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The Crystal Structure of the New Pyroelectric Phase $Bi_4Te_2O_9Br_2$

L. N. Kholodkovskaya, V. A. Dolgikh,[1,2] and B. A. Popovkin

Chemical Department, Moscow State University, Leninski Gory, Moscow, GSP, 119899, Russia

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The crystal structure of $Bi_4Te_2O_9Br_2$—a new phase with pyroelectric properties—was determined by the single crystal X-ray diffractometer technique (*Pmm*2, Z = 1, a = 5.5231(8), b = 5.5511(8), c = 9.735(1) Å, R/R_W = 0.070/0.084 for 461 reflections, Mo$K\alpha$). The structure could be described as being built up of fluorite-like triple metal–oxygen $[Bi_4Te_2O_9]$ layers alternating with bromine layers along the z-axis. Each triple $[Bi_4Te_2O_9]$ layer consists of two bismuth and one tellurium cationic sublayer with oxygen atoms in tetrahedral voids among the cations; half of all octahedral voids are occupied by O3 atoms. The relation of this crystal structure with Bi_3O_4Br and $NdBi_5O_8Cl_2$ Sillen phases is discussed.

INTRODUCTION

Several new pyroelectrics were discovered among the earlier synthesized bismuth–tellurium oxybromides (1, 2). $Bi_4Te_2O_9Br_2$ is one of them and has promising pyroelectric characteristics (3). This paper deals with the crystal structure determination of $Bi_4Te_2O_9Br_2$. In our previous works (1, 2) based on the results of X-ray powder analyses this compound was considered as belonging to the Sillen phases. Crystal structures of the last ones are built up of fluorite-like bismuth–oxygen (or bismuth–metal–oxygen) layers alternating with single, double, or triple halogen or chalcogen layers (4, 5).

EXPERIMENTAL

Single crystals of $Bi_4Te_2O_9Br_2$ were grown from the gas phase. The stoichiometric mixture of Bi_2O_3 and TeO_2 in the ratio 4 : 3 was first annealed in evacuated quartz ampoules at 600° for 300 hr, and then ground in an agate mortar with simultaneous addition of synthesized-from-elements $TeBr_4$. The general ratio of the components was $Bi_2O_3 : TeO_2 : TeBr_4$ = 4 : 3 : 1. The prepared mixture, placed in the one end of an evacuated quartz ampoule (l = 80 mm, d = 20 mm), was put into the hot zone of the temperature gradient furnace (temperature 710°C). The other end of the ampoule was situated in the zone at 660°C. After 170 hr small yellow-green single crystals formed in the "cold" end of the ampoule.

A suitable single crystal was selected and mounted on an Enraf–Nonius CAD4 diffractometer. The orthorhombic unit cell dimensions were determined using 25 well-centered reflections.

No systematic absences were observed. Data collection parameters are listed in Table 1. According to second harmonic generation measurements (SHG method) (2, 3) there are two possible noncentrosymmetric space groups, *P*222 and *Pmm*2. Unsatisfactory results were obtained in the *P*222 space group, but the crystal structure refinement in the *Pmm*2 space group appeared to be successful.

All calculations were made using an ENX-SDP program system. The positions of all heavy atoms were obtained from a phase set derived by direct methods. Difference Fourier cycling was then used to find the remaining atoms. The DIFABS program was applied for a semiempirical absorption correction. The final refinement was R = 7.0%, R_W = 8.4%, esd = 0.889. Positional and isotropic thermal parameters obtained in the final least-squares refinement are listed in Table 2, and interatomic distances are given in Table 3.

DISCUSSION

The $Bi_4Te_2O_9Br_2$ crystal structure (Fig. 1) is related to the Bi_3O_4Br and $NdBi_5O_8Cl_2$ crystal structures. Investigated by Aurivillius (7), these were found to be built up of triple fluorite-like $[Bi_3O_4]^+$ or $[NdBi_5O_8]^{2+}$ metal–oxygen layers alternating with single halogen layers. In the crystal structure of $Bi_4Te_2O_9Br_2$, triple bismuth–tellurium–oxygen layers are interleaved by single bromine layers. That is why $Bi_4Te_2O_9Br$, as well as Bi_3O_4Br and $NdBi_5O_8Cl_2$, should be regarded as a Sillen phase. Each triple $[Bi_4Te_2O_9]^{2+}$ layer consists of two bismuth and one tellurium cationic sublayer. As in all fluorite structures oxygen atoms (O1 and O2) are situated in tetrahedral voids among the cations.

[1] To whom correspondence should be addressed.
[2] E-mail: DOLG@nns.admin.chem.msu.su.

