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The crystal structure of a new bismuth tellurium oxychloride $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$ from neutron powder diffraction data

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Abstract

A new bismuth tellurium oxychloride was obtained by reaction of BiOCl and TeO_2 in air. According to energy dispersive X-ray spectroscopy and neutron powder diffraction refinement the composition of the substance was determined as $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$. The new compound crystallizes in the trigonal system space group $R\bar{3}$ (#148), $Z = 6$, $a = 4.10793(4)$, $c = 31.1273(4)$ Å, $\chi^2 = 3.20$, $wR_p = 0.0369$. $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$ has a new type of layered structure constructed by Bi–Te–O layers separated by chloride ions. The Te atoms in $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$ show an unusual umbrella-like environment. A comparison with known related structures has been made.
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1. Introduction

Compounds containing *p*-elements in low oxidation states frequently exhibit stereochemically active lone electron pairs. Due to this, compounds of Sn(II), Pb(II), Bi(III), Sb(III), Se(IV) and Te(IV) adopt asymmetric or one-sided oxygen ion coordination environments. The lone pair acts as a structure-directing agent that frequently leads to low dimensional structures and noncentrosymmetric (NCS) materials with promising physical properties [1,2]. Both of these tendencies were shown for crystal structures of complex Bi–Te and Ln–Te oxyhalides (Ln = rare earth metals) [3–13]. Most of them adopt layered and NCS structures with interesting nonlinear optical properties.

Due to the peculiarities highlighted above, during the last 20 years oxybromides and oxyiodides of Bi–Te and Ln–Te have been extensively developed [3–13] and some of them may be attributed as different families with common structural features. On the contrary, previous information about Bi–Te oxychlorides has been poor. Only one work has been performed to establish phase relations in the system Bi_2O_3–$BiCl_3$–TeO_2 at 500 °C [14]. In this study only one ternary phase, $2BiOCl \cdot Bi_2Te_4O_{11}$ ($Bi_4Te_4O_{13}Cl_2$), was found and no structural data were given.

Our present work was performed to establish the crystal structure of a new Bi–Te oxychloride with composition close to $BiTe_2O_5Cl$ and to compare it with other known structures of related bismuth and rare earth compounds.

2. Experimental

2.1. Synthesis and preliminary characterization

A mixture of BiOCl (Aldrich, 99%) and TeO_2 (Aldrich, 99,99%) in a molar ratio 1:2 was heated in an alumina crucible with a lid from room temperature to 550 °C over 2 h and annealed at 550 °C for 6 h. Subsequently, the furnace was switched off and the sample was allowed to cool. After crushing the crucible the product was extracted as a crystalline, melted, colorless substance with a small amount of well formed crystals on the surface of the bulk sample and crucible pieces.

The powder X-ray pattern (Stoe STADI P, Cu$K\alpha_1$ radiation, Ge-monochromator) from the ground reaction product could not be attributed to starting materials or to $Bi_4Te_4O_{13}Cl_2$.

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It should be noted that when the reaction was performed at 500 °C only starting materials were found in the annealed product.

Energy dispersive X-ray spectroscopy (EDX) analyses of the plate-like crystals using a JEOL JEM 2011 HRTEM microscope with Oxford Instruments ISIS EDX Analysis System, showed that sample contained a slightly smaller amount of Bi and Cl, (at.% Bi—22.7($\pm$4.9), Cl—23.2($\pm$2.4) and Te—54.1($\pm$6.1)) compared to that in the original reaction mixture. According to this the formula of the compound may be written as approximately $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$.

2.2. Single crystal X-ray diffraction

Single crystal data were collected on a Rigaku AFC7S diffractometer.

