Synthesis, crystal and topological electronic structures of new bismuth tellurohalides Bi_2TeBr and Bi_3TeBr

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ABSTRACT Halogen substitution, i. e. bromine for iodine, in the series of topological Bi_nTeI ($n = 1, 2, 3$) materials is conducted in order to explore an impact of anion exchange on the topological electronic structure. In the proof-of-concept study we demonstrate the applicability of the modular view on the crystal and electronic structures of the new Bi_2TeBr and Bi_3TeBr compounds. Along with the isostructural telluroiodides, they constitute a family of layered structures that are stacked from two basic building modules, ${}_2^{\infty}[\text{Bi}_2]$ and ${}_2^{\infty}[\text{BiTeX}]$ ($X = \text{I}, \text{Br}$). We present solid-state synthesis, thermochemical studies, crystal growth and crystal-structure elucidation of Bi_2TeBr (sp.gr. $R\bar{3}m$ (no. 166), $a = 433.04(2)$ pm, $c = 5081.6(3)$ pm) and Bi_3TeBr (sp.gr. $R\bar{3}m$ (no. 160), $a = 437.68(3)$ pm, $c = 3122.9(3)$ pm). First-principles calculations establish the topological nature of Bi_2TeBr and Bi_3TeBr . General aspects of chemical bonding appear to be similar for Bi_nTeX ($X = \text{I}, \text{Br}$) with the same n , so that the alternation of the global gap size upon substitution is insignificant. The complex topological inversion proceeds between the states of two distinct modules, ${}_2^{\infty}[\text{Bi}_2]$ and ${}_2^{\infty}[\text{BiTeBr}]$; thus, the title compounds can be seen as heterostructures built via a modular principle. Furthermore, highly disordered as well as incommensurately modulated ternary phase(s) are documented near the Bi_2TeBr composition. Single-crystal X-ray diffraction experiments on BiTeBr and Bi_2TeI resolve some discrepancies in the prior published work.

INTRODUCTION

Bismuth tellurohalides BiTeX ($X = \text{Cl}, \text{Br}, \text{I}$) constitute a multi-purpose material platform offering an attractive combination of functionalities such as fair thermoelectric performance,^{1,2} giant Rashba splitting of bulk and surface bands due to strong spin-orbit coupling and a lack of inversion symmetry^{3–10}, ambipolar conduction on different surface terminations thanks to the polarity of the structural fragments and strong internal electric fields,^{11–13} pressure-induced quantum topological phase transitions and lattice dynamics^{14–23} as well as, possibly, topological superconductivity^{24–26}. An interplay of these qualities enhances relevance of BiTeX for future applications in

spintronics near room temperature and creates more space for novel phenomena.

Chemical modification of structure and composition is a versatile tool to map out rich phase diagrams of possible electronic and magnetic ground states. There are several examples how physical properties of BiTeX can be varied by chemical means.

Improved thermoelectric performance was reported for a Cu-intercalated derivative²⁷ of BiTeI and Br-substituted $\text{BiTeI}_{1-x}\text{Br}_x$ ($x = 0.06, 0.12$)²⁸. Higher Br doping rates have not been investigated. Pure BiTeBr has a twice higher ZT value near room temperature than BiTeI .¹¹ Moreover, the TE figure-of-merit decreased in polycrystalline CuI/BiTeI ,

$\text{Bi}_2\text{Te}_3/\text{BiTeI}$ and Bi/BiTeI composites.^{2,29} Magnetic doping of BiTeI by Mn and V has also been attempted.³⁰ Bulk Bi_2Te_3 has a low ZT value that can be moderately improved by Zn doping.³¹

The layered BiTeI structure type can be altered in a more complex way as it incorporates corrugated $\infty[\text{Bi}_2]$ layers into the van der Waals gaps and, thus, transforms into $\text{Bi}_2\text{TeI} = [\text{Bi}_2]_2[\text{BiTeI}]^{32,33}$ or $\text{Bi}_3\text{TeI} = [\text{Bi}_2]_3[\text{BiTeI}]^{33}$ structure types. Remarkably, these heterostructures are thermodynamically stable and can be synthesized as phase-pure powders and single-crystals.³³

Furthermore, this structural modification augments the topological properties of the resultant lattices. The first building module, $\infty[\text{Bi}_2]$ (also referred to as Bi-bilayer³⁴), is a two-dimensional topological insulator (2D TI).^{35,36} Elemental bismuth can be regarded as a stack of interacting Bi-bilayers. Hybridization of the states along the stacking direction may result in 3D topological properties, although there is so far no consent whether pure bismuth has a nontrivial topology.^{37–41} A rough estimation using the bond-length bond-strength correlation assigns about 20 % of bonding of every Bi atom in the structure of elemental bismuth to interlayer bonding. Both a single $[\text{BiTeX}]$ layer and the periodic BiTeX lattice are topologically trivial under ambient conditions. Hydrostatic pressure may induce a quantum topological transition in bulk BiTeI via a band inversion at the A point of the 3D Brillouin zone (BZ) between the states of all atomic sorts.^{14,16} Chemical bonding between the $\infty[\text{Bi}_2]$ and $\infty[\text{BiTeI}]$ modules in Bi_2TeI exceeds the van der Waals interactions in pristine BiTeI , so that a topological inversion is realized Bi_2TeI at the Z point of the 3D BZ under normal pressure.^{42–44} Enhanced hybridization between the states of the Bi-bilayer and the BiTeI matrix results in a dual topological insulator in the case of Bi_2TeI and in a topological metal in the case of Bi_3TeI . A similarly developing tendency in topological properties is observed in the $\text{Bi}_2\text{Te}_3 - \text{BiTe} - \text{Bi}_4\text{Se}_3$ series.³³

We have recently described the concurrent evolution of structural and topological properties in the $\text{BiTeI} - \text{Bi}_2\text{TeI} - \text{Bi}_3\text{TeI}$ series in terms of a modular principle.³³ Our main aim is to derive a phenomenological principle that could assist in the pursuit of new topological materials,⁴⁵ so we want to put the modular design to a further test. The structure-property relation cannot be established for topological materials in a straightforward way, since, in general, the topological properties of bulk cannot be reduced to a superposition of the topological properties of its structure modules. Chemical bonding leading to enhanced hybridization and the resulting k_z dispersion cannot be quantified by simple means. Since the classic concept of topological insulators⁴⁶ does not directly include crystallography or chemical bonding, it does not directly point out real materials with complex symmetries and bonding patterns. Attempts to establish such relations have recently started.⁴⁷ The proposed analysis utilizes a local orbital-based picture. Modular design of new materials proceeds on the level of larger structure fragments, i. e. complexes, clusters, chains, layers, etc., and is more

feasible for a chemist than on the level of atoms and local point symmetries. Modular organization of solids diversifies the means of control of physical properties, since single modules can be tuned separately. Modulation doping of semiconductor heterostructures and high-temperature superconductors as well as the phonon-glass electron-crystal concept in thermoelectrics illustrate successful applications of this very general idea.^{48–50}

Topological bismuth telluroiodides offer two structure modules, $\infty[\text{Bi}_2]$ and $\infty[\text{BiTeI}]$, the former being a 2D TI. Our goal was to examine the applicability of the modular principle to the crystal structure, i. e. to expand the Bi_nTeI structure family via bromine substitution in a selected module. We have synthesized stable Bi_2TeBr and Bi_3TeBr compounds and elucidated their crystal structures. Another aim was to explore if the modular principle is pertinent to topological properties. For that, we traced the changes in the electronic spectra of the entire heterostructure by first-principle calculations upon chemical modifications in the selected module. As a result, we present a proof-of-concept study of the modular principle applied to Bi_2TeBr and Bi_3TeBr and demonstrate the impact of anion exchange on the crystal structure and topological electronic structure. First-principles calculations indicate that the topological band inversions in Bi_2TeBr and Bi_3TeBr take place between the states of two distinct modules. The observed chemical and electronic flexibility let us believe that further new effects could be discovered in bismuth tellurohalides via exertion of external perturbations as well as chemical pressure.

RESULTS AND DISCUSSION

1. Synthesis and Thermal Stability of Bi_nTeBr

Large hexagonal platelets of BiTeI and BiTeBr were first obtained in 1951.⁵¹ Crystal-growth routes⁵² and phase relations in the pseudo-binary $\text{BiBr}_3 - \text{Bi}_2\text{Te}_3$ section^{53,54} have been studied in full detail. In contrast to that, syntheses of Bi_2TeI ^{32,33} and Bi_3TeI ³³ were reported quite recently. We have applied the following core principles, that were determined previously for the Bi-Te-I system,³³ to the present study of the Bi-Te-Br system:

1. Tribochemical pre-activation of the reactants by ball-milling.
2. Thermochemical analysis of the mechanically activated mixtures.
3. Solid-state synthesis in the sub-solidus temperature region.

The targeted ternary phases have formed in all starting mixtures with the nominal compositions Bi_nTeBr ($n = 1, 2, 3$) already after the ball-milling (Fig. S1). No sign of BiBr_3 evaporation or decomposition was observed at this stage. The previously unaccounted PXRD patterns of Bi_2TeBr and Bi_3TeBr were preliminary indexed by analogy with the respective Bi_nTeI .³³ The resultant powdered samples were divided in two batches, one to be analyzed by differential scanning calorimetry (DSC) and the other to be consequently annealed in the sub-solidus range.

Our thermochemical experiments (see Supporting Information for an extended discussion, Fig. S2–S4) show that Bi_2TeBr and Bi_3TeBr melt at lower temperatures than BiTeBr^{54} and by ca. 10 °C lower than their Bi_nTeI analogs³³. We establish incongruent melting of Bi_3TeBr at around 400 °C, resembling the behavior of $\text{Bi}_3\text{TeI}^{33}$. The exact melting behavior of Bi_2TeBr cannot be conclusively elucidated from the available data. Interpretation is hampered by presence of an “intermediate” phase that exhibits a shifted and broadened set of reflections with respect to Bi_2TeBr that hints at massive structural disorder or poor crystallinity with small particle or domain size (Fig. S5).

