New subvalent bismuth telluroiodides incorporating Bi_2 layers: the crystal and electronic structure of Bi_2TeI

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Two new subvalent bismuth telluroiodides, Bi_2TeI and $Bi_4TeI_{1.25}$, were prepared by the gas-phase synthesis. The compositions of these phases were determined by energy-dispersive X-ray spectroscopy. X-ray diffraction study of melt-grown Bi_2TeI single crystals demonstrated that the compound crystallizes in the monoclinic system (space group $C/2m$) with the unit cell parameters $a = 7.586(1)$ Å, $b = 4.380(1)$ Å, $c = 17.741(3)$ Å, $\beta = 98.20°$. The layered crystal structure of Bi_2TeI consists of weakly bonded two-dimensional blocks with a stoichiometry of the title compound. The blocks are stacked along the c axis. Each block consists of eight atomic layers alternating in the Te—Bi—I—Bi—Bi—I—Bi—Te order and includes a double layer of bismuth atoms. Based on the results of *ab initio* quantum-chemical calculations, the title compound is expected to possess a pronounced anisotropy of conductivity.

Key words: low-dimensional phases, layered compounds, main-group metal—metal bonding, bismuth telluroiodides.

Bismuth is one of a few p-metals, which can form crystalline compounds containing extended metal—metal bond systems. For example, the crystal structures of subvalent iodides Bi_4I_4,[1,2] $Bi_{14}I_4$,[3] and $Bi_{18}I_4$,[4] bromide Bi_4Br_4,[5] and mixed subvalent iodide bromides $Bi_4I_{4-n}Br_n$ [6] consist of one-dimensional fragments, which can be described as corrugated bismuth strips of width 4, 14, or 18 atoms, respectively, which are bounded on both sides by halogen atoms. The geometry of these strips is very similar to the atomic arrangement in the crystal structure of bismuth metal. In addition, two-dimensional electroneutral Bi_2 layers, which also retain the structure of bismuth metal, were found in the crystals of subvalent bismuth selenides[7—9] and tellurides.[7,10,11]

The structures of subvalent bismuth chalcogenides, for example, with compositions BiQ and Bi_4Q_3 (Q = Se, Te), can be considered as a result of intercalation of Bi_2 layers into the crystal structures of layered selenides and tellurides with composition Bi_2Q_3 formed by weakly bonded two-dimensional electroneutral Bi_2Q_3 blocks.

The aim of the present study was to intercalate bismuth double layers into the crystal structure of bismuth telluroiodide BiTeI. This compound crystallizes in the hexagonal system[12] (space group $P3m1$, $a = 4.3302(1)$ Å, $c = 6.854(1)$ Å) and can be described as a distorted 2H-CdI_2-type crystal structure, in which the tellurium and iodine atoms in the anion sublattice are completely ordered so that the tellurium atoms replace one layer of iodine atoms in the starting CdI_2 structure (Fig. 1).

The shortest Bi—Te and Bi—I bonding distances (3.039 and 3.272 Å, respectively) and the Te—I nonbonded distance (3.93 Å) suggest a layered character of the structure. Since the geometry of the Bi—Te and Bi—I bond systems in BiTeI (Te—Bi—Te and I—Te—I angles are 83° and 91°, respectively) is similar to that of the Bi—Bi bond system in the Bi_2 layer of subvalent bismuth tellurides (in BiTe[11] and Bi_4Te_3,[11] the Bi—Bi distances are 3.267 and 3.098 Å, and the Bi—Bi—Bi angles are 85° and 91°, respectively), the Bi_2 layers can be intercalated into the BiTeI structure.

It was demonstrated[13,14] that BiTeI is characterized by a narrow homogeneity region ($BiTe_{0.95}I_{1.08}$—$BiTe_{0.99}I_{1.01}$), which is associated with disordering upon the replacement in the tellurium and iodine sublattices, undergoes a polymorphic transformation at 470 °C, and melts congruently at 555 °C. To our knowledge, there are no evidence of the existence of ternary phases other than BiTeI in the Bi—Te—I system.