Shelxs97 and Shelxl97 programs were used for structure solution and refinement [15]. It was found that new compound crystallized in the trigonal system, probable space group $R\bar{3}$ (#148). Unfortunately, positions of only the Bi, Te, Cl and one oxygen atom could be found unambiguously. The reasons for the failure of this structure solution may be a common difficulty to determine positions of 'light' oxygen atoms correctly in the presence of bismuth ('heavy' element) due to the their contrast in X-ray scattering factors, and also a possible twinning of the crystal used in the refinement. However, this model was useful as the indexing could be used to confirm purity of the bulk polycrystalline sample and allowed to index the X-ray powder pattern fully with $a = 4.1131(5)$ and $c = 31.201(5)$ Å (figure of merit $F(22) = 32.2$). This partial structural model was subsequently used to elaborate a complete model from the neutron powder diffraction study. Using powder neutron diffraction we may determine oxygen atoms more precisely and neglect the quality of the single crystals.

2.3. Neutron powder diffraction study

NPD data were collected at the ISIS Facility, using the high-resolution instrument HRPD. Approximately 10 g of powder were loaded into a cylindrical vanadium can, and data collected for about 3 h. Data from both the 90° and 168° detector banks were used for Rietveld refinement using the GSAS software [16]. Some experimental parameters are listed in Table 1.

The initial model of the crystal structure was taken from the partial single crystal solution. Positions of the remaining oxygen atoms were found using Fourier synthesis. The final fit for the 90° detector bank is shown in Fig. 1. As follows from the EDX investigation, the compound under study contains smaller amounts of Bi and Cl than was expected, so their sites occupancies should be reduced accordingly. Attempts to refine Bi and Cl occupancies lead to instabilities due to correlations with the thermal parameters. In the final model occupancies of Bi and Cl

Table 1
Crystal data and structure refinement for $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$

Empirical formula	$Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$
Instrument	HRPD
Temperature	293(2)
Crystal system	Trigonal
Space group	$R\bar{3}$ (#148)
Unit cell dimensions (Å)	
a	4.10793(4)
c	31.1273(4)
Volume ($Å^3$)	454.903(13)
Z	3
Density (calculated) (Mg/m³)	5.982
Refinement method	Rietveld Refinement
Refinement software	GSAS [16]
Number of parameters	39
Goodness-of-fit, χ^2	3.20
R_p	0.0461
Rw_p	0.0369

positions were assigned as 0.87 in accordance with the EDX analysis results. The position of the Bi atom was shifted from ideal $3a$ $(0,0,0)$ to $6c$ $(0,0,z)$. There are three oxygen sites within the asymmetric unit, but during the initial refinements both O2 and O3 revealed anomalously large displacement parameters. In order to correspond to the EDX stoichiometry, the occupancies of these two atoms were allowed to refine, subject to the overall stoichiometry constraint. In addition, a tentative anisotropic refinement revealed very elongated ellipsoids in the xy plane for O3, when sited on the ideal $6c$ position. This atom was therefore displaced to a general $18f$ position, with correspondingly reduced occupancy. This improved the fit, and also produced more reasonable displacement parameters and bond lengths during the final isotropic refinement.

Atomic coordinates, isotropic displacement parameters and bond distances are presented in Tables 2 and 3.

3. Results and discussion

A new Bi–Te oxychloride has been found. From EDX composition analysis the formula of the new compound may be written as $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$ (i.e. 30 mol% BiOCl), which deviates slightly from that expected based on the synthesis: $BiTe_2O_5Cl$ (33 mol % BiOCl). Such a nonstoichiometry in complex Bi–Te oxyhalides was also observed previously for $Bi_{0.97}TeO_3Br_{0.90}$ [3].

As can be seen from Table 3 and Fig. 2, $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$ possesses a layered structure, as may have been predicted from the statements in Section 1.

Bi and Te atoms are coordinated by oxygen atoms only within the distances of 2–2.9 Å (Table 3) and form layers parallel to the ab plane of the unit cell. Such layers are separated by Cl^- anions, the shortest distance between the Te atom and the nearest Cl being 3.26 Å (Table 3).