Nevertheless, the DSC results enabled us to make an informed choice of the synthetic temperatures for phase-pure samples. The remaining parts of the ball-milled batches were annealed at the temperatures in the sub-solidus range, e. g. 385–450 °C depending on the sample composition. These solid-state reactions yield nearly phase-pure powder samples (Fig. 1) of Bi_nTeBr , whose reflections accord well with the theoretical patterns based on model Bi_nTeI analogs. The BiTeBr sample again shows admixtures of Bi_2Te_3 and for the sample of the nominal composition “ Bi_3TeBr ” a slight bismuth loss is observed that leads to formation of Bi_2TeBr admixture.

The crucial role of thorough homogenization (the above-listed synthetic principle 1) becomes apparent from the following example. The “intermediate” phase is obtained as the major product from a mixture of Bi, BiBr_3 and Te with the nominal composition “ Bi_2TeBr ” after annealing at 425 °C for 5 days and quenching (Fig. S6). As opposed to that, a similar mixture subjected to ball-milling and annealed at 400 °C for 5 days contains phase-pure Bi_2TeBr (Fig. 1). Furthermore, mixtures of Bi, BiBr_3 and Te with the nominal compositions “ $\text{Bi}_{2.5}\text{TeBr}$ ” and “ Bi_3TeBr ”, that were annealed at 425 °C for 5 days (i. e. above the melting point of Bi_3TeBr , cf. the principle 1 above) and quenched, contain phase mixtures of Bi_3TeBr , Bi_2TeBr and Bi.

Similar to $\text{Bi}_n\text{TeI}^{33}$, we did not find any Bi-rich ternaries or an extended homogeneity range on the bismuth-rich side. An annealed sample with the nominal composition “ Bi_4TeBr ” comprises a mixture of Bi_3TeBr , that does not show any changes in the unit cell parameters, and residual Bi (Fig. S7).

On this stage, a cautious conclusion can be drawn that the new Bi_nTeBr ($n = 2, 3$) are indeed structurally analogous to the telluroiodides (Table 1). No superstructure reflections and no notable deviations from the targeted compositions were observed.

The ED patterns of BiTeBr , Bi_3TeBr and Bi_2TeBr along the stacking direction (Fig. 2) strongly resemble the corresponding $\text{Bi}_n\text{TeI}^{33,43}$. The indexing concords with the lattice parameters (Table 1) and trigonal symmetry. The “intermediate” phase exhibits the same basic monoclinic subcell as Bi_2TeX (Fig. 2) but a different type of superstructure ordering along the c axis (see more experimental details about the “intermediate” phase in the Supplement, Fig. S8).

Fig. 1. PXRD patterns of the phase-pure Bi_nTeBr . Results of indexing: BiTeBr (sp. gr. $P3m1$) $a = 426.88(3)$ pm, $c = 648.86(2)$ pm; Bi_2TeBr (sp. gr. $R\bar{3}m$) $a = 433.01(1)$ pm, $c = 5085.2(2)$ pm; Bi_3TeBr (sp. gr. $R3m$) $a = 437.39(1)$ pm, $c = 3128.1(1)$ pm.

Table 1: The unit cell parameters (X-ray powder data) and volumes of the ternary compounds in the Bi–Te–X (X = I, Br) systems. The PXRD patterns of Bi_nTeBr were indexed by analogy with the respective Bi_nTeI . No superstructure reflections were observed.

n	Bi_nTeBr	$\text{Bi}_n\text{TeI}^{32,33,59}$
1	$a=427$ pm, $c=649$ pm $V = 102.5 \times 10^6$ pm ³	$a=434$ pm, $c=685$ pm $V = 111.7 \times 10^6$ pm ³
2	$a=433$ pm, $c=5085$ pm $V = 825.7 \times 10^6$ pm ³	$a=438$ pm, $c=5284$ pm* $V = 877.9 \times 10^6$ pm ³
3	$a=437$ pm, $c=3128$ pm $V = 517.3 \times 10^6$ pm ³	$a=440$ pm, $c=3223$ pm $V = 540.4 \times 10^6$ pm ³

* rhombohedral setting

Fig. 2. The main zone $[100]^*$ ED patterns of BiTeBr , Bi_3TeBr , Bi_2TeBr and the “intermediate” phase (left to right). Indexing accords with Table 1.

2. Crystal Structure Elucidation of Bi_nTeBr ($n = 1, 2, 3$)

2.1. Crystal Growth Experiments. As shown above, crystallization from melts is not applicable to Bi_2TeBr and Bi_3TeBr ; hence chemical-vapor-transport (CVT), auto-transport or mineralization could be the methods of choice to produce high-quality single crystals.

CVT methods are well-established for BiTeBr . Relying on the known growth mechanism, we obtained BiTeBr crystals of ca. 2 mm in diameter via autotransport at 450°C (plus a small temperature gradient due to internal convection in the tube furnace) for at least 10 days.

Single crystals of Bi_2TeBr and Bi_3TeBr (Fig. 3) suitable for X-ray diffraction studies (SCXRD) have grown, presumably via mineralization, directly on the phase-pure powder batches treated at 400°C and 385°C , respectively (see previous section). It was noticed that a longer annealing time favors the formation of larger crystals.

Fig 3. Single crystals of Bi_2TeBr (left) and Bi_3TeBr (right) used for SCXRD experiments. EDX data (averaged over 5 crystals (ca. 10 points per each), in at. %): Bi, 50.7(2); Te, 25.5(2); Br, 23.8(1) for Bi_2TeBr ; Bi, 60.3(6); Te, 19.3(6); Br, 20(1) for Bi_3TeBr .

2.2. Crystal Structure of BiTeBr . The first published Rietveld refinement characterized BiTeBr as a 2H-CdI_2 -type structure with mixed, statistical Te/Br occupancy of the anion positions (sp. gr. $P\bar{3}m1$), while BiTeI was found to crystallize in the polar space group (sp. gr. $P3m1$) with separated I and Te sites.⁵⁹ Addressing the Te/Br disorder issue, relativistic *ab initio* calculations predict the ordered BiTeBr to be by 180 meV/f. u. more energetically favorable.⁶⁰ Some recent contributions claim to have confirmed the non-centrosymmetric structure of BiTeBr experimentally by X-ray diffraction, but, as a matter of fact, either no experimental evidence was given,⁶¹ or a mere Le Bail fit

of the unit cell parameters was presented¹⁹. The absence of an inversion center within the ${}^2[\text{BiTeBr}]$ layers was deduced indirectly from group theory analysis and Raman scattering measurements.^{19,62}

Fig. 4. Ordered BiTeBr crystal structure. Ellipsoids comprise 99 % of the probability density of the atoms.

Our re-determination of the structure by X-ray diffraction on a single-crystal definitely proves that BiTeBr crystallizes in the polar spacegroup $P3m1$ (no. 156) and is isostructural to BiTeI . The lattice parameters at room temperature are $a = 426.77(1)$ pm and $c = 648.43(3)$ pm (Table S1) in good agreement with the previous data⁵⁹ ($a = 426.62(1)$ pm and $c = 648.7(1)$ pm). The trigonal structure of BiTeBr is closely related to the CdI_2 structure type and is assembled by ${}^2[\text{BiTe}_{3/3}\text{Br}_{3/3}]$ triple layers (Fig. 4). In contrast to the hitherto disputed mixed occupancy of Te and Br,⁵⁹ our refinement yields anionic ordering in two separate atomic positions (Table S2) in full accordance with [61]. Given the non-centrosymmetric structures of both BiTeBr and BiTeI , statistical Br/I mixing can be assumed in the $\text{BiTeI}_{1-x}\text{Br}_x$ series. Halogen ordering would result in the decreased symmetry and a different set of the unique reflections in PXRD.

2.3. Crystal Structures of Bi_2TeBr and Bi_3TeI . Our X-ray diffraction experiment on a Bi_2TeBr single crystal reveals a rhombohedral lattice with $a = 433.04(2)$ pm and $c = 5081.6(3)$ pm and the centrosymmetric space group $R\bar{3}m$ (no. 166) (Table 2). The crystal structure can be described, just like Bi_2TeI ^{32,33}, as a regular alternation of one buckled ${}^2[\text{Bi}_2]$ layer and two consecutive ${}^2[\text{BiTe}_{3/3}\text{Br}_{3/3}]$ trilayers (Fig. 5, Table S4).

Fig. 5. Bi_2TeBr crystal structure. Ellipsoids comprise 99 % of the probability density of the atoms.

The crystal structure of Bi_2TeI was initially solved in the C-centered monoclinic cell.³² We showed³³ a possible transformation into a cell with trigonal (rhombohedral) metrics. This transformation causes negligible deviations of angles ($<0.01^\circ$) and atomic positions (<0.1 pm) from the higher symmetric space group $R\bar{3}m$ ³³. Overlooked trigonal symmetry is found relatively often in the previously reported C-centered monoclinic structures.⁶³ We hereby revisit the single-crystal solution for Bi_2TeI and describe it in the centrosymmetric space group $R\bar{3}m$ (no. 166) with $a = 437.88(1)$ pm and $c = 5283.8(3)$ pm (Table 2, Table S6).

