2x/3}Te₇ ($x = 0.15 - 0.2$) (space group *P3m1* with GeBi₄Te₇-type structure) and Mn_{1-x}□_{x/3}Bi_{6+2x/3}Te₁₀ ($x = 0.19 - 0.26$) (space group *R3m* with GeBi₆Te₁₀-type structure) is comparable to the situation in the related compound 33R-Ge_{4x}Sb_{2y}Te₇ ($x, y \approx 0.1$), which is isostructural to Ge₃Sb₂Te₆ despite a different stoichiometry.⁸⁰ The manganese bismuth tellurides with GeBi₄Te₇- and GeBi₆Te₁₀-type structures are metastable and start decomposing at approximately 250 °C into a Mn-doped Bi₂Te₃-like structure, Bi-rich bismuth tellurides and a manganese-rich phase. This result is crucial concerning physical measurements at elevated temperatures. This decomposition was not observed in our DSC measurements, as it is very slow and extends over a wide temperature range (~70 K). Yet, the DSC measurements show that these phases are not accessible by slow cooling of melts. An annealing step in the solid state followed by quenching to room temperature is essential to obtain phase pure samples, as kinetic effects impede the immediate decomposition at elevated temperatures. Small variations in the annealing temperature may lead to different structures. The rather broad DSC signal for the GeBi₆Te₁₀-type structure might indicate other structure variants. The *zT* values of these layered manganese bismuth tellurides indicate decent thermoelectric properties and may be affected by the metastability, but have plenty of room for optimization. The first step towards optimization would be to increase the stability, e.g. by partial substitution of manganese with group 14 elements as preliminary experiments indicate that such substitution is possible. For an increased thermoelectric performance, doping should decrease the concentration of the charge carriers. Much beyond thermoelectrics, the access to single-phase compounds in this ternary system is crucial for various more specialized analyses such as ARPES and detailed investigations of magnetic effects. MnBi₂Te₄ has attracted much attraction as the first antiferromagnetic topological insulator, with special focus on theoretical calculations.^{33,81} As these may be questionable if they are based on simple ordered models, the crystal-structure data presented in this study should be the basis for realistic calculations that take into account vacancies and Mn/Bi disorder. The new layered manganese bismuth tellurides may be promising candidates for topologically non-trivial materials and thus for studies of mutual influence between long-range magnetic ordering at

low temperatures and non-trivial band-structure topology. The single-phase materials, which were only accessible by taking the non-stoichiometry into account, may also be a perspective for magnetic sensing if they should exhibit the anomalous Hall effect like, e.g., Mn-doped Bi₂Te₃.^{17,82}

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Supporting Information

for

Layered Manganese Bismuth Tellurides with GeBi_4Te_7 - and $\text{GeBi}_6\text{Te}_{10}$ -type Structures: Towards Multifunctional Materials

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Figure S1: Heat capacity C_p determined by DSC measurements (Netzsch DSC 404, Pt crucibles with alumina inlays) for samples $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (left) and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ (right) as used for thermoelectric characterization and comparison with the Dulong-Petit approximation.

Figure S2: PXRD pattern of a sample with the nominal composition MnBi_4Te_7 (black points); Rietveld refinement taking into account structure models for $\text{Mn}_{0.85}\text{Bi}_{2.1}\text{Te}_4$ (GeBi₂Te₄-type structure) [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.; Ünzelmänn, M.; Kaiser, M.; Scaravaggi, F.; Rellinghaus, B.; Nielsch, K.; Heß, C.; Büchner, B.; Reinert, F.; Bentmann, H.; Oeckler, O.; Doert, T.; Ruck, M.; Isaeva, A. Chemical Aspects of the Antiferromagnetic Topological Insulator MnBi_2Te_4 ; available at arxiv.org/abs/1812.03106] and $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (GeBi₄Te₇-type structure) based on SCXRD refinements (see chapter 3.3), sum of calculated patterns light gray and experimental data black points; difference plot (black) and reflection markers (black lines GeBi₂Te₄-type structure, gray lines GeBi₄Te₇-type structure).

Figure S3: PXRD pattern of a sample with the nominal composition $\text{MnBi}_6\text{Te}_{10}$ (black points); Rietveld refinement taking into account structure models for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (GeBi_4Te_7 -type structure) and $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ ($\text{GeBi}_6\text{Te}_{10}$ -type structure) based on the SCXRD refinements (see chapter 3.3), sum of calculated patterns light gray and experimental data black points; difference plot (black) and reflection markers (black lines $\text{GeBi}_6\text{Te}_{10}$ -type structure, gray lines GeBi_4Te_7 -type structure).