Statistically distributed Bi has a complex surrounding by oxygen atoms. It may be described as a distorted cubic like
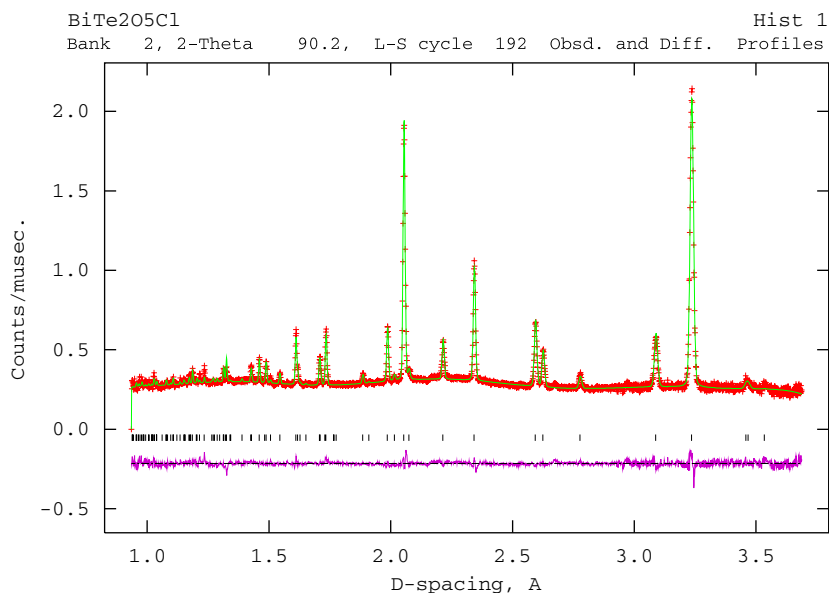
Fig. 1. Final Rietveld fits for NPD data of $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$, obtained on HRPD. Experimental curve marked as +, calculated − as continuous line. Difference curve and reflection positions are also depicted.

Table 2
Atomic coordinates and isotropic thermal parameters for $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$

Name	Site	Occupancy	X	Y	Z	Uiso × 100
Bi	6c	0.435[a]	0	0	0.01050(7)	5.73(9)
Te	6c	1.0	−1/3	1/3	0.09458(4)	6.63(6)
Cl	3b	0.87[a]	−2/3	−1/3	1/6	4.02(5)
O1	6c	1.0	1/3	2/3	−0.02985(5)	8.99(5)
O2	6c	0.7268(22)	0	0	0.08017(6)	8.78(8)
O3	18f	0.2411(7)	0.2022(7)	0.4643(7)	0.06865(8)	8.78(8)

[a]Occupancy of Bi and Cl sites were assigned in accordance with EDX data to 0.87.

Table 3
Bond distances (Å) for $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$

Bond			Distance
Bi	O1	× 3	2.683(1)
Bi	O1	× 3	2.4470(8)
Bi	O2	× 1	2.169(3)
Bi	O2	× 1	2.822(3)
Bi	O3	× 3	2.455(4)
Bi	O3	× 3	2.969(3)
Te	Cl	× 3	3.2651(9)
Te	O1	× 1	2.015(2)
Te	O2	× 3	2.4137(4)
Te	O3	× 3	2.368(1)
Te	O3	× 3	2.144(2)

environment formed by six O1 and two O2 atoms (Fig. 3a), positions of which are occupied fully or close to 3/4. The Bi atom has a position split from ideal into two sites close to the center of distorted cube. In addition, all faces of the cube are capped by the O3 atom, which has site occupancy close to 1/4. Finally, the full Bi environment may be described as a 14-vertex distorted polyhedron. The stereochemical activity of the Bi lone pair is manifested in the displacement of the atom away from the ideal 3a position towards one corner of the cube.

These polyhedra share their O1–O1 edges between each other and form layers perpendicular to direction [0 0 1] (Fig. 3b).