A search for new phases was performed by studying the phase compositions of several annealed samples in the BiTeI—Bi system by powder X-ray diffraction. Then,

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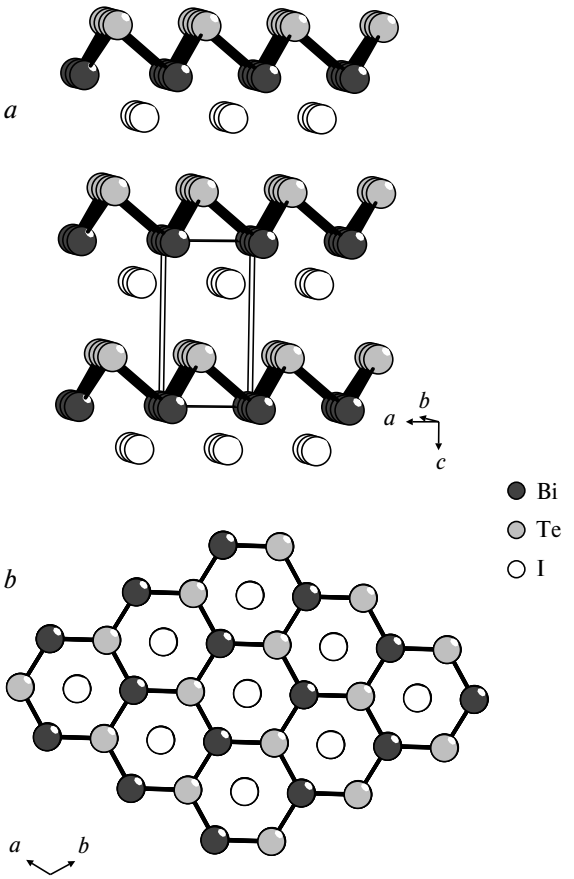

Fig. 1. Crystal structure of BiTeI[12]: *a*, an overall view; *b*, a projection onto the *ab* plane.

single crystals of compounds were grown from the gas phase and melt.

Experimental

Commercially available bismuth metal (99.999%), iodine (99.999%), tellurium (99.999%) BiI_3 (99.99%), and TeI_4 (99.999%) were used as purchased (all from Alfa Chemicals). Samples with compositions Bi_3TeI, $Bi_{5.5}TeI$, and $Bi_{6.5}TeI$ were prepared from the starting compounds and annealed in evacuated quartz tubes at 300 °C for 30 days. Powder X-ray diffraction study of the samples was carried out on an automated STOE STADI-P powder diffractometer (STOE GmbH, Germany; Cu-K-α1 radiation) using the JCPDS Powder Diffraction File[15] and the PDF-2 Database.[16]

Single crystals were grown from the gas phase in dual-temperature horizontal quartz tubes with an inner diameter of 13 mm and a length of 210 mm. In experiments, the temperature of the hot end of the tube was varied from 300 to 650 °C. The temperature difference between the hot and cold ends was varied from 50 to 100 °C. The starting mixtures (elemental bismuth, tellurium, and iodine or bismuth, tellurium, BiI_3, and TeI_4 in different ratios) were always placed at the hot end of the tube.

Melt-grown crystals were prepared by heating ground starting mixtures with different compositions in evacuated ($p \leq 10^{-2}$ Torr) quartz tubes to 550 °C followed by slow cooling to ~20 °C at a rate of ~2 K h^{-1}.

Energy-dispersive X-ray microanalysis. Quantitative energy-dispersive X-ray (EDX) microanalysis of the crystals was performed on a JEOL JSM-820 scanning electron microscope (Japan) equipped with a LINK AN-10000 energy-dispersive X-ray microanalyzer with a semiconducting detector (accelerating voltage was 20 kV, the counting time was 120 s, ZAF correction). The chemical composition of the crystal was determined by averaging the values measured at several points on its surface and then refined using the L and M lines for Bi and the L lines for Te and I.