Table S1: Details of the Rietveld refinements of samples with the nominal compositions $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ based on structure models for $\text{Mn}_{0.85}\text{Bi}_{4.1}\text{Te}_7$ (GeBi_4Te_7 -type structure) and $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ ($\text{GeBi}_6\text{Te}_{10}$ -type structure, the slightly different Mn content has no influence on the fit) from the SCXRD refinement (section 3.3).

formula	$\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$	$\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$
M (in g mol^{-1})	1796.715	7824.35
Z	1	3
$F(000)$	725.55	3154
crystal system	trigonal	trigonal
space group (no.)	$P3m1$ (164)	$R3m$ (166)
cell parameter (in Å)	$a = 4.3613(1)$ $c = 23.794(2)$	$a = 4.3694(2)$ $c = 101.870(7)$
cell volume (in Å ³)	391.95(3)	1674.3(2)
X-ray density (in g cm^{-3})	7.61	7.71
radiation	$\text{Cu-K}\alpha_1$ ($\lambda = 1.540596$ Å)	
2θ range (in °)	$4 \leq 2\theta \leq 100$	
number of reflections	216	310
refined parameter / thereof background	27 / 18	27 / 18
R_p / R_{wp}	0.0172 / 0.0269	0.0171 / 0.0264
R_{Bragg}	0.021	0.021
GooF	1.01	1.01

Table S2: Wyckoff positions and atomic parameters (coordinates $x y z$, site occupancy factors $s.o.f.$ and isotropic displacement parameters B_{eq} , all from single-crystal data and not further refined) used in the Rietveld refinement of $Mn_{0.85}Bi_{4.10}Te_7$.

Atom	Wyckoff	x	y	z	$s. o. f.$	B_{eq}
Mn1 / Bi1 / $\square$	1b	0	0	1/2	0.694 / 0.255 / 0.051	2.58
Mn2 / Bi2	2d	1/3	2/3	0.3423	0.0414 / 0.959	2.63
Mn3 / Bi3	2d	1/3	2/3	0.0860	0.035 / 0.965	2.51
Te1	2d	1/3	2/3	0.5680	1	2.54
Te2	2c	0	0	0.2703	1	2.38
Te3	2d	1/3	2/3	0.8413	1	2.34
Te4	1a	0	0	0	1	2.12

Table S3: Wyckoff positions and atomic parameters (coordinates $x y z$, site occupancy factors $s.o.f.$ and isotropic displacement parameters B_{eq} , all from single-crystal data and not further refined) used in the Rietveld refinement of $Mn_{0.81}Bi_{6.13}Te_{10}$.

Atom	Wyck.	x	y	z	$s. o. f.$	B_{eq}
Mn1/Bi1/ $\square$	3a	0	0	0	0.634 / 0.275 / 0.09	1.79
Mn2/Bi2	6c	0	0	0.29647	0.017 / 0.983	1.92
Mn3/Bi3	6c	0	0	0.23671	0.015 / 0.985	1.79
Mn4/Bi4	6c	0	0	0.47010	0.014 / 0.986	1.80
Te1	6c	0	0	0.34922	1	1.77
Te2	6c	0	0	0.05365	1	1.61
Te3	6c	0	0	0.41290	1	1.55
Te4	6c	0	0	0.11658	1	1.38
Te5	6c	0	0	0.17957	1	1.54

Table S4: Lattice parameters of $Mn_{1-x}\square_{x/3}Bi_{4+2x/3}Te_7$ with $x = 0.15, 0.167$ and 0.2 from Rietveld refinements compared with single crystal data of $Mn_{0.85}\square_{0.05}Bi_{4.10}Te_7$.

nominal composition	a (in Å)	c (in Å)	R_{wp}
$Mn_{0.80}Bi_{4.13}Te_7$	4.3610(1)	23.792(2)	0.028
$Mn_{0.833}Bi_{4.11}Te_7$	4.3606(2)	23.794(2)	0.029
$Mn_{0.85}Bi_{4.10}Te_7$	4.3613(1)	23.794(2)	0.027
SCXRD $Mn_{0.85}Bi_{4.10}Te_7$	4.3591(3)	23.769(2)	0.033 ($R1$ for $I > 2\sigma(I)$)
GeBi ₄ Te ₇ -type phase in a heterogeneous sample with nominal composition $MnBi_6Te_{10}$	4.3612(6)	23.769(4)	0.025

Table S5: SEM-EDX results for samples with the nominal compositions $Mn_{0.85}Bi_{4.10}Te_7$ and $Mn_{0.81}Bi_{6.13}Te_{10}$ (data averaged from 7-8 point measurements), compared with the nominal compositions $MnBi_4Te_7$ and $MnBi_6Te_{10}$, respectively.

