

Natural Sulfur-Containing Minerals as Topological Insulators with a Wide Band Gap

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Received July 25, 2012

The electronic structure of quaternary natural minerals $\text{PbBi}_2\text{Te}_2\text{S}_2$ (aleksite), $\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$ (saddlebackite), and $\text{PbBi}_4\text{Te}_4\text{S}_3$ (*C* phase) has been theoretically studied. These compounds have a layered structure: aleksite and saddlebackite are formed by seven- and nine-layer blocks, respectively, and *C* phase consists of five- and seven-layer blocks separated by van der Waals gaps. It has been shown that all studied materials are three-dimensional topological insulators with a wide band gap in the electronic spectrum and have a high spin polarization. For these reasons, they are promising for applications.

DOI: 10.1134/S0021364012170158

The new research field concerning topological insulators is one of the most rapidly developing fields in solid state physics [1–5] because of the prospect of using these materials in fundamentally new spintronic devices [6, 7] and quantum computers [8, 9]. Physical effects caused by the interaction of topological insulators with superconductors and ferromagnets [10, 11] are of fundamental interest.

The feature of topological insulators is the existence of a conduction band of electronic states with a linear dispersion law caused by a strong spin–orbit interaction on the surface of a bulk insulator. These states are Kramers doublets topologically protected by the time reversal symmetry from backscattering from local distortions and from weak disorder in the crystal lattice [3–5]. The latter means that electrons in these states can move along the surface of the bulk material without dissipation of energy.

The main criteria of applicability of topological insulators are a high spin polarization of charge carriers and a wide band gap in their spectrum. The compound that currently best satisfies these criteria is Bi_2Se_3 with a band gap of about 300 meV [4] and a spin polarization of about 80% [12–14]. Most of the known topological insulators have a band gap of about 50–250 meV [15–17] and can hardly be used in devices at room temperature. These materials have a narrow band gap primarily because of the strong spin–

orbit interaction splitting the states forming the edges of the gap, which is thereby narrowed. At the same time, the strong spin–orbit interaction is responsible for the inversion of the edges of the band gap of the material and for the appearance of electronic topological properties. In this situation, the replacement of some heavy atoms by lighter isoelectronic analogs can lead to an increase in the band gap, conserving its the topology of material. For this reason, we focus on the search for new topological insulators in which Te layers would be partially replaced by layers of the lighter S element. As parent compounds, we used well-known topological insulators PbBi_2Te_4 , $\text{Pb}_2\text{Bi}_2\text{Te}_5$, and PbBi_4Te_7 [17–19]. The partial replacement of Te atoms in these materials by S atoms provides $\text{PbBi}_2\text{Te}_2\text{S}_2$, $\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$, and $\text{PbBi}_4\text{Te}_4\text{S}_3$ compounds.

In this work, we report the *ab initio* calculations of the electronic structure of abundant natural minerals $\text{PbBi}_2\text{Te}_2\text{S}_2$ (aleksite), $\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$ (saddlebackite), and $\text{PbBi}_4\text{Te}_4\text{S}_3$ (conditionally called *C* phase) [20]. We show that these materials are topological insulators whose band gap exceeds 300 meV and spin polarization is about 70–80%.

The electronic structure was calculated using the density functional theory by the full-potential linearized augmented plane wave method [21], which was implemented in the FLEUR code [22]. In order to

Table 1. Experimental hexagonal lattice parameters a and c [20], optimized interlayer distances $d_{i,i+1}$ for the compounds under consideration, and width d_{vdW} of van der Waals gap. All values are given in angstroms. The central layer of a block is considered as zeroth ($i = 0$). In the case of the C phase, the central layer of the seven-layer block is considered as zeroth

	PbBi ₂ Te ₂ S ₂	Pb ₂ Bi ₂ Te ₂ S ₃	PbBi ₄ Te ₄ S ₃
a	4.230	4.230	4.241
c	39.830	16.710	23.121
d_{vdW}	2.773	2.791	2.758
d_{01}	1.680 (Pb–S)	1.698 (S–Pb)	1.678 (Pb–S)
d_{12}	1.754 (S–Bi)	1.680 (Pb–S)	1.749 (S–Bi)
d_{23}	1.819 (Bi–Te)	1.759 (S–Bi)	1.818 (Bi–Te)
d_{34}		1.823 (Bi–Te)	d_{vdW} (Te–Te)
d_{45}			1.822 (Te–Bi)
d_{56}			1.736 (Bi–S)

describe the exchange–correlation energy, we used the generalized gradient approximation [23]. Scalar-relativistic corrections were included in the Hamiltonian. The spin–orbit interaction was taken into account self-consistently [24]. The values 2.2, 2.7, 3.0, and 2.7 au were taken for the radii of the muffin-tin spheres for sulfur, tellurium, lead, and bismuth, respectively. The cutoff parameter in the plane wave basis was $k_{\text{max}} = 3.3 \text{ au}^{-1}$. The a and c lattice parameters, as well as the sequence of the atomic layers, are known for all compounds under study [20]. However, information concerning the interlayer distances is absent. For this reason, using the pseudopotential method implemented in the VASP code [25, 26], we optimized these distances at the fixed experimental values of lattice parameters. The lattice parameters and optimized interlayer distances are given in Table 1.