X-ray diffraction analysis. X-ray diffraction study of the samples was carried out on an automated SIEMENS P3 four-circle diffractometer (Germany, 293 K, Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique). The ψ-scan absorption correction was applied.

Quantum-chemical calculations. The electronic structure was calculated in terms of the band model by the restricted Hartree—Fock (RHF) method and the density functional theory (DFT) using the Hay—Wadt effective core potentials[17] to take into account the inner-shell electrons. The DFT calculations were carried out with the B3LYP exchange-correlation functional.[18] *Ab initio* calculations were carried out using the CRYSTAL98 program[19] and the Hay—Wadt basis sets[17] modified for performing calculations of infinite systems.

Results and Discussion

Powder X-ray diffraction study demonstrated that all three annealed samples, which were prepared as black bulks, contained three phases, *viz.*, bismuth metal, subvalent bismuth iodide $Bi_{14}I_4$, and a previously unknown phase. Taking into account the existence of subvalent bismuth iodide $Bi_{18}I_4$, the simultaneous presence of bismuth and $Bi_{14}I_4$ in the mixtures indicates that the equilibrium was not reached even upon annealing for such a long period of time. Therefore, individual single crystals of the new phase were obtained using the gas-phase and melt-growth techniques.

Gas-phase synthesis starting from a mixture of bismuth, tellurium, BiI_3, and TeI_4 taken in a 25.6 : 2.5 : 1 : 1 molar ratio at 650 and 550 °C for the hot and cold ends of the tube, respectively, afforded two types of small single crystals in very small amounts. The composition of needle-like single crystals grown in the cold zone (EDX analysis data) was similar to $Bi_4TeI_{1.25}$ (average values in at.%: Bi, 63.1; Te, 16.8; I, 21.0), whereas the composition of thin platelets grown at the surface of the starting mixture was close to Bi_2TeI (average values in at.%: Bi, 48.6; Te, 24.8; I, 24.6). The latter crystals were also grown at higher temperatures of the cold zone (600 and 620 °C) and a somewhat different component ratio (47 : 9 : 1 : 3).

Both types of crystals were unsuitable for X-ray diffraction study because of strong twinning. For the $Bi_4TeI_{1.25}$ crystals, we determined only the hexagonal unit cell parameters ($a = 4.387(3)$ Å and $c = 6.52(1)$ Å), which

were used for indexing the main lines in the powder X-ray diffraction pattern of the new phase, which was found in the samples annealed earlier. Annealing of the samples with 4 : 1 : 1.25 and 2 : 1 : 2 compositions in evacuated quartz tubes at 300 °C for 30 days did not afford single-phase samples.

Attempts to grow crystals of new phases from melt using the starting mixtures with different compositions and at different initial cooling temperatures led to success in the only case. Aggregates of platelet crystals were grown from the flux mixture with composition $Bi_4TeI_{1.25}$ cooled to 550 °C. We succeeded in separating a crystal suitable for X-ray diffraction (in a Vaseline oil) from these aggregates. To determine the composition with higher accuracy, single crystals were also analyzed on a CAMEBAX SX-50 electron probe microanalyzer (France) equipped with a wavelength dispersive X-ray system (accelerating voltage was 15.6 kV, the counting time was 200 s), which was calibrated against bismuth (Bi_2S_3), tellurium (Bi_2Te_3), and iodine (SbSI). The experiment confirmed that the atomic ratio of the elements in the sample is 2 : 1 : 1. The results of EDX analysis of the crystal used for X-ray diffraction study are given in Table 1.

