

Synthesis in Ionic Liquids: $[\text{Bi}_2\text{Te}_2\text{Br}](\text{AlCl}_4)$, a Direct Gap Semiconductor with a Cationic Framework

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Abstract: The Lewis acidic ionic liquid EMIMBr-AlCl₃ (EMIM = 1-ethyl-3-methylimidazolium) allows a novel synthetic route to the semiconducting layered metal chalcogenides halide $[\text{Bi}_2\text{Te}_2\text{Br}](\text{AlCl}_4)$ and its Sb analogue. $[\text{Bi}_2\text{Te}_2\text{Br}](\text{AlCl}_4)$ is a direct band gap, strongly anisotropic semiconductor and consists of cationic infinite layers of $[\text{Bi}_2\text{Te}_2\text{Br}]^+$ and $[\text{AlCl}_4]^-$ anions inserted between the layers.

Ionic liquids are unique alternatives to traditional aqueous or organic solvents.¹ Room-temperature ionic liquids generally are organic salts with high thermal stability, wide liquidus range, negligible vapor pressure, good ionic conductivity, and tunable solubility of both organic and inorganic molecules. Uses of ionic liquids in solvent extraction and organic catalysis have been extensive, but their use in the synthesis of inorganic materials is relatively recent.^{2,3} Recently, ionic liquids have been used as media for the syntheses of zeolites,⁴ metal-organic frameworks (MOFs),⁵ clathrates,⁶ metal nanoparticles and nanorods,⁷ and microporous and mesoporous carbon and graphene,^{8,9} as well as in electrochemical nanotechnology¹⁰ and polymer science.¹¹

Although the synthesis of metal chalcogenides in molten salts (i.e., inorganic ionic liquids) is well established,^{12,13} syntheses in organic or acidic ionic liquids are very few. Jiang and Zhu used ethylene glycol, aqueous acid, and ionic liquid as a reaction medium to prepare single-crystalline Bi₂S₃ and Sb₂S₃ nanorods.¹⁴ Recently, Rao and co-workers synthesized binary metal-chalcogenides nanoparticles and nanorods in different imidazolium-based ionic liquids,¹⁵ but research to discover new compounds in such media has been scarce. Recently, we reported the synthesis of the novel cluster compound $[\text{Sb}_7\text{S}_8\text{Br}_2](\text{AlCl}_4)_3$ with cationic chalcogenide clusters in ionic liquids.¹⁶

Here, we report the discovery of $[\text{Bi}_2\text{Te}_2\text{Br}](\text{AlCl}_4)$, a unique chalcogenide-halide solid with an extended layered structure and semiconducting properties, prepared in an ionic liquid containing Lewis acid or strong acceptors, EMIMBr-AlCl₃ (EMIM = 1-ethyl-3-methylimidazolium). The acidic character of this ionic liquid arises from the AlCl₃. This is the first example of a cationic chalcogenide framework synthesized in acidic organic ionic liquids. Chalcogenide polycationic compounds and clusters are a very interesting subgroup, and they adopt a variety of structures.¹⁷ There are several methods for their synthesis, including the use of electrophilic and acidic media, such as liquid SO₂ and H₂SO₄, or strong oxidizing agents, such as WCl₅,¹⁸ SbF₅, and AsF₅,¹⁹ or in the presence of strong acceptors, such as AlCl₃²⁰ and ZrCl₄.²¹

The black compound $[\text{Bi}_2\text{Te}_2\text{Br}](\text{AlCl}_4)$ (**1**) was synthesized by the reaction of elemental Bi with elemental Te in EMIMBr-AlCl₃ at 165 °C for 7 days.²² The reaction produced black needle-like crystals of **1**, and the structure was determined from single-crystal X-ray diffraction data collected at 100 K on a STOE 2 X-ray diffractometer. The isostructural Sb analogue $[\text{Sb}_2\text{Te}_2\text{Br}](\text{AlCl}_4)$ (**2**) was also synthesized similarly. Compounds **1** and **2** both crystallize in the space group C2/c.²³ Figure 1a shows the crystal structure of **1** down the *b*-axis. The structure consists of cationic infinite layers of $[\text{Bi}_2\text{Te}_2\text{Br}]^+$ with $[\text{AlCl}_4]^-$ anions inserted between the layers. The layers themselves are made of infinite chains of $[\text{Bi}_2\text{Te}_2]^{2+}$ which are connected by Br⁻ ions along the crystallographic *c*-axis (Figure 1b). The chains of $[\text{Bi}_2\text{Te}_2]^{2+}$ are made of (BiTe)₂ rhombic units having Te-Bi-Te angles ranging from 87.06(2) to 92.16(2)°. Bi1 and Bi2 atoms are five-fold-coordinated by three telluriums and two bridging bromides to form distorted square-pyramidal geometry. The oxidation state of Bi atoms is 3+, and the inert lone pair of electrons is clearly stereochemically expressed. The Bi-Te bond lengths range from 2.9475(8) to 2.9779(8) Å.²⁰