Topological phases in the compounds under study were identified by calculating the \mathbb{Z}_2 invariant [3, 27]. The Pb₂Bi₂Te₂S₃ and PbBi₄Te₄S₃ compounds are crystallized in a hexagonal structure, whereas PbBi₂Te₂S₂, in a rhombohedral structure. Since the rhombohedral structure can be represented as a hexagonal structure, we considered all three compounds in the hexagonal structure for convenient comparison. The crystal lattice of each mineral is a sequence of multilayer blocks separated by van der Waals gaps (Fig. 1). These blocks are seven- and nine-layer in the PbBi₂Te₂S₂ and Pb₂Bi₂Te₂S₃ compounds, respectively. In PbBi₄Te₄S₃, five- and seven-layer blocks alternate. As a result, surfaces with different terminations can be formed.

The calculated \mathbb{Z}_2 invariant shows that all three materials are three-dimensional topological insulators. Figure 2 shows the electron energy spectra of bulk crystals. It can be seen that the compounds under consideration are narrowband semiconductors. In partic-

Table 2. Band gaps (in meV) at the symmetric Γ and A points, as well as the minimum indirect band gap, in bulk crystals. The values obtained with the VASP code are given in parentheses

	Γ	A	Indirect band gap
PbBi ₂ Te ₂ S ₂	395 (440)	324 (418)	307 (341)
Pb ₂ Bi ₂ Te ₂ S ₃	234 (322)	602 (543)	– (304)
PbBi ₄ Te ₄ S ₃	427 (428)	400 (492)	318 (313)

ular, the PbBi₂Te₂S₂ and PbBi₄Te₄S₃ compounds have indirect band gaps of 307 and 318 meV, respectively, and the Pb₂Bi₂Te₂S₃ compound has a direct band gap of 234 meV. The results obtained with the FLEUR and VASP codes are generally in good agreement with each other (Table 2).

The surface electronic structure of the compounds under study was calculated within the slab model. The thicknesses of PbBi₂Te₂S₂ and Pb₂Bi₂Te₂S₃ slabs were 35 and 36 atomic layers, respectively, whereas two slabs with five-layer (29 layers) and seven-layer (31 layers) terminations were considered for the PbBi₄Te₄S₃ slab. Figure 3 shows the calculated electronic spectra of the (0001) surface. It can be seen that the band gap of the materials under consideration contains the Dirac cone. In contrast to Bi₂Te₃ and Sb₂Te₃ binary topological insulators, the upper half of the Dirac cone in the compounds under study is well isolated from the bulk states. As a result, scattering of electrons from surface states to bulk states will be absent in them. The Dirac

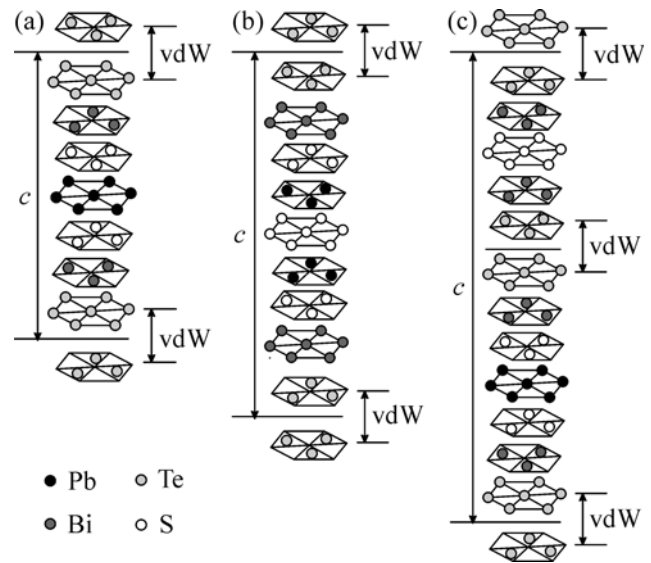


Fig. 1. Crystal structures of (a) PbBi₂Te₂S₂, (b) Pb₂Bi₂Te₂S₃, and (c) PbBi₄Te₄S₃ bulk compounds. The Pb, Bi, Te, and S atoms are shown in black, dark gray, light gray, and white, respectively.