X-ray diffraction data for Bi_2TeI were interpreted in the monoclinic system (space group $C2/m$). The bismuth atoms were located by direct methods using the SHELXS-97 program package.[20] The positions of the Te and I atoms were revealed from difference Fourier syntheses. The structure refinement presented a problem because of the similar atomic scattering factors of all atoms involved in the structure (particularly, of Te and I). Therefore, we used data on the crystal chemistry of binary bismuth iodides and tellurides for the construction of a chemically consistent structural model (in particular, to decide between the I and Te atoms for the description of the occupancies of the positions), which would be consistent with the EDX analysis data. Notwithstanding the fact that the EDX analysis revealed a somewhat higher tellurium content compared to the iodine content (apparently, because iodine atoms in the corresponding sublattice can be partially replaced by tellurium atoms and due to the possible existence of a homogeneity region in the phase, analogously to BiTeI [14] and BiSe [8]), we chose the model in which the corresponding positions are completely occupied by Te and I atoms, because it makes no sense to quantitatively estimate the possibility of the partial replacement of I atoms with Te based on the available X-ray diffraction data set. The possible replacement of a small number of Bi atoms (less than 1.5 at.% based on the results of EDX analysis)* in the double layer (Bi(1) position) with Te atoms cannot be completely ruled out. However, such a low degree of replacement cannot be reliably quantitatively characterized based on our experimental data. The final refinement of the crystal structure was performed by the full-matrix least-squares method first with isotropic and then with anisotropic displacement parameters for all atoms. The crystallographic data and main parameters of the structure refinement for Bi_2TeI are given in Table 2. The atomic coordinates and atomic displacement parameters are listed in Tables 3 and 4. The crystal structure of Bi_2TeI is shown in Fig. 2. The relatively high R_{int} and R_1 factors are attributable to the fact

Table 1. Energy-dispersive X-ray analysis data for the Bi_2TeI crystal

Element	Element content at different points of the crystal (at.%)*			
	1	2	3	Average/ideal
Te	26.9	27.8	27.6	27.4/25.0
Bi	48.8	48.7	48.7	48.7/50.0
I	24.3	24.5	23.6	24.1/25.0
Total (%)	100.0	101.0	99.9	100.3/100.0

* The accuracy of analysis was ±1%.

Table 2. Crystallographic data and main parameters of structure refinement of Bi_2TeI

Parameter	Characteristic
Crystal system	Monoclinic
Space group	$C2/m$ (№ 12)
Crystal dimensions/mm	0.5×0.5×0.05
Unit cell parameters	
a/Å	7.586(1)
b/Å	4.380(1)
c/Å	17.741(3)
β/deg	98.20
V/Å^3	583.4(1)
Z	4
μ/cm^{-1}	475.9
ρ_{calc}/g cm^{-3}	7.655
Scanning mode	ω—2θ
Scan range/θ	5.39—32.06
Total number of reflections	2012
Number of independent reflections	1101
R_{int}	0.124
R_σ	0.074
Number of parameters in refinement	26
Method of refinement	Full-matrix against F^2
Number of reflections with $I > 2\sigma(I)$	931
R_1 ($I > 2\sigma(I)$)/R (for all reflections)	0.066/0.078
wR^2 ($I > 2\sigma(I)$)/wR^2 (for all reflections)	0.193/0.204
GOOF	1.008
Program for refinement	SHELXL-97 [21]

* The accuracy of the method is about 1 at.%.

Table 3. Fractional atomic coordinates and isotropic displacement parameters (U_{iso}) for the crystal structure of Bi_2TeI

Atom	*x/a*	*z/c*	U_{iso}/Å^2
Bi(1)	0.6837(1)	0.0511(1)	0.0334(4)
Bi(2)	0.4426(1)	0.3274(1)	0.0257(3)
Te	0.8084(2)	0.4249(1)	0.0174(4)
I	0.0666(2)	0.1997(1)	0.0217(4)

Note: $y/b = 0$ for all atoms.