The final R values and the residual electron density indicate crystallographic problems in both isostructural

Bi_2TeX , likely stemming from structural disorder. It may be caused by the presence of an inversion center in the Bi_2TeX structures, which is generated via the flipping of every second ${}^2[\text{BiTe}_{3/3}\text{X}_{3/3}]$ trilayer, in contrast to the polar stacking of BiTeX . Calculations demonstrate that both mutual orientations of the trilayers, $[\text{I-Bi-Te-Te-Bi-I}]$ and $[\text{I-Bi-Te-I-Bi-Te}]$ differ negligibly by 0.5 meV⁶⁴, making stacking disorder in bulk highly probable. On the other hand, the calculated formation energy of stacking faults in bulk BiTeBr is about 50 times higher than in BiTeI .⁶⁵

The shapes and sizes of the displacement ellipsoids (Table S4, Table S6) suggest a certain type of stacking disorder in Bi_2TeX that is associated with varying stacking sequences of modules with different chemical identity rather than shifts of modules. Our TEM study do not, however, lend a corroboration for this assumption.

2.4. Crystal Structure of Bi_3TeBr . The most Bi-rich compound of the presented series, Bi_3TeBr , crystallizes in the polar space group $R3m$ (no. 160) with lattice parameters $a = 437.68(3)$ pm and $c = 3122.9(3)$ pm (Table 3) and is isostructural to Bi_3TeI ³³. It is built up by alternating corrugated ${}^2[\text{Bi}_2]$ bilayers and ${}^2[\text{BiTe}_{3/3}\text{Br}_{3/3}]$ trilayers (Fig. 6, Table S8). Bi_3TeI was described with the aid of a pseudo-inversion center in order to explain the conspicuous displacement parameters.³³ Thanks to larger domains in Bi_3TeBr promoting higher resolution, it is now possible to improve this description to some extent. The crystal structure of Bi_3TeBr was refined with reverse-obverse (a result of two settings in the rhombohedral cell) and inversion twinning. Additionally, a split position was introduced on both the Te1 and the Bi3 site, and the respective occupancies of the split atoms were refined to 40 % of Bi in the Te1 site, and 40 % of Te in the Bi3 site, respectively (Fig. S10). Regardless of the applied description, this recurring crystallographic problem is most likely caused by ubiquitous stacking disorder, originating from the small energy differences between various stacking variants of the ${}^2[\text{BiTe}_{3/3}\text{X}_{3/3}]$ trilayers with respect to each other and to the ${}^2[\text{Bi}_2]$ layers. The sizes of the thermal displacement parameters for Te and Br compared between BiTeBr (Table S2) and Bi_3TeBr (Table S8) may point at such disorder type as flipping of ${}^2[\text{BiTe}_{3/3}\text{Br}_{3/3}]$ trilayers.

We have also considered yet another possible stacking sequence for Bi_3TeBr with two ${}^2[\text{BiTe}_{3/3}\text{Br}_{3/3}]$ trilayers followed by two ${}^2[\text{Bi}_2]$ bilayers that face only the Br atomic planes along the c axis. This model bears more similarity to the Bi_2TeX stacking since the interlayer Bi-Te contacts would be also avoided. This structure hypothesis complies with the X-ray diffraction data, but is not supported by the HRTEM imaging (cf. Fig S7).

Table 2: Crystallographic data for Bi₂TeBr and Bi₂TeI (refined in a rhombohedral cell).

Compound	Bi ₂ TeBr	Bi ₂ TeI
Crystal system, space group	Trigonal, $R\bar{3}m$ (no. 166)	
Formula units	$Z = 6$	
Lattice parameters	$a = 433.04(2)$ pm $c = 5081.6(3)$ pm $V = 825.3(1) \times 10^6$ pm ³ $\rho_{\text{calc.}} = 7.55$ g cm ⁻³	$a = 437.88(1)$ pm $c = 5283.8(2)$ pm $V = 877.4(1) \times 10^6$ pm ³ $\rho_{\text{calc.}} = 7.64$ g cm ⁻³
Range for data collection; index ranges	$4.81^\circ \leq 2\theta \leq 49.71^\circ$ ($\lambda = 71.073$ pm); $-5 \leq h \leq 5$, $-5 \leq k \leq 4$, $-60 \leq l \leq 54$;	$6.94^\circ \leq 2\theta \leq 49.99^\circ$ ($\lambda = 71.073$ pm); $-5 \leq h \leq 5$, $-5 \leq k \leq 5$, $-62 \leq l \leq 62$;
Collected reflections	3230 measured, 230 unique	3742 measured, 403 unique
R indices of merging	$R_{\text{int}} = 0.033$, $R_\sigma = 0.013$	$R_{\text{int}} = 0.030$, $R_\sigma = 0.015$
Structure refinement	Full-matrix least-squares based on F^2 , anisotropic displacement parameters;	
Data/restraints/parameters	230/0/13	403/0/14
Final R indices and goodness-of-fit on F^2	$R_1[181 F_o > 4\sigma(F_o)] = 0.036$ wR_2 (all F_o^2) = 0.065 $\text{Goof} = 1.223$	$R_1[181 F_o > 4\sigma(F_o)] = 0.042$ wR_2 (all F_o^2) = 0.092 $\text{Goof} = 1.101$
Min./max. residual electron density	$-3.22/2.05 \text{ e} \times 10^{-6} \text{ pm}^{-3}$	$-5.26/4.05 \text{ e} \times 10^{-6} \text{ pm}^{-3}$

Fig. 6. Bi_3TeBr crystal structure. Ellipsoids comprise 99 % of the probability density of the atoms.

Table 3: Crystallographic data for Bi_3TeBr .

Crystal system, space group	Trigonal, $R\bar{3}m$ (no. 160)
Formula units	$Z = 3$
Lattice parameters	$a = 437.68(3)$ pm $c = 3122.9(3)$ pm $V = 518.1(1) \times 10^6$ pm ³ $\rho_{\text{calc.}} = 8.03$ g cm ⁻³
Range for data collection; index ranges	$3.92^\circ \leq 2\theta \leq 72.62^\circ$ $(\lambda = 71.073$ pm); $-7 \leq h \leq 7, -7 \leq k \leq 7, -51 \leq l \leq 49$;
Collected reflections	8650 measured, 1193 unique
R indices of merging	$R_{\text{int}} = 0.051, R_\sigma = 0.033$
Structure refinement	Full-matrix least-squares based on F^2 , anisotropic displacement parameters;
Data/restraints/parameters	1193/0/22
Final R indices and goodness-of-fit on F^2	$R_1[289 F_o > 4\sigma(F_o)] = 0.022$ wR_2 (all F_o^2) = 0.045 $\text{Goof} = 1.005$
Min./max. residual electron density	$-1.02/0.60$ e $\times 10^{-6}$ pm ⁻³

An in-depth theoretical and spectroscopic study of structural disorder in Bi_nTeX could be highly relevant for their physical properties. Theory has found a connection

between such defects as flipped trilayers and topological properties.^{64,66} For instance, two adjacent $\infty[\text{BiTeI}]$ trilayers connected via an inversion center and facing their Te atomic planes across the van der Waals gap would form a 2D topological defect in the trivial non-centrosymmetric BiTeI bulk. Moreover, a hypothetical periodic lattice built by regularly stacked $[\text{Br-Bi-Te}\cdots\text{Te-Bi-Br}]$ fragments could be a strong 3D TI. It is, however, notably less favorable (by ca. 20 meV / f. u.) than the non-centrosymmetric bulk BiTeBr . This prediction was confirmed by an STM study of BiTeBr ⁶⁵ revealing two single-domain (001) surfaces with opposite terminations. On the contrary, BiTeI has a multi-domain (001) surface with co-existing Te- and I-terminations on the scale of 100 nm.^{11,67-69} Consequently, BiTeBr is believed to be the most homogeneous of all BiTeX tellurohalides and a well-suited candidate for future spintronic applications. We also did not observe any signs of stacking disorder, domains or flipped layers in BiTeBr . As opposed to that, both Bi-rich tellurobromides and telluroiodides are prone to stacking disorder. Nevertheless, new Bi_nTeBr may become a better playground for forthcoming investigations, because twinning phenomena can be resolved better than in Bi_nTeI .

Comparison of the interatomic distances in Bi_nTeX ($X = \text{I}, \text{Br}$) hints at similar bonding scenarios in the respective compounds (Table 4, Table S3, Table S5, Table S7, Table S9). The Bi-Te distances are virtually unchanged as one moves from a telluroiodide to the corresponding tellurobromide. An exception observed for Bi_3TeBr is most likely a consequence of the refinement of a split position that entails a small shift of the Te atom towards the Bi atom. Since Bi_3TeI was refined without a split position, the estimated interatomic distance is slightly longer. As can be expected from the electronegativity values, the Bi-X distances are significantly shorter for $X = \text{Br}$ than for $X = \text{I}$. A general tendency towards elongation of pairwise bonds and diminishing van der Waals gaps upon increasing n is observed for all compounds. Interlayer and intralayer Bi-X contacts become almost equal in Bi_3TeBr as an effect of the introduced inversion twin (50/50), but also due to strengthening metallicity and interlayer interactions within the stack (cf. next section). A larger portion of Bi-bilayers enhances the metallic character of the discussed compounds.

We analyzed changes in the unit cell volumes upon bromine substituting for iodine in the entire Bi_nTeX series by comparison with *Biltz* volume increments⁵⁵. The values for Br^- (25 cm³/mol) and I^- (34 cm³/mol) amount to 41.5 Å³ and 56.5 Å³, respectively.⁵⁵ Thus, a simple size effect by iodine substitution for bromine would yield ca. 36 % increase in volume. However, the experimentally observed volume increments per $\infty[\text{BiTeX}]$ layer are 9.2 Å³ for $n = 1$, 8.7 Å³ for $n = 2$, and only 7.7 Å³ for $n = 3$, when moving from Bi_nTeBr to the respective Bi_nTeI . The observed tendencies of decreasing increments upon increasing n could indicate successive strengthening of bonding between the $\infty[\text{BiTeX}]$ and $\infty[\text{Bi}_2]$ layers across the van der Waals gap that goes beyond electrostatic anion-anion repulsion and weak van der Waals bonding in pristine

BiTeX. In other words, differences in electronegativity and polarizability between iodide and bromide become less prominent with increasing n and growing metallicity (see next section).