nominal composition	at.-% measured (8 points)	at.-% calc. for $Mn_{0.85}Bi_{4.10}Te_7$	at.-% calc. for $MnBi_4Te_7$
$Mn_{0.85}Bi_{4.10}Te_7$	Mn: 6.6(6); Bi: 34.7(3); Te: 58.7(4)	Mn: 7.1; Bi: 34.3; Te: 58.6	Mn: 8.33; Bi: 33.33; Te: 58.33
	at.-% measured (7 points)	at.-% calc. for $Mn_{0.81}Bi_{6.13}Te_{10}$	at.-% calc. for $MnBi_6Te_{10}$
$Mn_{0.81}Bi_{6.13}Te_{10}$	Mn: 4.5(3); Bi: 36.5(5); Te: 59.1(5)	Mn: 4.78; Bi: 36.19; Te: 59.03	Mn: 5.9; Bi: 35.3; Te: 58.8

Figure S4: SEM images (backscattered electrons) of samples with the nominal compositions $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (left) and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ (right); the minor phase (black spots, bottom left) corresponds to a manganese telluride; the main phase (gray) to $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (the influence of the minor phase on the composition is negligible) and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$, respectively.

Figure S5: PXRD pattern of samples with the nominal compositions $\text{Mn}_{0.89}\text{Bi}_{4.11}\text{Te}_7$ (left) and $\text{Mn}_{0.85}\text{Bi}_{6.15}\text{Te}_{10}$ (right); Rietveld refinements taking into account structure models for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (GeBi_4Te_7 -type structure, section 3.3), $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ ($\text{GeBi}_6\text{Te}_{10}$ -type structure, section 3.3) and $\text{Mn}_{0.85}\text{Bi}_{2.1}\text{Te}_4$ [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.; Ünzelmänn, M.; Kaiser, M.; Scaravaggi, F. Rellinghaus, B.; Nielsch, K.; Heß, C.; Büchner, B.; Reinert, F.; Bentmann, H.; Oeckler, O.; Doert, T.; Ruck, M.; Isaeva, A. Chemical Aspects of the Antiferromagnetic Topological Insulator MnBi_2Te_4 ; available at arxiv.org/abs/1812.03106] based on SCXRD refinements; sum of calculated patterns light gray and experimental data as black points; difference plot (gray) and reflection markers below, gray markers for GeBi_4Te_7 -type structure, black markers $\text{GeBi}_6\text{Te}_{10}$ -type structure (right) and GeBi_2Te_4 -type structure (left).

Figure S6: PXRD patterns of samples $\text{Mn}_{1-x}\square_{x/3}\text{Bi}_{6+2x/3}\text{Te}_{10}$ with $x = 0.19, 0.23$ and 0.26 (top row) and $\text{Mn}_{1-x}\square_{x/3}\text{Bi}_{4+2x/3}\text{Te}_7$ with $x = 0.15, 0.167$ and 0.2 (bottom row); Rietveld refinements taking into account structure models for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (GeBi_4Te_7 type) and $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ ($\text{GeBi}_6\text{Te}_{10}$ type) based on SCXRD (section 3.3); difference plots (gray), sum of calculated patterns light gray, experimental data as black points; reflection markers: black lines for GeBi_4Te_7 type (top) and $\text{GeBi}_6\text{Te}_{10}$ type (bottom), respectively.

Table S6: SEM-EDX data of $\text{Mn}_{1-x}\square_{x/3}\text{Bi}_{4+2x/3}\text{Te}_7$ with $x = 0.15, 0.167$ and 0.2 (top) and $\text{Mn}_{1-x}\square_{x/3}\text{Bi}_{6+2x/3}\text{Te}_{10}$ with $x = 0.19, 0.23$ and 0.26 (bottom) (averaged from eight point measurements) compared with the nominal composition MnBi_4Te_7 and $\text{MnBi}_6\text{Te}_{10}$.