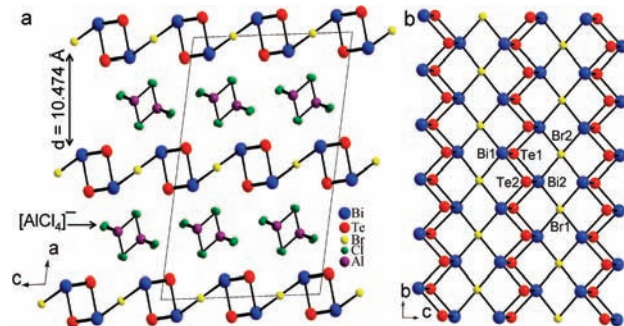


Figure 1. (a) Crystal structure of compound **1**, viewed down the *b*-axis. (b) View of cationic $[\text{Bi}_2\text{Te}_2\text{Br}]^+$ down the *a*-axis. The Bi-Br bridging distances range from 3.1983(15) to 3.2205(15) Å.

The layers of $[\text{Bi}_2\text{Te}_2\text{Br}]^+$ stack along the crystallographic *a*-axis with an interlayer distance of 10.474 Å. The tetrachloroaluminate ions have a moderately distorted tetrahedral structure (Figure 1a) in which the Al-Cl bond lengths range from 2.139(4) to 2.171(4) Å and the Cl-Al-Cl angles from 104.75(17) to 117.29(16)°.

The $[\text{AlCl}_4]^-$ ions render the compounds air- and moisture-sensitive because of the hydrolytic instability of Al-Cl bonds. The electronic absorption spectrum of compound **1** (taken with care to minimize air exposure) shows an absorption edge at ~0.8 eV (Figure 2), consistent with the black color. Thermogravimetric analysis (TGA) under N₂ atmosphere (Figure S2, Supporting

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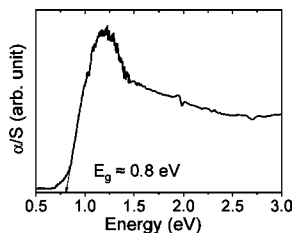


Figure 2. Electronic absorption spectrum of compound **1**. The energy gap is indicated. The electronic spectra were obtained as described elsewhere.²⁴

Information) showed that compound **1** starts to lose weight at 350 K and undergoes a sharp weight loss at 600 K. The loss is attributed to AlCl_3 or $\text{AlCl}_{3-x}\text{Br}_x$ ¹⁶ and gives rise to a $\text{BiTeBr}_x\text{Cl}_{(1-x)}$ species (eq 1).



Differential thermal analysis (DTA) (Figure S2, Supporting Information) indicates a melting event at ~ 844 K. The powder X-ray diffraction (PXRD) pattern measured after the DTA can be best matched with the theoretical PXRD pattern of the compound BiTeBr (ICSD 79363), but the pattern is shifted to a higher 2θ angle, indicating the incorporation of chlorine, $\text{BiTeBr}_x\text{Cl}_{(1-x)}$ (Figure S3, Supporting Information).

The room-temperature electrical conductivity measured along the crystallographic b -direction (parallel to the layers) was found to be ~ 40 S/cm, while along the a -direction (perpendicular to the layers) it was negligible, at $\sim 8 \times 10^{-5}$ S/cm (see Supporting Information). This high anisotropy is consistent with the lamellar structure of the material.

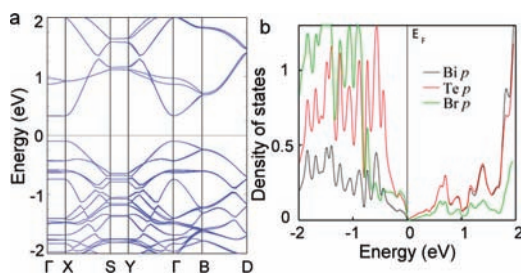


Figure 3. (a) Electronic band structure and (b) projected density of states for the p-orbital of the individual elements (Bi, Te, and Br) of compound **1**.