Table 4: Interatomic distances of Bi_nTeX ($X = \text{I}, \text{Br}$; $n = 1, 2, 3$).

n	Bond	Bi_nTeBr / pm	Bi_nTeI / pm
1	Bi-Te	301.1(1) [#]	303.9 ⁺
	Bi-X	312.1(1) [#]	327.3 ⁺
2	Bi-Te	304.8(2) [#]	305.9(2) [#]
	Bi-X	321.6(2) [#]	339.1(2) [#]
	Bi-Bi	309.2(2) [#]	309.9(2) [#]
3	Bi-Te	298.8(5) [#]	311.9 [*]
	Bi-X	334.4(2) [#]	343.6 [*]
	Bi-Bi	310.4(4) [#]	304.8 [*]

[#]: this work, ^{*}: [26], ⁺: [43]

4. Electronic Structures of Bi_nTeBr ($n = 2, 3$)

The bulk electronic structure of Bi_2TeBr with spin-orbit coupling (Fig. 7) has a nearly semimetallic character with electron pockets along the Γ -M and A-L directions of the 3D Brillouin zone (BZ). It can be concluded that a single pocket is projected onto the $\bar{\Gamma}$ - $\bar{M}$ direction of the 2D BZ. A complex inversion involving several groups of bands close to the Fermi level is observed near the Γ point. Two band groups reside in the occupied and another two at the unoccupied part of the spectrum. These groups are formed by the states of two different types of building modules: $\infty[\text{BiTeBr}]$ trilayers (magenta in Fig. 7) and $\infty[\text{Bi}_2]$ bilayers (blue in Fig. 7). The trilayer states mostly have the p_z symmetry, whereas the bilayer states possess the p_{xy} symmetry. The inversion of these states is caused by a complex hybridization and results in new insulating local band gaps out of the time-reversal invariant momenta (Fig. 7, red dashed ovals). The same inversion scheme has been previously observed for a dual topological insulator Bi_2TeI .⁴³ However, the distance between the electron and the hole part of the spectrum is larger in Bi_2TeI , which leads to a semiconductor-like band structure. Such complex inversion of the bulk states in Bi_2TeBr is a direct indication of the non-trivial topology. Subsequently, topological surface states emerge.

The stacking sequence of the structure modules in Bi_2TeBr offers three plausible terminations of the natural cleaving, i. e. by Te, Br and $[\text{Bi}_2]$ -layers.

The electronic structure of the Te-terminated surface is given in Fig. 8a. It features a topological surface state (TSS) in the local bulk band gap close to the Fermi level along the $\bar{\Gamma}\bar{K}$ and $\bar{\Gamma}\bar{M}$ directions. The state originates from the complex band inversion and the details of its formation were discussed for the identical Te-termination in Bi_2TeI .⁴³ The TSS is gapless along $\bar{\Gamma}\bar{M}$, whereas there is a tiny gap (~ 7 meV) in the $\bar{\Gamma}\bar{K}$ direction. In contrast to the earlier monoclinic description of Bi_2TeI ,^{32,43} the trigonal

crystal symmetry of Bi_2TeX necessitates the equivalence of all $\bar{\Gamma}\bar{M}$ directions and the gapless degeneracy of TSS along them.

Fig. 7. a) Bulk electronic structure of Bi_2TeBr with spin-orbit coupling. The states of the $\infty[\text{Te-Bi-Br}]$ trilayers ($\infty[\text{Bi}_2]$ -layers) are marked in magenta (blue). The local gap formed via a complex hybridization is outlined by dashed red ovals. **b)** The corresponding 3D BZ.

Fig. 8. (a) Surface electronic structure of Bi_2TeBr for the Te-termination. The bulk band continuum is shown in grey. For surface states, the radii of the red and blue circles symbolize the values of the in-plane components of spin eigenvalues perpendicular to the shown direction of the 2D Brillouin zone. **(b)** Spatial distribution of the charge density for the b_1 branch in the (1120) plane near the cross point (left panel). The maximum and minimum charge-density value of the state are marked by red and white, respectively. The charge density $\rho(z)$ of the branch integrated over the xy plane is shown in orange (right panel). Lila

and grey dotted rectangles outline the topmost surficial trilayer and bilayer modules. (c) *Ibid*, for the b2 branch.

The TSS has two branches (marked b1 and b2 in Fig. 8a) with different spatial localization and symmetry of the atomic orbitals. The outer branch (marked by b1) is strongly localized in the topmost ${}^2_{\infty}[\text{Te-Bi-Br}]$ layer and is mostly formed by the p_z orbitals of the topmost Te atoms and the Bi p -orbitals of this trilayer (see Fig. 8b). The more remote Br atoms and ${}^2_{\infty}[\text{Bi}_2]$ -layers make only a minor contribution to b1. The inner branch b2 is localized in both ${}^2_{\infty}[\text{Te-Bi-Br}]$ and adjacent ${}^2_{\infty}[\text{Bi}_2]$ modules (Fig. 8b-c) and is composed of the p -orbitals of both the topmost trilayer and bilayer modules. In contrast to b1, the contributing orbital symmetry in the topmost ${}^2_{\infty}[\text{Te-Bi-Br}]$ trilayer and ${}^2_{\infty}[\text{Bi}_2]$ -bilayer changes: the Te-states have the p_{xy} symmetry, the Br-states have the p_z symmetry, and the $[\text{Bi}_2]$ -states have the p_{xy} symmetry.

The complex inversion of the bulk states also fosters additional spin-polarized TSS with the Dirac-like dispersion in the valence and conduction bands (denoted TS2 and TS3 in Fig. 8a).

The surface electronic structure of the Br-terminated surface of Bi_2TeBr is shown in Fig. 9. It is characterized by both trivial and topological surface states. The former (SS1) sits in the local bulk band gap near the Fermi level and stems from an effective electric field gradient that is normal to the surface plane. The gradient occurs in the topmost asymmetric trilayer, and, consequently, the SS1 is predominantly localized in there (lila profile in Fig. 9b). In agreement with the electric field gradient, the spin-splitting and the dispersion of SS1 have a Rashba-like character. The TSS resides in both electron and hole local band gaps. In contrast to the Te-termination, the state is present in the local gap near the Fermi level only along the $\bar{\Gamma}\bar{M}$ directions of the 2D BZ. The spatial distribution profiles for both branches (b1 and b2) resemble those at the Te-terminated surface, but the state at the Br-surface penetrates much deeper into the $[\text{Br-Bi-Te}]$ topmost trilayer. Actually, a gapless spin-helical TSS is found only on the Te-terminated surface. On the Br-surface, it survives only along the $\bar{\Gamma}\bar{M}$ direction due to hybridization with the trivial Rashba-type surface state.

An additional spin-polarized TSS (TS2, Fig. 9) exists in the local valence band gap. It is also caused by the complex inversion involving several bulk bands. In contrast to the TSS close to the Fermi level, the state in the electron part of the spectrum has a linear dispersion and forms a Dirac cone with branches uniformly localized within the outer trilayer fragments (Fig. 9b).

The bulk electronic structure of Bi_3TeBr without spin-orbit coupling is similar to that for $\text{Bi}_3\text{TeI}^{33}$ (Fig. S12). When spin-orbit coupling is taken into account, the semimetallic electronic spectrum of Bi_3TeBr transforms into a metallic one (Fig. 10). Interactions between the two structure fragments, ${}^2_{\infty}[\text{Bi}_2]$ and ${}^2_{\infty}[\text{BiTeBr}]$, trigger a complex hybridization of the bulk states. In particular, this hybridization produces several local gaps with inverted edges

(marked by green ovals in Fig. 10). Like Bi_2TeBr and $\text{Bi}_2\text{TeI}^{33}$ and in contrast to isostructural Bi_3TeI , the inversion in Bi_3TeBr occurs between the states of two distinct structure fragments, corroborating the modular principle. The inversion close to the Fermi level proceeds predominately between the p_x - and the p_y -states of the ${}^2_{\infty}[\text{BiTeBr}]$ trilayer and the p_z -states of ${}^2_{\infty}[\text{Bi}_2]$ (Fig. 10).

Fig. 9. (a) Surface electronic structure of Bi_2TeBr for the Br-termination. The bulk band continuum is shown in grey. For surface states, the radii of the red and blue circles symbolize the values of the in-plane components of spin eigenvalues perpendicular to the shown direction of the 2D Brillouin zone. (b) Charge density of states integrated over the xy plane for the points shown by arrows in the panel (a).

Fig. 10. Bulk electronic structure of Bi_3TeBr with spin-orbit coupling with atomic orbital contributions. The dark green ovals encircle local gaps formed via complex hybridization.

Fig. 11 and Fig. 12 present the surface electronic structure of Bi_3TeBr with spin texture for all four possible surface terminations. The terminations of all types host spin-polarized TSS that stem from the above discussed bulk-band inversion. A topological surface state on the Te-terminated surface represents the upper part of a Dirac cone and is formed by two branches propagating in the $\bar{\Gamma}\bar{K}$ and $\bar{\Gamma}\bar{M}$ directions (Fig. 11a). The Dirac point is submerged into the bulk continuum of the valence band. The

surface states on the Br-terminated (Fig. 11b) and two types of the Bi-terminated (Fig. 12) surfaces are localized over a wide energy range (from -0.6 to 0 eV) in the local valence band gap. These states have a cone-like dispersion with the Dirac point at the center of the Brillouin zone. The energy position of the cone is directly determined by the near-surface band-bending effect, which can be traced by a comparison of the DFT and the tight-binding results (right panels in Fig. 11, 12). The latter data do not comprise the band-bending contribution. The Br-terminated surface exhibits positive band-bending, while the remaining Te- and Bi₂-terminations demonstrate a negative effect. Due to particularly large negative band bending at the Te-terminated surface, the cone dispersion is distorted by interaction with the bulk-band continuum at approx. -0.6 eV. Hence the Te-terminated surface is characterized by maximal negative band-bending, whereas the type-I $\infty[\text{Bi}_2]$ -termination exhibits the largest positive band-bending. Note that the band-bending effect is larger on the type-II $\infty[\text{Bi}_2]$ -terminated surface than on the type-I one.