Table 4. Anisotropic displacement parameters (Å^2) for the crystal structure of Bi_2TeI

Atom	U_{11}	U_{22}	U_{33}	U_{13}
Bi(1)	0.0256(5)	0.0243(6)	0.0510(8)	0.0078(4)
Bi(2)	0.0219(5)	0.0215(5)	0.0341(6)	0.0054(4)
Te	0.0106(6)	0.0100(7)	0.0322(9)	0.0054(5)
I	0.0224(7)	0.0221(8)	0.0209(8)	0.0038(5)

Note: $U_{12} = U_{23} = 0$ for all atoms.

that reliable absorption corrections were difficult to apply, because the X-ray data were collected from a platelet crystal.

Microcrystallites of Bi_2TeI were examined for the presence of an incommensurate modulation by electron diffraction on a JEOL JEM-2000 FX-II transmission electron microscope. The experiment confirmed the crystal system and the unit cell parameters. No satellite reflections characteristic of incommensurate modulation were observed.

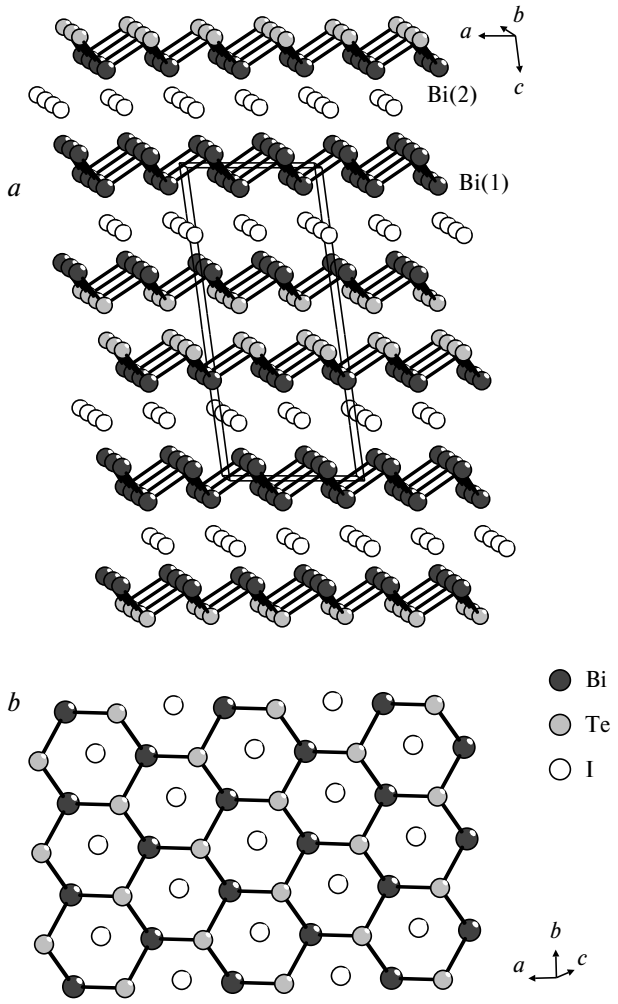

Fig. 2. Crystal structure of Bi_2TeI: *a*, an overall view; *b*, corrugated BiTe layers against the background of planar iodine layers.

The crystal lattice of Bi_2TeI (see Fig. 2) is formed by two-dimensional blocks stacked along the *c* axis. The blocks are slightly shifted with respect to one another along the *a* axis, have the stoichiometry of the title compound, and are weakly bonded to one another. The Te—Te distances between the blocks are 3.665 Å, which suggests that these distances are nonbonded. The layered structure of the phase was supported by the crystal shape and the ease of crystal cleavage. Each block consists of eight atomic layers alternating in the Te—Bi—I—Bi—Bi—I—Bi—Te order and includes a bismuth double layer.