Te has an umbrella-like environment formed by 10 oxygen atom sites, which may be regarded as '4 + 6', due to 4 ordered sites (O1 and O2) plus 6 disordered and partially occupied sites (O3) (Table 3 and Fig. 3c). Three O_2 and six O3 atoms build a hexagonal base and Te is situated on one side of it (Fig. 3c). From the other side of the hexagonal base one O1 is situated with shortest bond length Te–O1 about 2.015 Å. Distant from Te atom is oxygen site O_2 at about 2.41 Å. This oxygen, according to our refinement has site occupancy near 3/4. O_3 has closest distance 2.14 Å with site occupancy 1/4. An environment with an open polyhedron is common for Te(IV) compounds. This may be explained as due to the stereochemical activity of the Te^{4+} lone pair, as occurs in $Bi_2TeO_{4.5}Br$ [4] and other $LnTe_2O_5X$ ($Ln = $ Nd, Gd, Ho, X = Cl, Br) layered compounds [5,8,11]. Te umbrellas connected via shared the O2–O3 edge form sublayers parallel to the ab plane, above and below the Bi sublayer, which has common O–O edges with the Te polyhedra. The Bi and Te polyhedra build up metal–oxygen layers which are separated by chloride anions. Te atoms are situated in the outer regions of the Bi–Te–O layer (Fig. 2).

The crystal structure of $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$ represents a new type of structure for complex Te–M oxyhalides. However, it is pertinent to draw some analogies with the so-called Sillén phases. Within Sillén's family of layered materials, the structures vary by the thickness of the fluorite-like metal oxygen block, $[M_2O_2]$ or $[M_3O_4]$, and by

the thickness of the separating halide anion layers (one, two or three anion sublayers thick). From this point of view our new compound $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$ may be considered as related to the $NdTe_2O_5Br$ structure type [5] (Fig. 4a), which exhibits triple metal–oxygen blocks constructed by two Te sublayers and a central Nd sublayer. In the case of $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$ similar triple metal–oxygen blocks are separated by chloride anion layers; however, $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$ represents a significantly different variant, having both different symmetry (trigonal

rather than pseudo-tetragonal) and a different Te environment (Fig. 4).

From the symmetry point of view the $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$ structure is more closely related to the SmSI-type [17]. The crystal structure of YOCl (SmSI-type, space group $R\bar{3}m$ (#166), $a = 3.776$, $c = 27.95$ Å) [18] is displayed in Fig. 4b together with the crystal structure of $NdTe_2O_5Br$, mentioned above (Fig. 4a) and may be compared with the crystal structure of $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$ (Fig. 2). It can be seen that the key difference between the $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$
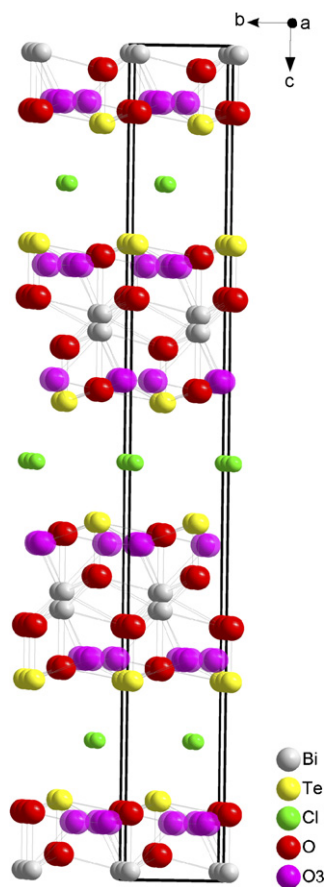

