JOURNAL OF SOLID STATE CHEMISTRY 96, 154–161 (1992)

Synthesis and Structure of New Bismuth Containing Oxychlorides: $BiSr_3O_3Cl_3$ and $BiCa_3O_3Cl_3$

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Received July 29, 1991

A new bismuth strontium oxychloride $BiSr_3O_3Cl_3$ has been synthesized and structurally characterized from single crystal X-ray diffraction data. The compound crystallizes in the orthorhombic space group *Pnma* (#62) with $a = 6.687(2)$ Å, $b = 11.4618(8)$ Å, $c = 11.565(2)$ Å, $V = 886.4(3)$ Å^3, and $Z = 4$. From the formula weight of 626.20, the density is calculated to be 4.693 g/cm^3. The structure of $BiSr_3O_3Cl_3$ can be described as a layered structure arranged in sequence Cl/Sr–O/Bi–Sr–O–Cl/Sr–O/Cl along the *b* axis. The Bi–Sr–O–Cl layer is unique among all the known bismuth oxyhalides in that oxygen and halide are mixed in one layer. Two types of Sr atom and one type of Bi atom are found. Strontium of the Sr–O layer is coordinated by three O atoms with Sr–O distances ranging from 2.404(7) to 2.557(6) Å and by five Cl atoms with Sr–Cl distances from 3.010(2) to 3.394(3) Å. Strontium of the Bi–Sr–O–Cl layer is coordinated to three oxygen atoms with Sr–O distances in the range of 2.419(8) to 2.505(6) Å and to six chlorine atoms with Sr–Cl distances in the range 2.922(3) to 3.796(4) Å. The Bi atom is coordinated by three O atoms and two Cl atoms with Bi–O bond lengths ranging from 2.062(8) to 2.071(6) Å and Bi–Cl bond lengths of 3.472(3) Å. The isostructural compound $BiCa_3O_3Cl_3$ was also synthesized; the cell dimensions from single crystal data are $a = 6.383(3)$ Å, $b = 10.803(3)$ Å, and $c = 11.422(3)$ Å. © 1992 Academic Press, Inc.

Introduction

Oxyhalides frequently have interesting optical properties leading to potential applications. One good example is LaOBr, which is isostructural with BiOCl. Lanthanum oxybromide exhibits highly efficient luminescence under X-ray, UV, and cathode-ray excitation if doped with various rare-earth activators (*1–6*). The precise mechanism of the photostimulated luminescence is not completely understood. However, from studies of the isostructural compound BaFCl, it is suggested that this luminescence may be strongly dependent upon the electron states arising from F-centers consisting of a chloride or fluoride ion vacancy occupied by an electron (*7, 8*) and hole states that have been identified as a V_k center represented by a Cl_2^- species (*9, 10*). An attempt to use Bi oxyhalides as light-sensitive photograph layers for Ag-free development has been reported (*11*).

By fusing bismuth oxyhalides with excess of one of the halides of Li, Na, Ca, Sr, Ba, Cd, and Pb, Sillén and co-workers prepared a large number of complex oxyhalides (*12*). All the compounds form tetragonal leaflets with a similar *a* axis (from 3.85 to 4.10 Å) but with various *c* axes (from 12 to 50 Å). The structures of these compounds are closely related to the simple bismuth oxy-

0022-4596/92 $3.00

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halides. The metal–oxygen sheets alternate with single, double, or triple halogen layers forming /*M*–O/*X*/*M*–O/, /*M*–O/*X*/*X*/*M*–O/ or /*M*–O/*X*/*X*/*X*/*M*–O/ layer structures. None of these oxyhalides are structurally related to those described in this paper.

Synthesis

The reagents used in the synthesis of $BiSr_3O_3Cl_3$ were $BiCl_3$ (J. T. Baker) and SrO (obtained by heating $SrCO_3$ at 1400°C for 3 days). They were mixed together in a mole ratio of Bi : Sr = 1 : 3 by grinding under hexane in an agate mortar. Synthesis was carried out by heating this reagent mixture in air in alumina containers. The mixture was heated at 220°C (below the melting point of $BiCl_3$) for 4 hr then at 400°C (below the boiling point of $BiCl_3$) for another 4 hr at 600°C for 4 hr, and finally at 800°C for 12 hr. The reagent CaO (J. T. Baker) and similar reaction conditions were used for synthesis of the Ca substituted compound $BiCa_3O_3Cl_3$. Both $BiSr_3O_3Cl_3$ and $BiCa_3O_3Cl_3$ are white powders that are not readily attacked by or soluble in either cool or hot water. The estimated melting points are about 850 and 910°C, respectively.