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TABLE 1
Crystal Data for $Bi_4Te_2O_9Br_2$

Formula	$Bi_4Te_2O_9Br_2$
Space group	*Pmm*2
Cell parameters	
a (Å)	5.5231(8)
b (Å)	5.5511(8)
c (Å)	9.735(1)
Z	1
Crystal dimensions (mm)	0.08 × 0.12 x 0.03
$\mu(cm^{-1})$	679.7
$\rho_{calc}(g/cm^3)$	7.76
λ (Mo$K\alpha$)	0.71073 Å
Temperature of measurement	293 K
Scan mode	ω/θ
θ_{max}	28°
No. of measured reflections	672
No. of unique reflections	461
No. of reflections used with $I > 3\sigma(I)$	343
No. of refined parameters	27
Weights	see Ref. (6)
R	0.070
R_w	0.084

According to Aurivillius (7), in the crystal structures of Bi_3O_4Br and $NdBi_5O_8Cl_2$ there is room for an extra oxygen atom in the octahedral voids in the middle of the triple metal–oxygen layer. In the crystal structure of $Bi_4Te_2O_9Br_2$ half of all octahedral voids are occupied by O3 atoms, so it differs from the fluorite-type structures where all octahedral voids are empty. In addition, one of the three sublayers consists of Te1 and Te2 atoms whose *z* coordinates are not equal, and the sublayer is slightly corrugated.

Bismuth atoms in the middle of the triple metal–oxygen layer (Bi1 and Bi2) are surrounded by eight oxygen atoms (4 × O1 and 4 × O2) forming a distorted cube, as in the crystal structure of Bi_3O_4Br. It is interesting that the distortions are not so strong as in the structure of Bi_3O_4Br. In the crystal structure of $Bi_4Te_2O_9Br_2$ each cube is completed by two O3 "caps." Sharing common triangle faces O1–O3–O2, Bi1 and Bi2 polyhedra form layers parallel to the (001) plane.

The nearest environment of the bismuth atoms of both lateral sublayers in the crystal structure of Bi_3O_4Br (7) is typical for Sillen phases and corresponds to an Archimedian antiprism with four oxygen atoms in one base and four bromine atoms in another one. Nevertheless, Bi–Br bond lengths are rather long (Table 3) and Aurivillius did not include the bromine atoms in the coordination polyhedra of the Bi atoms. Looking along the *z*-axis in the crystal structure of $Bi_4Te_2O_9Br_2$ O1 atoms are situated only below Bi3 and Bi4 atoms, so that each of them is coordinated by a square of four O1 atoms only from one side. In addition, in Bi3 coordination each 4 × O1 square is completed by an O3 "cap." There is a $[Br]^-$ layer above the Bi3 and Bi4 atoms but the Bi–Br bond lengths are too long to be included in the coordination polyhedra of Bi3 and Bi4 atoms.

TABLE 2
Positional and Thermal Parameters for $Bi_4Te_2O_9Br_2$

Atom	*x/a*	*y/b*	*z/c*	B_{iso}	*N*
Bi1	0	0	0.5	1.73(8)	1
Bi2	0.5	0.5	0.5245(4)	1.9(1)	1
Bi3	0	0.5	0.7644(4)	1.78(8)	1
Bi4	0.5	0	0.7976(5)	1.6(1)	1
Te1	0.5	0	0.346(1)	2.2(1)	1
Te2	0	0.5	0.291(1)	2.9(2)	1
Br1	0.5	0.5	0.047(1)	3.8(3)	1
Br2	0	0	0.079(1)	2.4(2)	1
O1	0.26(1)	0.26(1)	0.670(2)	0.8(3)	4
O2	0.24(1)	0.23(2)	0.321(5)	1.6(9)	4
O3	0	0.5	0.495(9)	2.4(9)	1

TABLE 3
Interatomic Distances (Å) for $Bi_4Te_2O_9Br_2$ and Bi_3O_4Br (7)

$Bi_4Te_2O_9Br_2$			Bi_3O_4Br		
Atom–atom		Distance	Atom–atom		Distance
Bi1	4 × O1	2.62(5)			
	4 × O2	2.54(7)	Bi1	2 × O2′	2.19(3)
	2 × O3	2.776(2)		2 × O2	2.37(2)
Bi2	4 × O1	2.35(5)		2 × O1′	2.71(2)
	4 × O2	2.87(7)		2 × O1′	2.86(2)
	2 × O3	2.776(9)			
Bi3	4 × O1	2.16(5)			
	1 × O3	2.62(9)			
	2 × Br1	3.897(7)			
	2 × Br2	4.133(8)	Bi2	2 × O2′	2.07(2)
Bi4	4 × O1	2.32(5)		2 × O2	2.12(2)
	2 × Br1	3.688(7)		2 × O1′	2.13(2)
	2 × Br2	3.890(8)		2 × O1	3.45(2)
Te1	4 × O2	1.94(8)		1 × Br′	3.30(0)
	2 × Br1	4.022(10)		1 × Br	3.43(0)
	2 × Br2	3.792(9)		1 × Br″	3.60(0)
Te2	4 × O2	2.02(9)		1 × Br‴	3.70(0)
	1 × O3	1.99(9)			
	2 × Br1	3.643(9)			
	2 × Br2	3.459(8)			
	O1–O1	2.65(8)			
	O1–O1	2.67(8)			
	O1–O1	2.89(8)			
	O1–O3	2.60(7)			
	O2–O2	2.55(16)			
	O2–O2	2.65(8)			
	O2–O2	2.87(8)			
	O2–O3	2.62(10)			