Fig. 11. Surface electronic structures of the Te- and Br-terminations of Bi_3TeBr . For surface states, the radii of the red and blue circles symbolize the values of the in-plane components of spin eigenvalues perpendicular to the shown direction of the 2D Brillouin zone. The results of DFT calculations are presented in the left column, the results of TB calculations – in the right column.

Fig. 12. Surface electronic structures of the two Bi₂-terminations (I and II type) of Bi_3TeBr . For surface states, the radii of the red and blue circles symbolize the values of the in-plane components of spin eigenvalues perpendicular to the shown direction of the 2D Brillouin zone. The results of DFT calculations are presented in the left column, the results of TB calculations – in the right column.

To conclude, the topological character of new tellurobromides coincides with the corresponding telluroiodides³³. Bi_3TeBr is essentially a dual topological insulator, i. e. a topological crystalline insulator owing to the mirror planes and a weak 3D topological insulator with $Z_2 = 0; (001)$. The topological band gap in Bi_3TeBr crosses the Fermi level almost in the full 3D BZ with an exception of a small electronic pocket along the Γ -M direction, that makes the electronic spectrum of Bi_3TeBr semimetallic. Bi_3TeBr is a topological metal with a complex hybridization of the states. A larger band gap is expected for elements with higher electronegativity, i. e. bromides vs. iodides, in the case of trivial insulators. It is, however, opposite in the topological regime due to the inverted (or negative) character of the gap. A transition between a topological and a trivial insulator proceeds via gap closing, and a topological semimetal may form at the boundary. Consequently, doping of topological insulators with lighter elements may cause the bulk band gap to close first and then to invert, as was observed for $\text{TlBiSe}_{2-x}\text{S}_x$ and $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$.⁷⁰ Another example of this effect is a small-

er gap in Bi_2Se_3 in comparison with Bi_2Te_3 , as calculated within the GW-approach.⁷¹

CONCLUSIONS

Ternary bismuth tellurohalides Bi_nTeX ($X = \text{I}, \text{Br}$; $n = 1, 2, 3$) constitute a structurally flexible materials' base for exploration of topological properties. Their structure and composition can be modified via incorporation of $[\text{Bi}_2]$ modules and anionic substitutions, similarly to topologically non-trivial bismuth tellurides⁷². We have developed synthetic routes for bulk samples and crystals of Bi_nTeBr ($n = 2, 3$) layered heterostructures. Further stacking variants may exist as evidenced by the "intermediate" phase.

In many aspects, both structural and electronic, the discovered tellurobromides have appeared the same as the telluroiodides³³. Ubiquitous stacking disorder, however, can be better resolved in the Bi_nTeBr series, so that these compounds are most suitable for forthcoming studies of topological defects in the spirit of [64, 66]. In contrast to a trivial insulator BiTeBr , Bi_2TeBr and Bi_3TeBr are predicted to have topologically non-trivial electronic spectra by our calculations. They exemplify how enhanced chemical bonding along the stacking direction, exceeding van den Waals interactions, can drastically alter the electronic properties of the trivial insulating matrix of BiTeBr , which has a larger gap than BiTeI . In some sense, this is an alternative to "physical" pressure proposed to modify the properties of bulk BiTeI .¹⁴ Chemical bonding in Bi_nTeX is realized through overlaps of the p -orbitals and structural/chemical similarity of the structure modules. For instance, $(\text{BiTe})^+$ is isoelectronic to Bi_2 in terms of the valence electrons.⁵⁹ This complementarity ensures the structural and compositional richness provided by various combinations of building units, i.e. the applicability of the modular approach to the crystal structures.

The modular view on Bi_nTeX is not limited by structure aspects. The Bi_nTeX lattices are not mere stacks of independent 2D TI modules, but instead realize a topological band inversion as a result of interlayer bonding. The ${}^\infty[\text{Bi}_2]$ module incorporated into the BiTeX matrix is not an ionic spacer, like bismuth-iodide fragments in $\text{Bi}_{14}\text{Rh}_3\text{I}_9$ ⁷³, but a rightful player in the game. Relatively low polarity of chemical bonding and highly diffuse p -orbitals of Bi support strong hybridization of the states between the adjacent modules along the stacking direction. Moreover, differences in the electronegativity between I and Br do not significantly affect the electronic properties of Bi_nTeX with inverted topological gaps. The topological band inversion takes place between the states of two distinct structure fragments, ${}^\infty[\text{Bi}_2]$ and ${}^\infty[\text{BiTeX}]$, as found for Bi_2TeI ³³, Bi_2TeBr and Bi_3TeBr .

EXPERIMENTAL SECTION

Powder synthesis. Similar to Bi_nTeI ³³, the target tellurobromides were synthesized from the stoichiometric

mixtures of bismuth, tellurium and bismuth tribromide. Subsequent oxidation and occasional formation of BiOBr (transparent yellow, $T_m = 620^\circ\text{C}$) posed a much stronger issue for the bromides than for iodides. Additionally, high volatility of BiBr_3 likely accounted for small deviations from the target compositions in some cases.

Polycrystalline samples were obtained by annealing of a stoichiometric mixture of Bi, Te, and BiBr_3 (bismuth, MERCK, treated at 220°C in H_2 -flow; tellurium, MERCK, > 99.9%; bismuth(III)-bromide, synthesized from the elements and sublimated twice). The starting materials were pulverized by ball milling ("Pulverisette 23", Fritsch) for 25 minutes under argon atmosphere in a glovebox. The homogeneous powder was sealed in an evacuated silica ampoule. The samples of Bi_nTeBr ($n = 2, 3$) were annealed at 400°C and 385°C , respectively, for at least three days.

Crystal Growth. Phase-pure powders synthesized via the above described procedure were used as batches for the crystal-growth experiments. Small single crystals (up to $200\ \mu\text{m}$) for single-crystal X-ray diffraction studies were obtained via mineralization for 2 weeks at 400 and 385°C for Bi_2TeBr and Bi_3TeBr , respectively.

X-ray diffraction experiments. Single-crystal X-ray diffraction was measured on a four-circle Kappa APEX II CCD diffractometer (Bruker) with a graphite(002)-monochromator and a CCD-detector at $T = 296(2)\ \text{K}$. $\text{Mo-K}\alpha$ radiation ($\lambda = 71.073\ \text{pm}$) was used. A numerical absorption correction based on an optimized crystal description⁷⁴ was applied and the initial structure solution was performed in JANA2006⁷⁵. The structures were refined in SHELXL against F_o^2 .^{76,77} Further details on the crystal structure investigation of BiTeBr , Bi_2TeBr , Bi_3TeBr and Bi_2TeI can be obtained from the Supporting Information (Tables S1–S9) and from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-434404, 434405, 434406, and 434407, respectively.

Powder X-ray diffraction data were measured using a X'Pert Pro diffractometer (PANalytical) with Bragg-Brentano geometry, a curved Ge(III) monochromator, and $\text{Cu-K}\alpha$ radiation ($\lambda = 154.06\ \text{pm}$). Variable divergence slits were used to keep the illuminated sample area constant.

Graphics of the structures were developed with Diamond⁷⁸ software.

Thermal properties of BiTeBr , Bi_2TeBr and Bi_3TeBr were analyzed by means of differential scanning calorimetry (DSC) using a Setaram Labsys ATD-DSC device with a k-probe (Ni-Cr/Ni-Al ; $T_{\text{max}} = 800^\circ\text{C}$) and Al_2O_3 as a reference compound. Heating and cooling rates of $2^\circ/\text{min}$ were employed. The substance was sealed in an evacuated silica glass ampoule.

Transmission and Scanning Electron Microscopy. SEM images were collected on a Hitachi SU8020 microscope. Acceleration voltages of 10 to 20 kV and current of

10 μA were used to create the SEM images. Energy dispersive X-ray spectra (EDX) were collected using an Oxford Silicon Drift X-Max^N detector at an acceleration voltage of 20 kV and a 100 s accumulation time. The EDX analysis was performed using the P/B-ZAF standardless method (where Z = atomic no. correction factor, A = absorption correction factor, F = fluorescence factor, P/B = peak to background model).

High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) studies were performed on a FEI Titan F20 microscope with CS-correction operating at 80 kV and on a CM20 microscope (Philips) operating at 200 kV. For image acquisition, a 2k $\times$ 2k Slow-Scan CCD-Camera (Gatan) was used. Image simulations were done with the JEMS software⁷⁹. Samples were ground in ethanol and deposited on a lacey carbon grid. In addition, thin lamellas were cut from a single crystal of Bi₃TeBr and a crystal of the “intermediate” phase perpendicular to the largest facets, i.e. along the stacking direction, with an ultramicrotome (Ultracut, Leica Microsystems) equipped with a diamond knife. Prior to it, the crystals were embedded in the epoxy resin Epon (Fluka) that was then polymerized at 60 °C. The nominal lamella thickness was approx. 50 nm while locally crystalline flakes with lower thickness were observed.

Computational details. Electronic structure calculations were carried out within the density functional theory using the projector augmented-wave method⁸⁰ as implemented in the VASP code^{81,82}. 11 $\times$ 11 $\times$ 1 (7 $\times$ 7 $\times$ 1) *k*-point mesh has been employed in the case of surface (bulk) calculations. The exchange-correlation energy was treated using the generalized gradient approximation⁸³. Exchange-correlation functional Perdew-Becke-Ernzerhof (PBE) was used. The Hamiltonian contained the scalar relativistic corrections and the spin-orbit coupling was treated by second variation method. The cut-off plane-wave basis was chosen to be 300 meV.