Composition	at.-% measured	at.-% calculated (nominal)	at.-% calculated for MnBi_4Te_7
$\text{Mn}_{0.80}\text{Bi}_{4.13}\text{Te}_7$ ($x = 0.2$)	Mn: 6.5(5) Bi: 34.2(7) Te: 59.3(7)	Mn: 6.7 Bi: 34.6 Te: 58.7	Mn: 8.3 Bi: 33.3 Te: 58.3
$\text{Mn}_{0.833}\text{Bi}_{4.11}\text{Te}_7$ ($x = 0.167$)	Mn: 6.7(5) Bi: 34.6(5) Te: 58.7(5)	Mn: 7.0 Bi: 34.4 Te: 58.6	Mn: 8.3 Bi: 33.3 Te: 58.3
$\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ ($x = 0.15$)	Mn: 6.6(6); Bi: 34.7(3); Te: 58.7(4)	Mn: 7.1; Bi: 34.3; Te: 58.6	Mn: 8.3 Bi: 33.3 Te: 58.3

Compositon	at.-% measured	at.-% calculated (nominal)	at.-% calculated for $\text{MnBi}_6\text{Te}_{10}$
$\text{Mn}_{0.74}\text{Bi}_{6.18}\text{Te}_{10}$ ($x = 0.26$)	Mn: 4.2(7); Bi: 36.5(4); Te: 59.4(4)	Mn: 4.4 Bi: 36.5 Te: 59.1	Mn: 5.9 Bi: 35.3 Te: 58.8
$\text{Mn}_{0.77}\text{Bi}_{6.15}\text{Te}_{10}$ ($x = 0.23$)	Mn: 4.5(6); Bi: 36.4(4); Te: 59.2(7)	Mn: 4.5 Bi: 36.4 Te: 59.1	Mn: 5.9 Bi: 35.3 Te: 58.8
$\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ ($x = 0.19$)	Mn: 4.5(3); Bi: 36.5(5); Te: 59.1(5)	Mn: 4.8; Bi: 36.2; Te: 59.0	Mn: 5.9 Bi: 35.3 Te: 58.8

Table S7: Lattice parameters of $\text{Mn}_{1-x}\square_{x/3}\text{Bi}_{6+2x/3}\text{Te}_{10}$ with $x = 0.19, 0.23$ and 0.26 from Rietveld refinements compared with single-crystal data of $\text{Mn}_{0.73}\square_{0.09}\text{Bi}_{6.18}\text{Te}_{10}$.

nominal composition	a (in Å)	c (in Å)	R_{wp}
$\text{Mn}_{0.74}\text{Bi}_{6.18}\text{Te}_{10}$	4.3739(1)	101.818(8)	0.027
$\text{Mn}_{0.77}\text{Bi}_{6.15}\text{Te}_{10}$	4.3697(2)	101.863(8)	0.027
$\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$	4.3694(1)	101.870(7)	0.030
SCXRD $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$	4.3698(3)	101.829(8)	0.0303 (R_1 for $I > 2\sigma(I)$)

Figure S7: PXRD for samples with the nominal compositions $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (left) and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ (right) after thermoelectric characterization; Rietveld refinements taking into account structure models for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (GeBi₄Te₇ type), $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ (GeBi₆Te₁₀ type) based on SCXRD (section 3.3), for Bi₂Te₃ [Atuchin, V. V.; Gavrilova, T. A.; Kokh, K. A.; Kuratieva, N.V.; Pervukhina, N.B.; Surovtsev, N. V. *Solid State Commun.* 2012, 152, 1119–1122] and for MnTe₂ (FeS₂-type structure, space group *Pa3*) [Fjellvåg, H.; Kjekshus, A.; Chattopadhyay, T.; Hochheimer, H. D.; Hönle, W.; von Schnering, H. G. *Phys. Lett.* 1985, 112A, 411–413]; experimental data (black points), refined curve (gray), difference plot (black) and reflection positions: black GeBi₄Te₇ type (left) and GeBi₆Te₁₀ type (right), respectively, dark gray Bi₂Te₃ type and light gray MnTe₂.

Figure S8: PXRD patterns (taken from Fig. 2, $\lambda = 0.18972 \text{ \AA}$) of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (left) and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ (right) at 120 °C (black curve) and 465 °C (gray curve; Bi₂Te₃ type resulting from decomposition); vertical black lines and dashed black lines indicate the reflection positions of GeBi₄Te₇-type structure (left) and of GeBi₆Te₁₀-type structure (right), respectively; vertical gray lines and gray dashed lines indicate reflection positions of a Bi₂Te₃-type structure; note that the strongest reflections may easily be confused with each other.

Table S8: Signals of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ in the DSC experiment and possible assignments.

Run	Signal	$T_{\text{peak}} / ^\circ\text{C}$	possible assignment
1st heating	shoulder of 1		melting of Bi_2Te_3
	1	590.2	melting of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$
	2	598.2	melting of Mn_2BiTe_4
1st cooling	1	588.7	solidification of Mn_2BiTe_4
	2	584.5	solidification of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$
	3	580.5	solidification of Bi_2Te_3
2nd heating	1	589.2	melting of Bi_2Te_3
	1'	590.5	melting of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$
	2	596.5	melting of Mn_2BiTe_4
2nd cooling	1	588.7	solidification of Mn_2BiTe_4
	2	584.5	solidification of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$
	3	580.5	solidification of Bi_2Te_3

Figure S9: DSC experiments (two heating-cooling cycles from 100-700 °C) for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$.