The geometry of the Bi—Te and Bi—I bond systems in Bi_2TeI is very similar to that in bismuth telluroiodide BiTeI,[12] and the Bi_2 double layer is structurally very similar to the analogous layers in subvalent bismuth tellurides[11] (Table 5). It should be noted that the geometry of the Bi_2 layers in Bi_2TeI is virtually identical to that in Bi_4Te_3.[11] The Bi—I distances in the Bi_2TeI structure are noticeably longer than the corresponding distances in BiTeI [12] and much exceed those in BiI_3 [22] (3.06 Å). To the contrary, the Bi—Te distances in the structures of both telluroiodides are very similar, being substantially shorter than the corresponding distances in subvalent bismuth tellurides[11] (3.11—3.33 Å).

In the structure under study, the coordination polyhedra of all types of atoms can be described as distorted octahedra. The Bi(1) atoms belonging to the double layers lie in the equatorial plane of the octahedron, are located at the shortest distances from two Bi(1) atoms, and have two iodine atoms as the nearest neighbors at a distance of 3.65 Å. Two Bi(1) atoms occupy the axial positions at distances of 4.38 Å from the central atom. The Bi(2) atoms in the equatorial plane of the octahedron are

Table 5. Interatomic distances (*d*) and bond angles (ω) in the crystal structure of Bi_2TeI

Distance	*d*/Å	Angle	ω/deg
Bi(1)—Bi(1)	3.101(2)	Bi(1)—Bi(1)—Bi(1)	89.87(7)
Bi(2)—Te	3.054(2)	Te—Bi(2)—Te	91.63(5)
Bi(2)—I	3.38(2)	I—Bi(2)—I	80.75(4)

Table 6. Calculated atomic charges in the Bi_2TeI structure

Atom	RHF	DFT
Bi(1)	+0.25	+0.25
Bi(2)	+1.00	+1.25
Te	−0.5	−0.7
I	−0.75	−0.8

located at the shortest distances from two Te atoms; the distances to two nearest neighbors (iodine atoms) are 3.38 Å. Two axial Bi(2) atoms are located at distances of 4.38 Å from the central atom.

To establish the crystal structure of Bi_2TeI, the atomic charges were calculated by the Hartree—Fock and DFT methods (Table 6). The results of these calculations are in good agreement with each other and consistent with the crystal structure of the phase. The Bi(1) atoms of the double layer have small positive charges, which confirms the assumption of nearly zero charge of the layer, whereas the Bi(2) atoms bound to the I and Te atoms bear a large positive charge.

Band diagrams for Bi_2TeI are shown in Fig. 3. They indicate that Bi_2TeI is expected to show a pronounced anisotropy of conductivity. Indeed, a rather high density of states at the Fermi level for the Γ—X and Γ—M directions is indicative of metallic conductivity in the *ab* plane, whereas the Γ—Z direction (along the *c* axis of the unit cell) is characterized by the zero density of states at the Fermi level, which indicates that compound Bi_2TeI must exhibit semiconducting properties along this direction.

Although the crystal structure of Bi_2TeI, includes a layer of bismuth atoms, it, strictly speaking, cannot be considered as a results of direct intercalation of this layer into the BiTeI lattice. The structure of Bi_2TeI differs from that of BiTeI in that the BiTeI blocks in the former structure alternate with their mirror images (related by the *ab* plane), resulting in two types of "gaps" alternating along the *c* axis, which are formed by the nonbonding I—I and Te—Te contacts. The former gaps are filled with Bi_2 layers, whereas gaps of the latter type remain unoccupied, which accounts for a layered structure and the Bi_2TeI composition.