A repeated slab model was used to calculate the surface electronic structures of the title compounds. A vacuum gap of about 15 Å was introduced between the slabs to prevent their interaction from both sides. 32 atomic planes were used to simulate one Te-terminated slab of Bi₂TeBr, and 30 atomic plane – to model a Br-terminated slab of Bi₂TeBr. Thus, finite-size effects for surface states were prevented. 38 atomic layers were used to simulate the [Te–Bi–Br...Bi–Bi]– and the [Bi–Bi...Br–Bi–Te]– terminations in Bi₃TeBr. 30 atomic layers were used to simulate the [Br–Bi–Te...Bi–Bi]– and the [Bi–Bi...Te–Bi–Br]– terminations in Bi₃TeBr.

The large slab Hamiltonian within tight-binding method derived from the bulk one was afterwards used to calculate surface Green functions.^{84–86} Hence the TB models were constructed using WANNIER90 code^{87,88}. The chosen basis consisted of six spinor p-type orbitals for each atom: $|p_x^\uparrow\rangle$, $|p_y^\uparrow\rangle$, $|p_z^\uparrow\rangle$, $|p_x^\downarrow\rangle$, $|p_y^\downarrow\rangle$, $|p_z^\downarrow\rangle$. The low-lying s-orbitals were not taken into consideration.

ASSOCIATED CONTENT

Supporting Information. PXRD of the synthesized samples, experimental DSC data and discussion, HRTEM data, unit cell parameters for BiTe_xBr_{1–x}, additional crystallographic data (incl. atomic parameters, isotropic displacement parameters and selected interatomic distances for Bi_nTeBr (*n* = 1, 2, 3), bulk band structures without spin-orbit coupling are available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

This work was supported by the German Research Foundation (DFG) in the framework of the Special Priority Program (SPP 1666) “Topological Insulators” and by the ERANET-Chemistry Program. We acknowledge support by Academic D. I. Mendeleev Fund Program of Tomsk State University (project No. 8.1.01.2018), by Saint Petersburg State University (project No. 15.61.202.2015), by Ministry of Education and Science of the Russian Federation within the framework of the governmental program “Megagrants” (State Task No. 3.8716.2017/P220 or 3.8716.2017/9.10), by Russian Science Foundation No. 18-12-00169 (for surface electronic structure within tight-binding method), by Spanish Ministry of Science and Innovation (Grants No. FIS 2013-48286-Co2-02-P, No. FIS 2013-48286-Co2-440 01-P, and No. FIS 2016-75862-P).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This research received its initial impetus and supervision from Prof. Boris A. Popovkin (1937–2008), to whom the authors are indebted for inspiration. We are grateful to Prof. C. T. Koch, Dr. Wouter Van den Broek (Humboldt-University Berlin, Germany) and Prof. U. Kaiser (University of Ulm, Germany) for the provided TEM facilities at the Physics Department of the University of Ulm, and to Mr. E. Schmid (Central facility for electron microscopy, University of Ulm) for ultramicrotomy of our samples.

ABBREVIATIONS

TI topological insulator; DSC differential scanning calorimetry; PXRD powder X-ray diffraction; SCXRD single-crystal X-ray diffraction; SEM scanning electron microscopy; TEM transmission electron microscopy; ED electron diffraction; HRTEM high-resolution transmission electron microscopy; SOC spin-orbit coupling; BZ Brillouin zone.

REFERENCES

- (1) Kulbachinskii, V. A.; Kytin, V. G.; Lavrukina, Z. V.; Kuznetsov, A. N.; Shevelkov, A. V. Galvanomagnetic and thermoe-

- lectric properties of BiTeBr and BiTeI single crystals and their electronic structure. *Semiconductors* **2010**, *44*, 1548–1553.
- (2) Kulbachinskii, V. A.; Kytin, V. G.; Kudryashov, A. A.; Kuznetsov, A. N.; Shevelkov, A. V. On the electronic structure and thermoelectric properties of BiTeBr and BiTeI single crystals and of BiTeI with the addition of BiI₃ and CuI. *J. Solid State Chem.* **2012**, *193*, 154–160.
- (3) Ishizaka, K.; Bahramy, M.S.; Murakawa, M.; Sakano, M.; Shimojima, T.; Sonobe, T.; Koizumi, K.; Shin, S.; Miyahara, M.; Kimura, A.; Miyamoto, M.; Okuda, M.T.; Namatame, H.; Taniguchi, M.; Arita, R.; Nagaosa, N.; Kobayashi, K.; Murakami, Y.; Kumai, R.; Kaneko, Y.; Onose, Y.; Tokura, T. Giant Rashba-type spin splitting in bulk BiTeI. *Nat. Mater.* **2011**, *10*, 521–526.
- (4) Bahramy, M. S.; Arita, R.; Nagaosa, N. Origin of giant bulk Rashba splitting: Application to BiTeI. *Phys. Rev. B* **2011**, *84*, 041202.
- (5) Eremeev, S. V.; Nechaev, I. A.; Koroteev, Yu. M.; Echenique, P. M.; Chulkov, E. V. Ideal Two-Dimensional Electron Systems with a Giant Rashba-Type Spin Splitting in Real Materials: Surfaces of Bismuth Tellurohalides. *Phys. Rev. Lett.* **2012**, *108*, 246802.
- (6) Rusinov, I. P.; Nechaev, I. A.; Eremeev, S. V.; Friedrich, C.; Blügel, S.; Chulkov, E. V. Many-body effects on the Rashba-type spin splitting in bulk bismuth tellurohalides. *Phys. Rev. B* **2013**, *87*, 205103.
- (7) Sakano, M.; Miyawaki, J.; Chainani, A.; Takata, Y.; Sonobe, T.; Shimojima, T.; Oura, M.; Shin, S.; Bahramy, M. S.; Arita, R.; Nagaosa, N.; Murakawa, H.; Kaneko, Y.; Tokura, Y.; Ishizaka, K. Three-dimensional bulk band dispersion in polar BiTeI with giant Rashba-type spin splitting. *Phys. Rev. B* **2012**, *86*, 085204.
- (8) Eremeev, S. V.; Nechaev, I. A.; Chulkov, E.V. Giant Rashba-type spin splitting at polar surfaces of BiTeI. *JETP Letters* **2012**, *96*, 437–444.
- (9) Rusinov, I. P.; Tereshchenko, O. E.; Kokh, K. A.; Shakhmamatova, A. R.; Azarov, I. A.; Chulkov, E. V. Role of anisotropy and spin-orbit interaction in the optical and dielectric properties of BiTeI and BiTeCl compounds. *JETP Letters* **2015**, *101*, 507–512.
- (10) Sklyadneva, I. Yu.; Heid, R.; Bohnen, K.-P.; Chis, V.; Volodin, V. A.; Kokh, K. A.; Tereshchenko, O. E.; Echenique, P. M.; Chulkov, E. V. Lattice dynamics of bismuth tellurohalides. *Phys. Rev. B* **2012**, *86*, 094302.
- (11) Crepaldi, A.; Moreschini, L.; Autès, G.; Tournier-Colletta, C.; Moser, S.; Virk, N.; Berger, H.; Bugnon, Ph.; Chang, Y. J.; Kern, K.; Bostwick, A.; Rotenberg, E.; Yazyev, O. V.; Grioni, M. Giant ambipolar Rashba effect in the semiconductor BiTeI. *Phys. Rev. Lett.* **2012**, *109*, 096803.
- (12) Landolt, G.; Eremeev, S.V.; Koroteev, Yu.M.; Slomski, B.; Muff, S.; Neupert, T.; Kobayashi, M.; Strocov, V.N.; Schmitt, T.; Aliev, Z.S.; Babanly, M.B.; Amiraslanov, I.R.; Chulkov, E.V.; Osterwalder, J.; Dil, J.H. Disentanglement of surface and bulk Rashba spin splittings in noncentrosymmetric BiTeI. *Phys. Rev. Lett.* **2012**, *109*, 116403.
- (13) Landolt, G.; Eremeev, S. V.; Tereshchenko, O. E.; Muff, S.; Slomski, B.; Kokh, K.A.; Kobayashi, M.; Schmitt, T.; Strocov, V.N.; Osterwalder, J.; Chulkov, E. V.; Dil, J. H. Bulk and surface Rashba splitting in single termination BiTeCl. *New J. Phys.* **2013**, *15*, 085022.
- (14) Bahramy, M. S.; Yang, B.-J.; Arita, R.; Nagaosa, N. Emergence of non-centrosymmetric topological insulating phase in BiTeI under pressure. *Nat. Commun.* **2012**, *3*, 679.
- (15) Chen, Y.; Xi, X.; Yim, W.-L.; Peng, F.; Wang, Y.; Wang, H.; Ma, Y.; Liu, G.; Sun, C.; Ma, C.; Chen, Z.; Berger, H. High-pressure phase transitions and structures of topological insulator BiTeI. *J. Phys. Chem. C* **2013**, *117*, 25677–25683.
- (16) Rusinov, I. P.; Menshchikova, T. V.; Sklyadneva, I. Yu.; Heid, R.; Bohnen, K.-P.; Chulkov, E.V. Pressure effects on crystal and electronic structure of bismuth tellurohalides. *New J. Phys.* **2016**, *18*, 113003.
- (17) Tran, M. K.; Levallois, J.; Lerch, P.; Teyssier, J.; Kuzmenko, A. B.; Autès, G.; Yazyev, O. V.; Ubaldini, A.; Giannini, E.; van der Marel, D.; Akrap, A. Infrared- and Raman-Spectroscopy Measurements of a Transition in the Crystal Structure and a Closing of the Energy Gap of BiTeI under Pressure. *Phys. Rev. Lett.* **2014**, *112*, 047402.
- (18) Ideue, T.; Checkelsky, J. G.; Bahramy, M. S.; Murakawa, H.; Kaneko, Y.; Nagaosa, N.; Tokura, Y. Pressure variation of Rashba spin splitting toward topological transition in the polar semiconductor BiTeI. *Phys. Rev. B* **2014**, *90*, 161107.
- (19) Sans, J. A.; Manjón, F. J.; Pereira, A. L. J.; Vilaplana, R.; Gomis, O.; Segura, A.; Muñoz, A.; Rodríguez-Hernández, P.; Popescu, C.; Drasar, C.; Ruleova, P. Structural, vibrational, and electrical study of compressed BiTeBr. *Phys. Rev. B* **2016**, *93*, 024110.
- (20) Park, J.; Jin, K.-H.; Jo, Y. J.; Choi, E.S.; Kang, W.; Kampert, E.; Rhyee, J.-S.; Jhi, S.-H.; Kim, J. S. Quantum Oscillation Signatures of Pressure-Induced Topological Phase Transition in BiTeI. *Sci. Rep.* **2015**, *5*, 15973.
- (21) Ohmura, A.; Higuchi, Y.; Ochiai, T.; Kanou, M.; Ishikawa, F.; Nakano, S.; Nakayama, A.; Yamada, Y.; Sasagawa, T. Pressure-induced topological phase transition in the polar semiconductor BiTeBr. *Phys. Rev. B* **2017**, *95*, 125203.
- (22) Xi, X.; Ma, C.; Liu, Z.; Chen, Z.; Ku, W.; Berger, H.; Martin, C.; Tanner, D. B.; Carr, G. L. Signatures of a pressure-induced topological quantum phase transition in BiTeI. *Phys. Rev. Lett.* **2013**, *111*, 155701.
- (23) Ponomarev, Yu. S.; Kuznetsova, T. V.; Tereshchenko, O. E.; Kokh, K. A.; Chulkov, E. V. Dynamics of the BiTeI lattice at high pressures. *JETP Lett.* **2014**, *98*, 557–561.
- (24) Ying, J. J.; Struzhkin, V. V.; Cao, Z. Y.; Goncharov, A. F.; Mao, H. K.; Chen, F.; Chen, X. H.; Gavriluk, A. G.; Chen, X. J. Realization of insulating state and superconductivity in the Rashba semiconductor BiTeCl. *Phys. Rev. B* **2016**, *93*, 100504.
- (25) Qi, Y.; Shi, W.; Naumov, P. G.; Kumar, N.; Sankar, R.; Schnelle, W.; Shekhar, C.; Chou, F. C.; Felser, C.; Yan, B.; Medvedev, S. A. Topological quantum phase transition and superconductivity induced by pressure in the bismuth tellurohalide BiTeI. *Adv. Mater.* **2017**, *29*, 1605965.
- (26) VanGennep, D.; Linscheid, A.; Jackson, D. E.; Weir, S. T.; Vohra, Y. K.; Berger, H.; Stewart, G. R.; Hennig, R. G.; Hirschfeld, P. J.; Hamlin, J. J. Pressure-induced superconductivity in the giant Rashba system BiTeI. *J. Phys. Condens. Matter* **2017**, *29*, 09LT02.
- (27) Wu, L.; Yang, J.; Chi, M.; Wang, S.; Wie, P.; Zhang, W.; Chen, L.; Yang, J. Enhanced thermoelectric performance in Cu-intercalated BiTeI by compensation weakening induced mobility improvement. *Sci. Rep.* **2015**, *5*, 14319.
- (28) Wu, L.; Yang, J.; Zhang, T.; Wang, S.; Wei, P.; Zhang, W.; Chen, L.; Yang, J. Enhanced thermoelectric performance in the Rashba semiconductor BiTeI through band gap engineering. *J. Phys. Condens. Matter* **2016**, *28*, 085801.
- (29) Kulbachinskii, V. A.; Kytin, V. G.; Lavruchina, Z. V.; Kuznetsov, A. N.; Markelov, A. V.; Shevelkov, A. V. Thermoelectric Properties of BiTeI with Addition of BiI₃, CuI, and Overstoichiometric Bi. *Semiconductors* **2011**, *45*, 845–849.
- (30) Klimovskikh, I.I.; Shikin, A.M.; Otrokov, M.M.; Ernst, A.; Rusinov, I.P.; Tereshchenko, O.E.; Golyashov, V.A.; Sanchez-Barriga, J.; Varykhalov, A. Yu.; Rader, O.; Kokh, K.A.; Chulkov, E.V. Giant Magnetic Band Gap in the Rashba-Split Surface State of Vanadium-Doped BiTeI: A Combined Photoemission and *Ab Initio* Study. *Sci. Rep.* **2017**, *7*, 3353.
- (31) Tu, K.; Wei, P.; Zhou, H.; Mu, X.; Zhu, W.; Nie, X.; Zhao, W. A thermoelectric performance study of layered Bi₂TeI weak topological insulator materials. *Energies* **2018**, *11*, 891.