Table S9: Signals of $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ DSC experiment and possible assignment.

Run	Signal	$T_{\text{peak}} / ^\circ\text{C}$	Possible assignment
1st heating	1	574.0	Melting Bi-rich Bi_xTe_y
	2	588.3	Melting $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$
	3	590.0	Melting $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$
	4	598.2	Melting Mn_2BiTe_4
1st cooling	1 (broad unstructured signal)		Bi_2Te_3 and Mn-poorer $\square_{0.06}\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ and $\square_{0.05}\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$
2nd heating	1		Bi_2Te_3 and Mn-poorer $\square_{0.06}\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ and $\square_{0.05}\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$
	2		Melting Mn_2BiTe_4
2nd cooling	1 (broad unstructured signal)		Bi_2Te_3 and Mn-poorer $\square_{0.06}\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ and $\square_{0.05}\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$

Figure S10: DSC experiments (two heating-cooling cycles from 100-700 °C) for $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$.

Figure S11: PXRD pattern of the decomposition product of a sample with the nominal composition $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ after DSC heating up to 400 °C; Rietveld refinements taking into account structure models for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (GeBi_4Te_7 type), $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ ($\text{GeBi}_6\text{Te}_{10}$ type) based on SCXRD refinements (section 3.3), for Bi_2Te_3 [Atuchin, V. V.; Gavrilova, T. A.; Kokh, K. A.; Kuratieva, N.V.; Pervukhina, N.B.; Surovtsev, N. V. *Solid State Commun.* **2012**, *152*, 1119–1122] and for MnTe_2 (FeS_2 -type structure, space group $Pa\bar{3}$) [Fjellvåg, H.; Kjekshus, A.; Chattopadhyay, T.; Hochheimer, H. D.; Hönle, W.; von Schnering, H. G. Pressure induced phase transition in MnTe_2 . *Phys. Lett.* **1985**, *112A*, 411–413]; experimental data (black points), refined curve (gray), difference plot (black) and reflection markers: black GeBi_4Te_7 type, dark gray Bi_2Te_3 type and light gray MnTe_2 .

Figure S12: PXRD of the decomposition product of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ after a DSC experiment with two consecutive cycles from RT up to 700 °C; Rietveld refinements taking into account structure models for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (GeBi_4Te_7 -type structure, section 3.3), $\text{Mn}_{0.85}\text{Bi}_{2.1}\text{Te}_4$ [GeBi_2Te_4 -type structure: [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.; Ünzelmann, M.; Kaiser, M.; Scaravaggi, F. Rellinghaus, B.; Nielsch, K.; Heß, C.; Büchner, B.; Reinert, F.; Bentmann, H.; Oeckler, O.; Doert, T.; Ruck, M.; Isaeva, A. Chemical Aspects of the Antiferromagnetic Topological Insulator MnBi_2Te_4 ; available at arxiv.org/abs/1812.03106]; experimental data (black points), for Bi_2Te_3 [Atuchin, V. V.; Gavrilova, T. A.; Kokh, K. A.; Kuratieva, N.V.; Pervukhina, N.B.; Surovtsev, N. V. *Solid State Commun.* **2012**, *152*, 1119–1122] and for MnTe (NiAs -type structure) [Efrem D'Sa, J.B.C.; Bhobe, P. A.; Riolkar, K. R.; Das, A.; Paranjpe, S. K.; Prabhu, R. B.; Sarode, P. R. *J. Magn. Mater.* **2005**, *285*, 267–271], refined curve (gray), difference plot (black) and reflection positions (black GeBi_4Te_7 type; dark gray GeBi_2Te_4 type, gray Bi_2Te_3 type and light gray NiAs -type structure of MnTe).