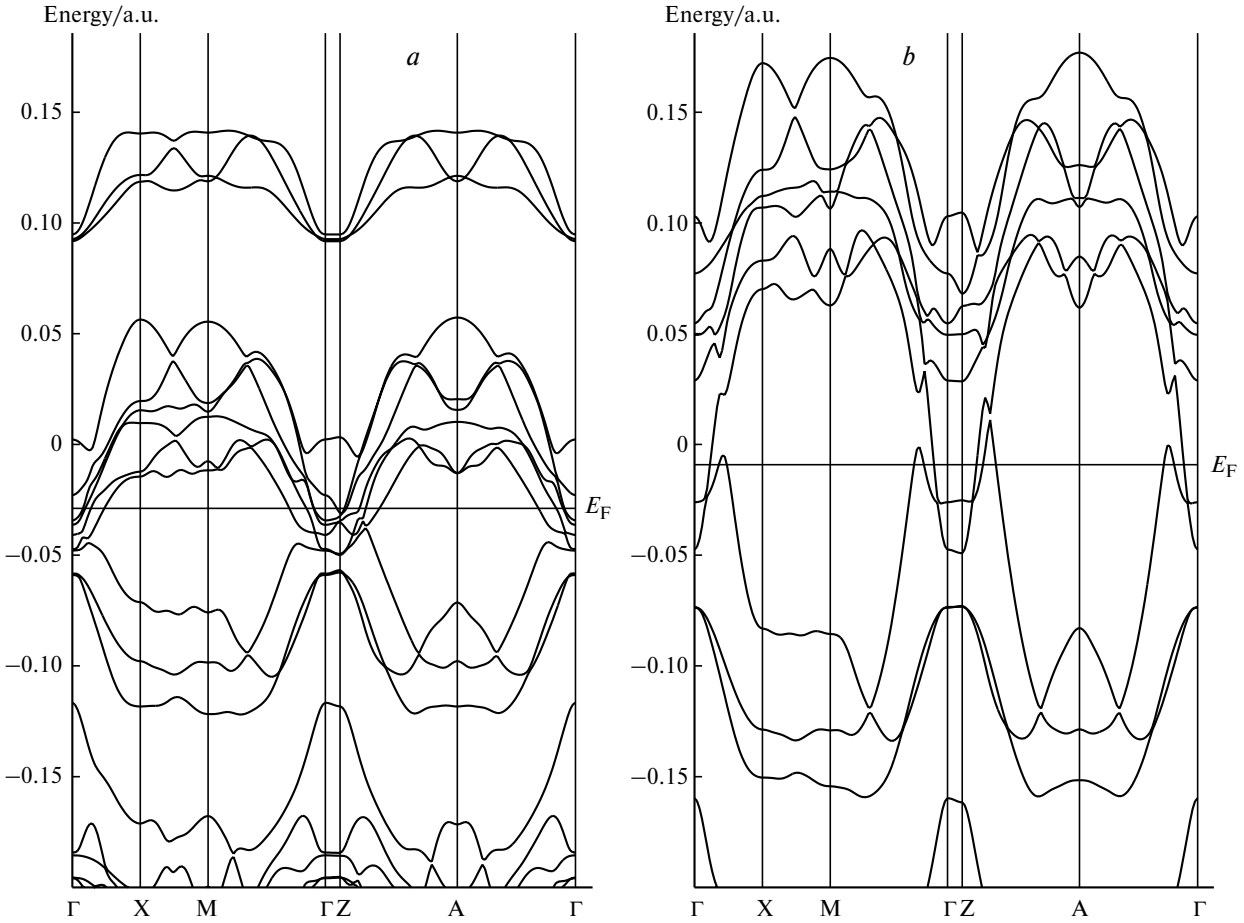

Fig. 3. Band diagrams for Bi_2TeI calculated by the RHF (*a*) and DFT (*b*) methods; E_F is the position of the Fermi level.

It is reasonable to assume that the compound with an unknown structure, which was found in the present study and which is similar in composition to $Bi_4TeI_{1.25}$, is formed by simple intercalation of the bismuth double layers into the Te—Te-type "gaps" in the Bi_2TeI structure (by analogy with the formation of, for example, the lattice of Bi_4Te_3 from Bi_2Te_3). This assumption is supported by the unit cell parameters of the phase under consideration, which apparently correspond to a subcell, and by the crystal shape, which rules out a pronounced layered structure. A high iodine content in the compound may be accounted for by both inaccuracy of chemical analysis and possible disordered substitution in the iodine and tellurium sublattices.