- (32) Savilov, S. V.; Khrustalev, V. N.; Kuznetsov, A. N.; Popovkin, B. A.; Antipin, M. Yu. New subvalent bismuth telluroiodides incorporating Bi₂ layers: the crystal and electronic structure of Bi₂TeI. *Russ. Chem. Bull.* **2005**, *54*, 87–92.
- (33) Zeugner, A.; Kaiser, M.; Schmidt, P.; Menshchikova, T.V.; Rusinov, I.P.; Markelov, A.V.; Van den Broek, W.; Chulkov, E.V.; Doert, T.; Ruck, M.; Isaeva, A. Modular design with 2D-topological-insulator building blocks: optimized synthesis and crystal growth, crystal and electronic structures of Bi_xTeI (x = 2, 3). *Chem. Mater.* **2017**, *29*, 1321–1337.
- (34) Murakami, S. Quantum spin Hall effect and enhanced magnetic response by spin-orbit coupling. *Phys. Rev. Lett.* **2006**, *97*, 236805.
- (35) Wada, M.; Murakami, S.; Freimuth, F.; Bihlmayer, G. Localized edge states in two-dimensional topological insulators: Ultrathin Bi films. *Phys. Rev. B* **2011**, *83*, 121310.
- (36) Drozdov, I.K.; Alexandradinata, A.; Jeon, S.; Nadj-Perge, S.; Ji, H.; Cava, R.J.; Bernevig, B.A.; Yazdani, A. One-dimensional topological edge states of bismuth bilayers. *Nat. Phys.* **2014**, *10*, 664–669.
- (37) Ohtsubo, Y.; Perfetti, L.; Goerbig, M. O.; Fevre, P. L.; Bertran, F.; Taleb-Ibrahimi, A. Non-trivial surface-band dispersion on Bi(111). *New J. Phys.* **2013**, *15*, 033041.
- (38) Perfetti, L.; Faure, J.; Papalazarou, E.; Mauchain, J.; Marsi, M.; Goerbig, M. O.; Taleb-Ibrahimi, A.; Ohtsubo, Y. New aspects of electronic excitations at the bismuth surface: topology, thermalization and coupling to coherent phonons. *J. Electron Spectrosc. Relat. Phenom.* **2015**, *201*, 60–65.
- (39) Ning, W.; Kong, F.; Xi, C.; Graf, D.; Du, H.; Han, Y.; Yang, J.; Yang, K.; Tian, M.; Zhang, Y. Evidence of topological two-dimensional metallic surface states in thin bismuth nanoribbons. *ACS Nano* **2014**, *8*, 7506–7512.
- (40) Ning, W.; Kong, F.; Han, Y.; Du, H.; Yang, J.; Tian, M.; Zhang, Y. Robust surface state transport in thin bismuth nanoribbons. *Sci. Rep.* **2014**, *4*, 7086.
- (41) Ito, S.; Feng, B.; Arita, M.; Takayama, A.; Liu, R.-Y.; Someya, T.; Chen, W.-C.; Iimori, T.; Namatame, H.; Taniguchi, M.; Cheng, C.-M.; Tang, S.-J.; Komori, F.; Kobayashi, K.; Chiang, T.-C.; Matsuda, I. Proving nontrivial topology of pure bismuth by quantum confinement. *Phys. Rev. Lett.* **2016**, *117*, 236402.
- (42) Tang, P.; Yan, B.; Cao, W.; Wu, S.-C.; Felser, C.; Duan, W. Weak topological insulators induced by the interlayer coupling: A first-principles study of stacked Bi₂TeI. *Phys. Rev. B* **2014**, *89*, 041409(R).
- (43) Rusinov, I.P.; Menshchikova, T.V.; Isaeva, A.; Ereemeev, S.V.; Koroteev, Y.M.; Vergniory, M.G.; Echenique, P.M.; Chulkov, E.V. Mirror-symmetry protected non-TRIM surface state in the weak topological insulator Bi₂TeI. *Sci Rep.* **2016**, *6*, 20734.
- (44) Avraham, N.; Norris, A.; Sun, Y.; Qi, Y.; Pan, L.; Isaeva, A.; Zeugner, A.; Felser, C.; Yan, B.; Beidenkopf, H. Coexisting surface states in the weak and crystalline topological insulator Bi₂TeI. Available online at arxiv.org: 1708.09062.
- (45) Isaeva, A.; Rasche, B.; Ruck, M. Bismuth-based candidates for topological insulators: Chemistry beyond Bi₂Te₃. *Phys. Status Solidi RRL*, **2013**, *7*, 39–49.
- (46) Hasan, M.Z.; Kane, C.L. Colloquium: Topological insulators. *Rev. Mod. Phys.* **2010**, *82*, 3045.
- (47) Bradlyn, B.; Elcoro, L.; Cano, J.; Vergniory, M. G.; Wang, Z.; Felser, C.; Aroyo, M.I.; Bernevig, B.A. Topological quantum chemistry. *Nature* **2017**, *547*, 298–305.
- (48) Takada, K.; Sakurai, H.; Takayama-Muromachi, E.; Izumi, F.; Dilanian, R. A.; Sasaki, T. Superconductivity in two-dimensional CoO₂ layers. *Nature* **2003**, *422*, 53–55.
- (49) Terasaki, I.; Iwakawa, M.; Nakano, T.; Tsukuda, A.; Kobayashi, W. Novel thermoelectric properties of complex transition-metal oxides. *Dalton Trans.* **2010**, *39*, 1005–1011.
- (50) Kimber, S. A.; Kreyssig, A.; Zhang, Y.-Z.; Jeschke, H. O.; Valenti, R.; Yokaichiya, F.; Colombier, E.; Yan, J.; Hansen, T.C.; Chatterij, T.; McQueeney, R. J.; Canfield, P. C.; Goldman, A. I.; Argyriou, D. N. Similarities between structural distortions under pressure and chemical pressure in superconducting BaFe₂As₂. *Nat. Mater.* **2009**, *8*, 471–475.
- (51) Dönges, E. Über Tellurohalogenide des dreiwertigen Antimons und Wismuts und über Antimon- und Wismut (III)-tellurid und Wismut(III)-Selenid. *Z. Anorg. Allg. Chem.* **1951**, *265*, 56–61.
- (52) Onopko, L.V.; Onopko, V.V.; Chepur, D.V.; Dovgoshei, N.I.; Turyanica, I.D.; Zayachkovskaya, N. F. Physical properties of BiTeI and BiTeBr. *Neorg. Mater.* **1974**, *10*, 1137–1138.
- (53) Onopko, L.V.; Turyanica, I.D.; Onopko, V.V.; Chepur, D.V.; Zayachkovskaya, N. F.; Gryadil, I.A. In: Physics and Technology of Thin Films of Complex Semiconductors. Uzhgorod State University, 1972.
- (54) Petasch, U.; Oppermann, H. Untersuchungen zum quasibinären System Bi₂Te₃/BiBr₃. *Z. Naturforsch.* **1999**, *54b*, 487–490.
- (55) Biltz, W. Raumchemie der festen Stoffe. Leopold Voss, Leipzig, 1934.
- (56) von Schnering, H. G.; von Benda, H.; Kalveram, Ch. Wismutmonoiodid Bil, eine Verbindung mit Bi(o) und Bi(II). *Z. Anorg. Allg. Chem.* **1978**, *438*, 37–52.
- (57) von Benda, H.; Simon, A.; Bauhofer, W. Zur Kenntnis von BiBr und BiBr_{1.67}. *Z. Anorg. Allg. Chem.* **1978**, *438*, 53–67.
- (58) Dikarev, E. V.; Popovkin, B. A.; Shevelkov, A. V. New poly-molecular bismuth monohalides. Synthesis and crystal structures of Bi₄Br_xI_{4-x} (x = 1, 2, or 3). *Russ. Chem. Bull. Int. Ed.* **2001**, *50*, 2304–2309.
- (59) Shevelkov, A.V.; Dikarev, E.V.; Shpanchenko, R.V.; Popovkin, B.A. Crystal structures of bismuth tellurohalides BiTeX (X = Cl, Br, I) from X-ray powder diffraction data. *J. Solid State Chem.* **1995**, *114*, 379–384.
- (60) Ereemeev, S. V.; Rusinov, I. P.; Nechaev, I. A.; Chulkov, E.V. Rashba surface split surface states in BiTeBr. *New J. Phys.* **2013**, *15*, 075015.
- (61) Sakano, M.; Bahramy, M.S.; Katayama, A.; Shimojima, T.; Murakawa, H.; Kaneko, Y.; Malaeb, W.; Shin, S.; Ono, K.; Kumigashira, H.; Arita, R.; Nagaosa, N.; Hwang, H.Y.; Tokura, Y.; Ishizaka, K. Strongly spin-orbit coupled two-dimensional electron gas emerging near the surface of polar semiconductors. *Phys. Rev. Lett.* **2013**, *110*, 107204.
- (62) Akrap, A.; Teyssier, J.; Magrez, A.; Bugnon, P.; Berger, H.; Kuzmenko, A. B.; van der Marel, D. Optical properties of BiTeBr and BiTeCl. *Phys. Rev. B* **2014**, *90*, 035201.
- (63) Cenxual, K.; Gelato, L. M.; Penzo, M.; Parthe, E. Overlooked symmetry in structures reported with monoclinic centred Bravais lattices; trigonal description of Li₈Pb₃, PtTe, Pt₃Te₄, Pt₂Te₃, LiFe₆Ge₄, LiFe₆Ge₅, CaGe₆Te₁₀ and La₃.266Mn₁₁S₆. *Z. Kristallogr.* **1990**, *193*, 217–242.
- (64) Nechaev, I. A.; Ereemeev, S. V.; Krasovskii, E. E.; Echenique, P. M.; Chulkov, E. V. Quantum spin Hall insulators in centrosymmetric thin films composed from topologically trivial BiTeI trilayers. *Sci. Rep.* **2017**, *7*, 43666.
- (65) Fiedler, S.; Bathon, Th.; Ereemeev, S. V.; Tereshchenko, O.V.; Kokh, K.A.; Chulkov, E.V.; Sessi, P.; Bentmann, H.; Bode, M.; Reinert, F. Termination-dependent surface properties in the giant-Rashba semiconductors BiTeX (X = Cl, Br, I). *Phys. Rev. B* **2015**, *92*, 235430.
- (66) Ereemeev, S. V.; Nechaev, I. A.; Chulkov, E. V. Two- and three-dimensional topological phases in BiTeX compounds. *Phys. Rev. B* **2017**, *96*, 155309.
- (67) Fiedler, S.; El-Kareh, L.; Ereemeev, S. V.; Tereshchenko, O. E.; Seibel, C.; Lutz, P.; Kokh, K. A.; Chulkov, E. V.; Kuznetsova, T. V.; Grebennikov, V. I.; Bentmann, H.; Bode, M.; Reinert, F. De-