Figure S13: PXRD pattern of the decomposition product of $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ after DSC (heating up to 400 °C); Rietveld refinement taking into account structure models for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (GeBi_4Te_7 -type structure), $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ ($\text{GeBi}_6\text{Te}_{10}$ -type structure) based on SCXRD (section 3.3), for Bi_2Te_3 [Atuchin, V. V.; Gavrilova, T. A.; Kokh, K. A.; Kuratieva, N. V.; Pervukhina, N. B.; Surovtsev, N. V. *Solid State Commun.* **2012**, *152*, 1119–1122] and for MnTe_2 (FeS_2 -type structure, space group $Pa\bar{3}$) [Fjellvåg, H.; Kjekshus, A.; Chattopadhyay, T.; Hochheimer, H. D.; Hönle, W.; von Schnering, H. G. *Phys. Lett.* **1985**, *112A*, 411–413]; experimental data (black points), refined curve (gray), difference plot (black) and reflection markers (black $\text{GeBi}_6\text{Te}_{10}$ type, dark gray Bi_2Te_3 type and light gray MnTe_2).

Figure S14: PXRD of the decomposition product of $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ after a DSC experiment with two consecutive cycles from RT up to 700 °C; Rietveld refinement taking into account structure models for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (GeBi_4Te_7 type), $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ ($\text{GeBi}_6\text{Te}_{10}$ type) based on SCXRD (section 3.3), and $\text{Mn}_{0.85}\text{Bi}_{2.1}\text{Te}_4$ [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.; Ünzelmann, M.; Kaiser, M.; Scaravaggi, F. Rellinghaus, B.; Nielsch, K.; Heß, C.; Büchner, B.; Reinert, F.; Bentmann, H.; Oeckler, O.; Doert, T.; Ruck, M.; Isaeva, A. Chemical Aspects of the Antiferromagnetic Topological Insulator MnBi_2Te_4 ; available at arxiv.org/abs/1812.03106] and for Bi_2Te_3 [Atuchin, V. V.; Gavrilova, T. A.; Kokh, K. A.; Kuratieva, N. V.; Pervukhina, N. B.; Surovtsev, N. V. *Solid State Commun.* **2012**, *152*, 1119–1122]; experimental data (black points), refined curve (gray), difference plot (black) and reflection markers (black GeBi_4Te_7 type; dark gray GeBi_2Te_4 type, gray Bi_2Te_3 type and light gray $\text{GeBi}_6\text{Te}_{10}$ type).

Figure S15: SEM images (backscattered electrons) after thermoelectric measurements (3 cycles; RT – 400 °C) of samples with the nominal composition $\text{Mn}_{0.85}\text{Bi}_{4.1}\text{Te}_7$ (left) and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ (right) with increasing magnification from top to bottom; black areas (lines, spots) correspond to manganese tellurides and possibly other Mn-rich phases, light gray areas to Mn-doped Bi_2Te_3 and the dark gray main phase to $\text{Mn}_{0.85}\text{Bi}_{4.1}\text{Te}_7$ and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$, respectively; EDX results are given in Table S10.

Table S10: Results of SEM-EDX analyses (marked in Fig. S15) for samples with the nominal compositions $\text{Mn}_{0.85}\text{Bi}_{4.1}\text{Te}_7$ and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ after thermoelectric measurements (3 cycles; RT-400 °C) taking into account formed precipitates; data averaged from 2-5 point measurements; the small size of the precipitates can result in large errors as surrounding matrix material may contribute to point measurements.

formula	$\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (point 6-9)	MnTe_2 (point 1-5)	Bi_2Te_3 (point d-g)	Mn-rich phase(point a-c)
at.-% meas.	Mn: 6.4(10); Bi: 35.0(9); Te: 59.2(7)	Mn: 33.1(5); Te: 66.9(5)	Mn: 2.1(11); Bi: 37.7(10); Te: 60.23(6)	Mn: 19(2); Bi: 19(2); Te: 62.6(1)
at.-% calc.	Mn: 7.1; Bi: 34.3; Te: 58.6	Mn: 33.3; Te: 66.7	Bi: 40; Te: 60	" $\text{MnTe}_2 + \text{Bi}_2\text{Te}_3$ "
formula	$\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ (1-5)	Bi_2Te_3 (6-9)		Mn-rich phase (a-b)
at.-% meas.	Mn: 4.6(3); Bi: 36.2(5); Te: 59.2(5)	Mn: 1.7(6); Bi: 38.2(8); Te: 60.2(12)		Mn: 23(3); Bi: 13(2); Te: 64(2)
at.-% calc.	Mn: 4.78; Bi: 36.19; Te: 59.03	Bi: 40; Te: 60		" $\text{MnTe}_2 + \text{Bi}_2\text{Te}_3$ "

Figure S16: Temperature-dependent PXRD patterns of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ during cooling (decomposition into a Bi_2Te_3 -like structure took place during heating): the starting materials were not regained during cooling and the Bi_2Te_3 -like structure remains ($\lambda = 0.18972 \text{ \AA}$, synchrotron radiation).