To better understand the charge transport properties, the electronic band structure of compound **1** was calculated using the full potential linearized augmented plane wave (FLAPW) method with the screened-exchange local density approximation (sX-LDA) and the Hedin–Lundqvist (LDA) forms of the exchange–correlation potential.²⁵ Figure 3a shows the electronic band structure of compound **1**. The nearly perfectly flat band edges along the Γ -to- X direction (related to the a -direction in the crystal) confirm the highly anisotropic transport properties. This comes from the fact that the tetrahedral anions $[\text{AlCl}_4]^-$ do not play an important role in bonding with the layers, except for making charge neutrality, and do not provide facile hopping paths for carriers. This flat band results in very high effective masses along the a -axis, which predicts that the out-of-plane electronic conductivity is expected to be negligible compared to in-plane, consistent with experiments. The sX-LDA calcula-

tions with spin–orbit interaction (SOC) included give a direct band gap of 0.43 eV, which is smaller than the experimentally estimated value of ~ 0.8 eV. The projected angular-momentum-resolved density of states for Bi, Te, and Br p-orbitals (Figure 3b) shows the p–p mixing effect on the electronic structure. All states contribute significantly to both the valence and conduction band edges, but with slightly higher Te and Br p-orbital contribution to the valence band maximum due to the ionic characteristics. Therefore, the bad gap transition shown in Figure 2 is mainly associated with interlayer excitations from Te and Br atoms to Bi atoms.

Bismuth/antimony telluride-based materials have not only diverse structures but also fascinating properties, such as thermoelectric and topological insulation.²⁶ The chalcogenides, $[\text{Bi}_2\text{Te}_2\text{Br}](\text{AlCl}_4)$ and $[\text{Sb}_2\text{Te}_2\text{Br}](\text{AlCl}_4)$, with novel cationic two-dimensional frameworks and anisotropic electrical transport properties, can be synthesized in a Lewis acidic organic ionic liquid. Organic acidic ionic liquids enhance the reactivity of normally inert reactants such as Bi, Sb, and Te to generate saturated solutions. Thus, they provide a promising synthetic strategy toward new chalcogenides with cationic frameworks rather than the familiar anionic frameworks observed in molten salt reactions.

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Supporting Information Available: Experimental methods, physical characterization, and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Synthesis of $[\text{Bi}_2\text{Te}_2\text{Br}](\text{AlCl}_4)$ (**1**): 105 mg (0.5 mmol) of Bi, 64 mg (0.5 mmol) of Te, 250 mg (1.87 mmol) of AlCl_3 , and 75 mg (0.39 mmol) of EMIMBr were loaded in a 20 mL glass vial inside a glovebox. The vial was closed and put in a preheated oven at 165°C for 7 days. After completion of the reaction, the vial was opened inside the glovebox, and the product was washed with chloroform. Black needle-like crystals were obtained (71% yield). The compound is moisture-sensitive and stable in air up to 1 h.

- (23) Crystal data for $[\text{Bi}_2\text{Te}_2\text{Br}](\text{AlCl}_4)$ (1) at 100 (2) K: STOE IPDS2 diffractometer, Mo $K\alpha$ radiation, monoclinic; $C2/c$; $Z = 8$; $a = 21.2247(13)$ Å, $b = 8.4778(3)$ Å, $c = 13.2264(10)$ Å, $\beta = 99.280(5)^\circ$; $V = 2348.8(2)$ Å³. Collection and refinement data: $2\theta_{\text{max}} = 55^\circ$; $d_{\text{calc}} = 5.214$ g/cm³; $F(000) = 3088$; 9479 total reflections; 2688 unique reflections [$F_o^2 > 2\sigma(F_o^2)$]; 92 parameters; GOF = 1.055; $R1 = 4.35\%$ and $wR2 = 11.04\%$ for $I > 2\sigma(I)$.
- Crystal data for $[\text{Sb}_2\text{Te}_2\text{Br}](\text{AlCl}_4)$ (2) at 100 (2) K: monoclinic; $C2/c$; $Z = 8$; $a = 21.216(4)$ Å, $b = 8.2816(17)$ Å, $c = 13.126(3)$ Å, $\beta = 98.71(3)^\circ$; $V = 2279.7(8)$ Å³. Collection and refinement data: $2\theta_{\text{max}} = 53.48^\circ$; $d_{\text{calc}} = 4.355$ g/cm³; $F(000) = 2576$; 8378 total reflections; 2413 unique reflections [$F_o^2 > 2\sigma(F_o^2)$]; 93 parameters; GOF = 1.012; $R1 = 2.45\%$ and $wR2 = 6.45\%$ for $I > 2\sigma(I)$.
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