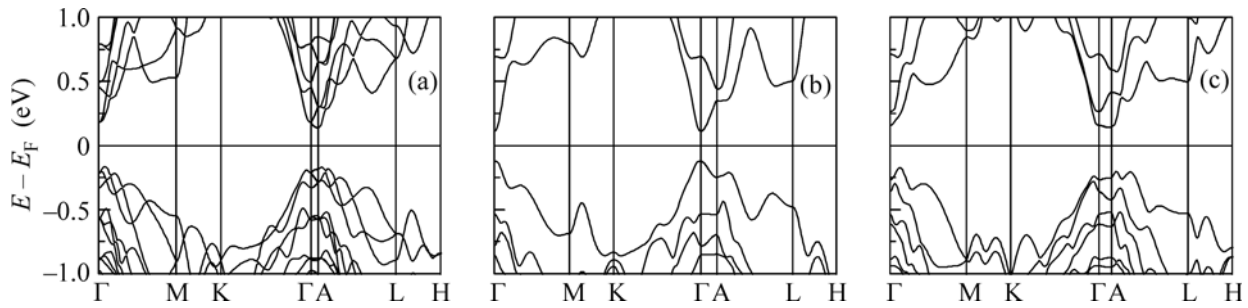


Fig. 2. Bulk electronic spectra of (a) $\text{PbBi}_2\text{Te}_2\text{S}_2$, (b) $\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$, and (c) $\text{PbBi}_4\text{Te}_4\text{S}_3$ compounds.