Figure S17: Temperature-dependent PXRD patterns of $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ during cooling (decomposition into a Bi_2Te_3 -like structure took place during heating): the starting materials were not regained during cooling and the Bi_2Te_3 -like structure remains ($\lambda = 0.18972 \text{ \AA}$, synchrotron radiation).

Figure S18: PXRD patterns of the decomposition products of $\text{Mn}_{0.85}\text{Bi}_{4.15}\text{Te}_7$ (left) and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ (right) after 1d at 300 °C; Rietveld refinements taking into account structure models for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (GeBi_4Te_7 type), $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ ($\text{GeBi}_6\text{Te}_{10}$ type) based on SCXRD data (section 3.3), for Bi_2Te_3 [Atuchin, V. V.; Gavrilova, T. A.; Kokh, K. A.; Kuratieva, N. V.; Pervukhina, N. B.; Surovtsev, N. V. *Solid State Commun.* **2012**, 152, 1119–1122] and for MnTe_2 (FeS_2 -type structure, space group $Pa3$) [Fjellvåg, H.; Kjekshus, A.; Chattopadhyay, T.; Hochheimer, H. D.; Hönle, W.; von Schnering, H. G. *Phys. Lett.* **1985**, 112A, 411–413]; experimental data (black points), refined curve (gray), difference plot (black) and reflection markers black GeBi_4Te_7 type (left) or $\text{GeBi}_6\text{Te}_{10}$ type (right), dark gray Bi_2Te_3 type and light gray MnTe_2).

Figure S19: The decomposition products of Figure S18 were again treated like during the initial melt synthesis (section 2) and result in phase pure samples again: $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (left) and $\text{Mn}_{0.81}\text{Bi}_{6.13}\text{Te}_{10}$ (right); Rietveld refinements taking into account structure models for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (GeBi_4Te_7 type) and $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ ($\text{GeBi}_6\text{Te}_{10}$ type) based on SCXRD refinements (section 3.3); calculated patterns light gray, experimental data black points; difference plot (black) and reflection markers (black lines for GeBi_4Te_7 type and $\text{GeBi}_6\text{Te}_{10}$ type, respectively).

Figure S20: SEM SE image of the $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ single crystal used for structure analysis.

Table S11: SEM-EDX data of the $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ crystal used for structure analysis (averaged from five point measurements).

at.-% measured	at.-% for $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$	calculated	at.-% for MnBi_4Te_7	calculated
Mn: 5.8(5); Bi: 35.9(5); Te: 58.3(3)	Mn: 7.1; Bi: 34.3; Te: 58.6		Mn: 8.33 Bi: 33.33 Te: 58.33

Figure S21: TEM image of the $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ single crystal used for structure analysis.

Table S12: TEM-EDX data of the $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ crystal used for structure analysis (averaged from two point measurements).

at.-% measured	at.-% calculated for $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$	at.-% calculated for $\text{MnBi}_6\text{Te}_{10}$
Mn: 5.4(4); Bi: 36.4(4); Te: 58.2(2)	Mn: 4.3; Bi: 36.5; Te: 59.1	Mn: 5.9 Bi: 35.3 Te: 58.8

Table S13: Selected interatomic distances (in Å) for $\text{Mn}_{0.85}\text{Bi}_{2.10}\text{Te}_4$ [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.; Ünzelmann, M.; Kaiser, M.; Scaravaggi, F. Rellinghaus, B.; Nielsch, K.; Heß, C.; Büchner, B.; Reinert, F.; Bentmann, H.; Oeckler, O.; Doert, T.; Ruck, M.; Isaeva, A. Chemical Aspects of the Antiferromagnetic Topological Insulator MnBi_2Te_4 ; available at arxiv.org/abs/1812.03106], Bi_2Te_3 [Mansour, A. N.; Wong-Ng, W.; Huang, W.; Tang, W.; Tompson, A.; Sharp, J. J. *Appl. Phys.* 2014, *116*, 083513] as well as $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ and $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ (this work).