The Bi_2TeI compound would be expected to serve as a parent compound of intercalation phases formed by intercalation of five-layer Bi_2Te_3 blocks or seven-layer Bi_3Te_4 blocks into the Te—Te "gap." However, it should be noted that the synthesis of such phases by prolonged annealing of solid components will, apparently, always afford multiphase samples, as in the present study. All researchers working with subvalent bismuth chalcogenides[7—11] also noted that heterogeneous samples were formed regardless of the annealing conditions. Most probably, this is associated with the fact that the related phases are similar in crystallographic characteristics and energy.

To summarize, we demonstrated for the first time that bismuth double layers can be in principle intercalated not only between layers of selenium or tellurium atoms (this situation is observed in subvalent bismuth chalcogenides) but also between iodine layers. This gives prospects of searching for new metal—insulator (semiconductor) "molecular composites" of this type.

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References

1. H. G. von Schnering, H. von Benda, and C. Kalveram, *Z. Anorg. Allg. Chem.*, 1978, **438**, 37.
2. E. V. Dikarev and B. A. Popovkin, *Vestn. Mosk. Univ., Ser. Khim.*, 1990, **31**, 496 [*Moscow Univ. Bull., Ser. Chem.*, 1990, **31** (Engl. Transl.)].
3. E. V. Dikarev, B. A. Popovkin, and A. V. Shevelkov, *Z. Anorg. Allg. Chem.*, 1992, **612**, 118.
4. E. V. Dikarev and B. A. Popovkin, *Dokl. Akad. Nauk SSSR,* 1990, **310**, 117 [*Dokl. Chem.*, 1990 (Engl. Transl.)].
5. H. von Benda, A. Simon, and W. Bauchofer, *Z. Anorg. Allg. Chem.*, 1978, **438**, 53.
6. E. V. Dikarev, A. V. Shevel´kov, and B. A. Popovkin, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 2201 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2304].
7. N. Frangis, S. Kuypers, C. Manolikas, G. van Tendeloo, J. van Landuyt, and S. Amelinckx, *J. Solid State Chem.*, 1990, **84,** 314.
8. E. Gaudin, S. Jubic, M. Evain, R. Brec, and J. Rouxel, *Mat. Res. Bull.,* 1995, **30**, 549.
9. H. Lind and S. Lidin, *Solid State Sciences*, 2003, **5**, 47.
10. H. Shimazaki and T. Ozawa, *American Mineralogist*, 1978, **63**, 1162.
11. K. Yamana, K. Kihara, and T. Matsumoto, *Acta Crystallogr.*, 1979, **B35**, 147.
12. A. V. Shevelkov, E. V. Dikarev, R. V. Shpanchenko, and B. A. Popovkin, *J. Solid State Chem.*, 1995, **114**, 379.
13. N. R. Valitova, V. A. Aleshin, B. A. Popovkin, and A. V. Novoselova, *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.*, 1976, **12**, 225[*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1976, **12** (Engl. Transl.)].
14. A. Tomokiyo, T. Okada, and S. Kawano, *Jpn J. Appl. Phys.*, 1977, **16**, 291.
15. *Joint Comission for Powder Diffraction Standarts (JCPDS), Inorganic Substances*, International Centre for Diffraction Data, USA, 1997.
16. *Powder Diffraction File-2 (PDF-2), Database for Powder Diffraction Data*, International Centre for Diffraction Data (ICDD)), USA, 1999.
17. P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270.
18. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
19. V. R. Saunders, R. Dovesi, C. Roetti, M. Causa, N. M. Harrison, R. Orlando, and C. M. Zicovich-Wilson, *CRYSTAL98 User's Manual*, University of Torino, Torino, 1998.
20. G. S. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution,* Göttingen, Germany, 1997.
21. G. S. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, Göttingen, Germany, 1997.
22. G. Tropper and T. Zobel, *Z. Kristallogr.*, 1966, **123**, 67.

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