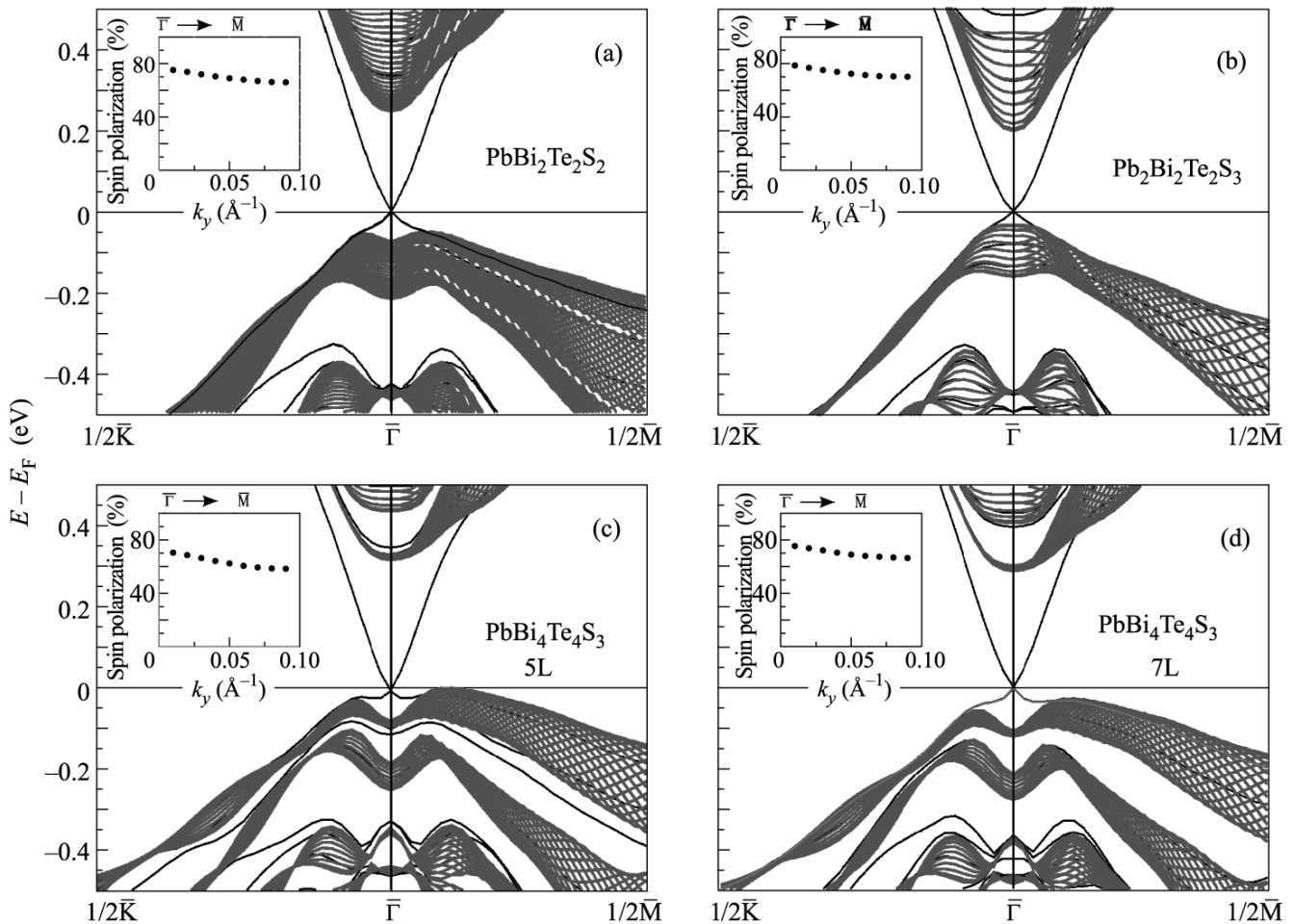


Fig. 3. (Black lines) Electronic spectra and (gray lines) projections of bulk states on the two-dimensional Brillouin zone of the (a) $\text{PbBi}_2\text{Te}_2\text{S}_2$ slab, (b) $\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$ slab, and (c, d) $\text{PbBi}_4\text{Te}_4\text{S}_3$ slab with five- and seven-layer terminations, respectively. The insets show the spin polarization versus the wave vector k_y .

point in the $\text{PbBi}_2\text{Te}_2\text{S}_2$ and $\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$ compounds, as well as in the $\text{PbBi}_4\text{Te}_4\text{S}_3$ compound with the seven-layer termination, lies noticeably above the top of the valence band, whereas the Dirac point in the $\text{PbBi}_4\text{Te}_4\text{S}_3$ compound with the five-layer termination is 9 meV lower than the top of the valence band, in

contrast to the situation in the related PbBi_4Te_7 compound [16]. Estimates show that the group velocity of charge carriers in the Dirac cone in the $\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$ compound is almost the same as in the Bi_2Se_3 compound, whereas the group velocity for the $\text{PbBi}_2\text{Te}_2\text{S}_2$ and $\text{PbBi}_4\text{Te}_4\text{S}_3$ compounds is somewhat higher.

The band gap in the $\text{PbBi}_2\text{Te}_2\text{S}_2$, $\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$, and $\text{PbBi}_4\text{Te}_4\text{S}_3$ compounds is much wider than that in the known PbBi_2Te_4 , $\text{Pb}_2\text{Bi}_2\text{Te}_5$, and PbBi_4Te_7 topological insulators, where the band gap is narrower than 200 meV [17–19]. For this reason, the former family of compounds can be used in a wider temperature range and therefore is promising for applications.

The insets in Fig. 3 show the dependence of the mean value of the spin operator on the wave vector $\mathbf{k} = (0, k_y)$, oriented along the $\bar{\Gamma} - \bar{M}$ direction. The k_y component of this vector varies from 0 \AA^{-1} ($\bar{\Gamma}$ point) to a value of about 0.1 \AA^{-1} , at which the states of the Dirac cone are in the bulk continuum region. It can be seen that the dependence of the spin polarization on the wave vector k_y is the same for all minerals under study. The spin polarization is maximal near the center of the Brillouin zone and minimal near the bottom of the conduction band. The spin polarization near $\bar{\Gamma}$ is maximal ($\sim 80\%$) in $\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$, minimal ($\sim 70\%$) in $\text{PbBi}_4\text{Te}_4\text{S}_3$ with the five-layer termination, and intermediate ($\sim 75\%$) in $\text{PbBi}_4\text{Te}_4\text{S}_3$ with the seven-layer termination and in $\text{PbBi}_2\text{Te}_2\text{S}_2$. Such a high spin polarization and its weak dependence on the wave vector promote the applications of these compounds. This makes it possible to increase the number of electrons (owing to a change in the Fermi level) involved in transport in a wide energy range without a significant decrease in the polarization.

To summarize, it has been shown theoretically that $\text{PbBi}_2\text{Te}_2\text{S}_2$, $\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$, and $\text{PbBi}_4\text{Te}_4\text{S}_3$ sulfur-containing minerals are three-dimensional topological insulators with a wide band gap. For this reason, they are favorable over PbBi_2Te_4 , $\text{Pb}_2\text{Bi}_2\text{Te}_5$, and PbBi_4Te_7 parent compounds, where the band gap is narrower than 200 meV. The Dirac cone in the compounds under investigation is well isolated from bulk states and has a high spin polarization ($\sim 70\text{--}80\%$). Owing to wide band gaps and a high spin polarization, these materials are promising for various applications at room temperature along with the well-studied Bi_2Se_3 compound.

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Translated by R. Tyapaev