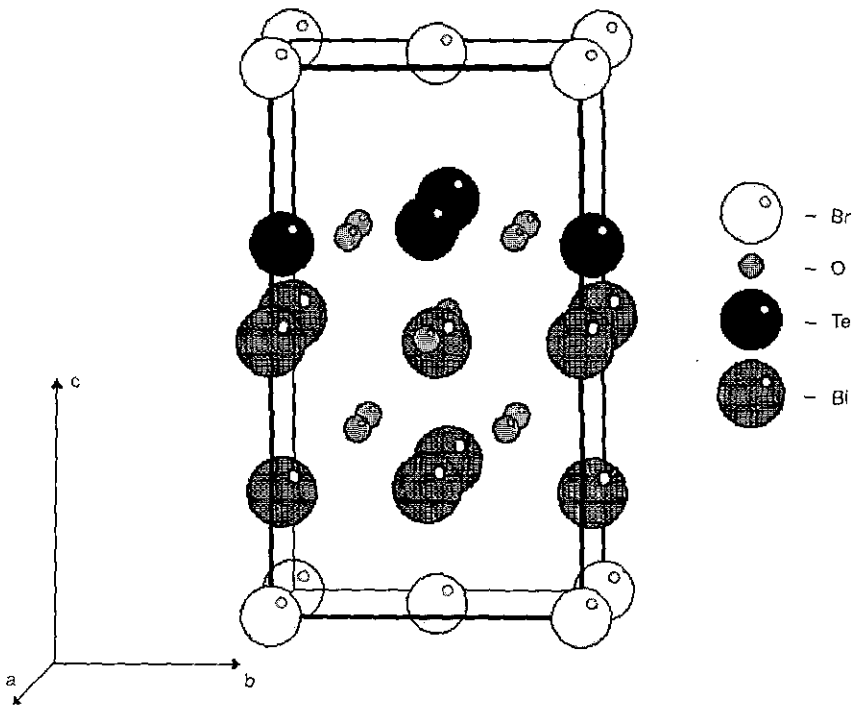

FIG. 1. The crystal structure of $Bi_4Te_2O_9Br_2$.

Te1 and Te2 atoms have the same coordination as Bi3 and Bi4 atoms. If the Te–Br distances were not so long, the coordination polyhedra of Te1 and Te2 atoms could also be described as distorted tetragonal antiprisms but with four O2 atoms in their bottoms and four bromine atoms in their upper bases with an O3 "cap" above the 4 × O2 square in the Te2 polyhedron.

It is interesting that such "opened" polyhedra are rather typical for cations possessing lone electron pairs.

For instance, the coordination environment of Bi atoms in the structures of sillenites $Bi_{12}M_xO_{20\pm\delta}$ (8) includes five oxygen atoms. Four of them lie in the same plane and the fifth Bi–O bond is perpendicular to that plane. The Bi atom is shifted from this plane in the direction opposite to the fifth oxygen atom. As reported in (9), the Bi atom polyhedron is completed to a distorted octahedron by its lone $6s^2$ electron pair oriented opposite the fifth oxygen atom. As for the Te^{IV} environment, TeO_3E pyramids and TeO_4E trigonal bipyramids with all oxygen atoms situated also to one side of the central cation are the most typical ones (10).

As reported in (7), statistical substitution of $\frac{1}{6}$ of the bismuth atoms for Nd atoms killed the lone pair influence. As a result the $[Bi_3O_4]$ layers undergo a transition into the nearly undistorted tetragonal fluorite structure. In the crystal structure of $Bi_4Te_2O_9Br_2$ the Te^{IV} cations, which also possess lone pair electrons, form their own slightly distorted sublayer in each triple metal–oxygen layer.

REFERENCES

1. V. A. Dolgikh, L. N. Kholodkovskaya, and B. A. Popovkin, *in* "Proceedings of The International Symposium on Solid State Chemistry, Karlovy Vary, October 28–31, 1986," pp. 376–377.
2. L. N. Kholodkovskaya, V. A. Dolgikh, A. P. Leonov, and B. A. Popovkin, *Zh. Neorg. Khim.* **32**, 2363 (1987).
3. V. A. Dolgikh, L. N. Kholodkovskaya, S. Yu. Stephanivich, and B. A. Popovkin, Inventor's Certificate N4812479, USSR with priority of 12.04.90.
4. L. G. Sillen, *Naturwissenschaften*, **22**, 318 (1942).
5. V. A. Dolgikh and L. N. Kholodkovskaya, *Zh. Neorg. Khim.* **36**, 970 (1992).
6. R. C. G. Killean and J. L. Laurence, *Acta Crystallogr. Sect. B* **25**, 1750 (1969).
7. B. Aurivillius, *Chem. Scr.* **24**, 125 (1984).
8. S. F. Radaev and V. I. Simonov, *Butll. Soc. Catalana Cien. Fis. Quim. Mat.* **XII** 247 (1991).
9. D. C. Craig and N. C. Stephenson, *J. Solid State Chem.* **15**, 1 (1975).
10. V. A. Dolgikh, *Zh. Neorg. Khim.* **35**, 1979 (1991).