$\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$	bond length in Å	$\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$	bond length in Å	$\text{Mn}_{0.85}\text{Bi}_{2.1}\text{Te}_4$	bond length in Å	Bi_2Te_3	bond length in Å
septuple layer		septuple layer		septuple layer			
Mn2/Bi2 – Te2	3.0473(5)	Mn2/Bi2 – Te2	3.0436(7)	Bi1/Mn1 – Te2	3.027(1)		
Mn2/Bi2 – Te1	3.3055(6)	Mn2/Bi2 – Te1	3.2987(9)	Bi1/Mn1 – Te1	3.291(1)		
Mn1/Bi1 – Te1	2.9969(4)	Mn1/Bi1 – Te1	2.9909(7)	Bi2/Mn2 – Te1	2.977(1)		
van der Waals gap		van der Waals gap		van der Waals gap		van der Waals gap	
Te2 ... Te3	3.6516(5)	Te2 ... Te3	3.6559(7)	Te2 ... Te2	3.699(1)	Te2 – Te2	3.630
Te5 ... Te5	3.6432(5)						
quintuple layers		quintuple layer		quintuple layer		quintuple layer	
Mn3/Bi3 – Te3	3.0628(5)	Mn3/Bi3 – Te3	3.0543(7)			Bi – Te2	3.067
Mn3/Bi3 – Te4	3.2395(5)	Mn3/Bi3 – Te4	3.2410(4)			Bi – Te1	3.254
Mn4/Bi4 – Te4	3.2536(5)						
Mn4/Bi4 – Te5	3.0594(5)

Figure S22: Reconstructed reciprocal lattice sections $0kl$ (top) and $h0l$ (bottom) from the data of the crystals used for structure analysis: a) $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ single crystal (GeBi_4Te_7 -type structure) and b) $\text{Mn}_{0.73}\text{Bi}_{6.18}\text{Te}_{10}$ single crystal ($\text{GeBi}_6\text{Te}_{10}$ -type structure). No pronounced diffuse streaks, which would suggest stacking disorder, are visible in the experimental diffraction patterns of both crystals.

Figure S23: HRTEM image (zone axis [100], Fourier filtered) of manganese bismuth tellurides with $\text{GeBi}_6\text{Te}_{10}$ structure type (space group $R\bar{3}m$, $a = 4.370 \text{ \AA}$, $c = 101.82 \text{ \AA}$, $\Delta f = -67 \text{ nm}$, $t = 0.88 \text{ nm}$; beam semiconvergence 1.2 mrad , defocus spread 15 nm), with a corresponding SAED pattern in the upper right corner; in order to symbolize the long-range order, white bars symbolize quintuple Bi_2Te_3 -like slab and black lines symbolize septuple layers characteristic of MnBi_2Te_4 .

Figure 24: HRTEM image (zone axis [100]) of a manganese bismuth telluride with GeBi_4Te_7 -type structure; inset: simulation based on single-crystal data of $\text{Mn}_{0.85}\text{Bi}_{4.10}\text{Te}_7$ (space group $P3m1$, $a = 4.359 \text{ \AA}$, $c = 23.77 \text{ \AA}$, $\Delta f = -85 \text{ nm}$, $t = 8.36 \text{ nm}$; beam semiconvergence 1.2 mrad , defocus spread 15 nm); in the upper part of the simulation, the atom positions of the GeBi_4Te_7 -type structure are illustrated (green = Te; yellow = Bi-rich cation position; red = Mn-rich cation position); for the exact cation distribution, including mixed sites, cf. Tables 2 and 4.

Modelling of transport properties and thermoelectric data

First, the electron chemical potential η was estimated from the measured Seebeck coefficient at a given temperature by numerical methods:

$$S(\eta) = \frac{k_B}{e} \left(2 \frac{F_1(\eta)}{F_0(\eta)} - \eta \right)$$

with the Fermi integrals $F(\eta)$ being defined as:

$$F_x(\eta) = \int f \varepsilon^x d\varepsilon = \int \frac{\varepsilon^x d\varepsilon}{1 + \exp(\varepsilon - \eta)}$$

From η and the measured electrical conductivity σ , the intrinsic electrical conductivity σ_{E0} was calculated:

$$\sigma_{E0} = \frac{\sigma}{\ln(1 + e^\eta)}$$

Further, the phononic part of thermal conductivity κ_{ph} was calculated from the measured σ and thermal conductivity κ :

$$\kappa_{ph} = \kappa - L(\eta) \sigma T$$

with the Lorenz number $L(\eta)$ being calculated as:

$$L(\eta) = \frac{k_B^2}{e^2} \frac{3F_0(\eta)F_2(\eta) - 4F_1(\eta)^2}{F_0(\eta)^2}$$

The quality factor B was obtained from the following equation:

$$B = \left(\frac{k_B}{e} \right)^2 \frac{\sigma_{E0}}{\kappa_{ph}} T$$

For a given B , η was varied in order to find the optimal doping level, obtaining ZT for different chemical potentials η (see chapter 3.6):

$$zT(\eta) = \frac{S^2(\eta)}{\frac{(k_B/e)^2}{B \ln(1 + e^\eta)} + L(\eta)}$$

Supporting_Information_MnBiTe_CHEMRXIV.pdf (1.88 MiB)

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