fect and structural imperfection effects on the electronic properties of BiTeI surfaces. *New J. Phys.* **2014**, *16*, 075013.

(68) Tournier-Colletta, C.; Autes, G.; Kierren, B.; Bugnon, Ph.; Berger, H.; Fagot-Revurat, Y.; Yazyev, O. V.; Grioni, M.; Malterre, D. Atomic and electronic structure of a Rashba p-n junction at the BiTeI surface. *Phys. Rev. B* **2014**, *89*, 085402.

(69) Butler, C. J.; Yang, H.-H.; Hong, J.-Y.; Hsu, S.-H.; Sankar, R.; Lu, C.-I.; Lu, H.-Y.; Yang, K.-H. O.; Shiu, H.-W.; Chen, C.-H.; Kaun, C.-C.; Shu, G.-J.; Chou, F.-C.; Lin, M.-T. Mapping polarization induced surface band bending on the Rashba semiconductor BiTeI. *Nat. Commun.* **2014**, *5*, 4066.

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

(71) Aguilera, I.; Friedrich, Ch.; Bihlmayer, G.; Blügel, S. GW study of topological insulators Bi₂Se₃, Bi₂Te₃ and Sb₂Te₃: Beyond the perturbative one-shot approach. *Phys. Rev. B* **2013**, *88*, 045206.

(72) Cava, R. J.; Ji, H.; Fuccillo, M. K.; Gibson, Q. D.; Hor, Y. S. Crystal Structure and Chemistry of Topological Insulators. *J. Mater. Chem. C* **2013**, *1*, 3176–3189.

(73) Rasche, B.; Isaeva, A.; Ruck, M.; Borisenko, S.; Zabolotnyy, V.; Büchner, B.; Koepernik, K.; Ortix, C.; Richter, M.; van den Brink, J. Stacked topological insulator built from bismuth-based graphene sheet analogues. *Nat. Mater.* **2013**, *12*, 422–425.

(74) X-Shape, Crystal Optimization for Numerical Absorption Correction Program. v. 2.12.2, Stoe & Cie GmbH, Darmstadt, 2009.

(75) Petricek, V.; Dusek, M.; Palatinus, L. JANA2006, The Crystallographic Computing System. Institute of Physics, Praha, Czech Republic, 2011.

(76) Sheldrick, G. M. SHELXL, Program for Crystal Structure Refinement – Multi-CPU v. 2014/7, Georg-August-Universität Göttingen, Göttingen, Germany, 2014.

(77) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112–122.

(78) Brandenburg, K. Diamond 3.2k, Crystal Impact GbR, Bonn, 2014.

(79) Stadelmann, P. JEMS software, v. 4.2731U2015, <http://cimewww.epfl.ch/people/stadelmann/jemsWebSite/jems.html>, 2012.

(80) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953–17979.

(81) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169–11186.

(82) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758–1775.

(83) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(84) Lopez Sancho, M. P.; Lopez Sancho, J. M.; Rubio, J. J. Quick iterative scheme for the calculation of transfer matrices: application to Mo(100). *J. Phys. F: Met. Phys.* **1984**, *14*, 1205–1215.

(85) Lopez Sancho, M. P.; Lopez Sancho, J. M.; Rubio, J. J. Highly convergent schemes for the calculation of bulk and surface Green functions. *J. Phys. F: Met. Phys.* **1985**, *15*, 851–858.

(86) Henk, J.; Schattke, W. A subroutine package for computing Green's functions of relaxed surfaces by the renormalization method. *Comput. Phys. Commun.* **1993**, *77*, 69–83.

(87) Marzari, N.; Vanderbilt D. Maximally localized generalized Wannier functions for composite energy bands. *Phys. Rev. B* **1997**, *56*, 12847.

(88) Zhang, W.; Yu, R.; Zhang, H.-J.; Dai, X.; Fang, Z. First-principles studies of the three-dimensional strong topological insulators Bi₂Te₃, Bi₂Se₃ and Sb₂Te₃. *New J. Phys.* **2010**, *12*, 065013.

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