Fig. 2. The crystal structure of $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$. O3 atoms are shown as transparent balls. Unit cell and Bi–O, Te–O bonds are marked. Thermal displacement parameters for all atoms are drawn with 50% probability factor.
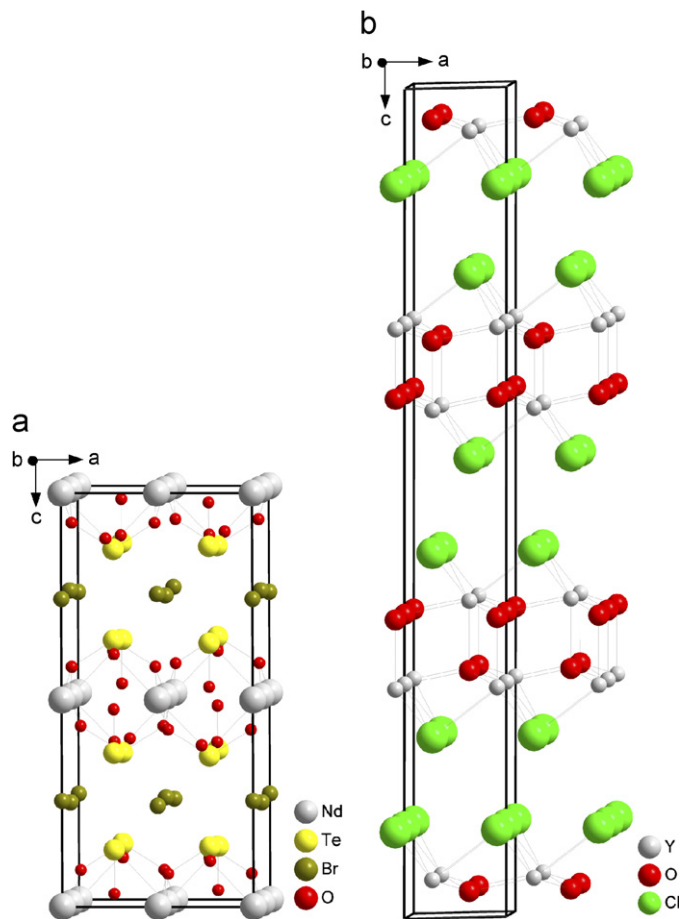

Fig. 4. Crystal structures of $NdTe_2O_5Br$ [5] (a) and YOCl [18] SmSI structure type (b) for comparison with $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$ presented in Fig. 2.
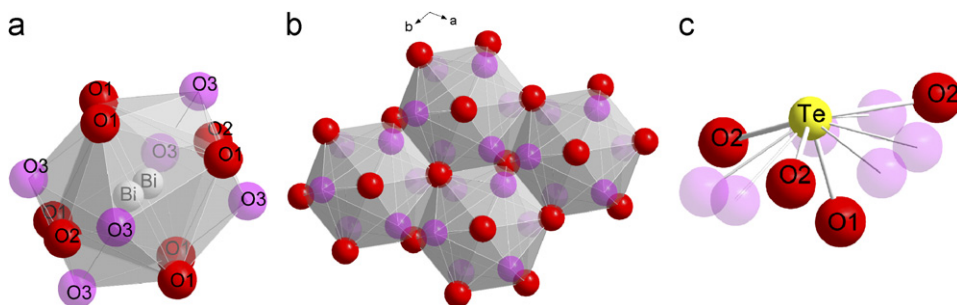

Fig. 3. Coordination environment of Bi (a) and Te (c) atoms in $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$. O3 atoms are shown as transparent balls. Fourteen-vertex Bi polyhedra forming layers in *ab* plane (b).

and YOCl structures is in the thickness of the metal–oxygen block (i.e. '[M_3O_4]' versus '[M_2O_2]' types). In both structures the metal–oxygen blocks are separated by anionic layers in accordance with charge balance. Significantly, the Y–Cl contact distances are shorter (2.76 Å) and the Cl atom is included in Y environment. In the case of $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$ this block consists of three cationic sublayers in the sequence Te–Bi–Te, whereas in the YOCl structure the metal–oxygen block contains only two cationic sublayers. In both cases the metal–oxygen blocks are separated by anionic layers in accordance with charge balance; a single layer for $Bi_{0.87}Te_2O_{4.9}Cl_{0.87}$ and a double layer for YOCl. In the Sillén family the same situation exists, for example it may be illustrated by BiOCl [19] and Bi_3O_4Br [20], where double and triple metal–oxygen blocks are separated by double and single layers of anions, respectively.

Acknowledgments

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