For crystal growth, the powder samples were heated to a temperature 30°C above the melting point, held at that temperature for 15 min, and then cooled to room temperature at rate of 15°C/h. Clear colorless crystals were obtained both for $BiSr_3O_3Cl_3$ and $BiCa_3O_3Cl_3$.

Composition of the crystals was determined on an SX-50 microprobe. Standards were Bi_2O_3, $SrCO_3$, and $CaFeSi_2O_6$ for Bi, Sr, and Ca, respectively. The analysis on different crystals gave Bi : Sr = 1 : 3 for $BiSr_3O_3Cl_3$ and Bi : Ca = 1 : 3 for $BiCa_3O_3Cl_3$. It was found that the chlorine content in the samples changed with time under the electron beam; therefore, the Cl content was determined from refinement of the single crystal X-ray data.

Structure Determination

A clear crystal of $BiSr_3O_3Cl_3$ having approximate dimensions 0.15 × 0.15 × 0.30 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated MoK_α radiation from a 12-KW rotating anode generator. Cell dimensions and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 22 carefully centered reflections in the range $30.25° < 2\theta < 38.28°$. This gave an orthorhombic cell with $a = 6.687(2)$ Å, $b = 11.4618(8)$ Å, $c = 11.565(2)$ Å, and $V = 886.4(3)$ Å^3. For $Z = 4$ and formula weight 626.20, the calculated density is 4.693 g/cm^3. The space group was uniquely determined to be *Pnma*(#62). Intensity data were collected at room temperature with the $\omega - 2\theta$ scan technique at a scan speed of 16°/min (in omega) and scan width $\Delta\omega = (1.30 + 0.3 \tan\theta)°$ to a maximum 2θ value of 70°. The weak reflections $[I < 10.0\sigma(I)]$ were rescanned (maximum of 3 rescans), and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting was 2 : 1. The diameter of the incident beam collimator was 0.5 mm, and the crystal to detector distance was 400.0 mm. Data were collected for reflections $0 \leq h \leq 6$ and $-11 \leq k \leq 11$, $-11 \leq l \leq 11$. Of the 8134 reflections which were collected, 2260 were unique ($R_{int} = 0.129$). Equivalent reflections were merged. The intensities of three representative reflections which were measured after every 300 reflections remained constant throughout data collection. The linear absorption coefficient for MoK_α is 380.2 cm^{-1}. An empirical absorption correction, using the program DIFABS (*13*), was applied; it resulted in transmission factors ranging from 0.76 to 1.33. The data were also corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.3945(4) × 10^{-6}).

The structure was solved and refined with the programs from TEXAN crystallographic software package (*14*). The positions of Bi and Sr(1) were determined from direct methods with SHELXS (*15*). The atoms Sr(2), Cl, and O were located from subsequent analyses of difference electron density maps. The final cycle of full-matrix least-square refinement based on $|F|$ for those data having $F_o^2 > 3\sigma(F_o^2)$ with 53 variables (anisotropic thermal parameters on each atom) and 1221 observations resulted in $R = 0.037$ and $R_w = 0.038$. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.04 and -2.91 e$^-$/Å^3 respectively.

The cell dimensions and the Laue symmetry of $BiCa_3O_3Cl_3$ were also determined on the Rigaku AFC6R diffractometer from a clear crystal of $BiCa_3O_3Cl_3$ with dimensions of 0.15 × 0.15 × 0.20 mm. $BiCa_3O_3Cl_3$ is isostructural with $BiSr_3O_3Cl_3$; the cell dimensions obtained are a = 6.383(3) Å, b = 10.803(3) Å, and c = 11.422(3) Å.

Powder X-ray diffraction data for $BiSr_3O_3Cl_3$ and $BiCa_3O_3Cl_3$ were collected on a Siemens D5000 diffractometer with Si as an internal standard. The diffraction pattern of $BiSr_3O_3Cl_3$ compares well to that calculated with the computer program Lazy-pulverix (*16*) based on the results from our single-crystal structure determination. Table I gives the experimental powder diffraction data for $BiSr_3O_3Cl_3$ and $BiCa_3O_3Cl_3$ and the calculated data for $BiSr_3O_3Cl_3$.

The final atomic positions and isotropic thermal parameters are given in Table II, the anisotropic thermal parameters are given in Table III, and selected interatomic distances and angles are listed in Table IV. A labeled drawing of the contents of the unit cell for $BiSr_3O_3Cl_3$ is shown in Fig. 1, and a perspective view along the a axis is shown in Fig. 2.

Discussion

The structure of $BiSr_3O_3Cl_3$ can be described as the stacking of layers arranged in sequence /Cl/Sr–O/Bi–Sr–O–Cl/Sr–O/Cl/. The layers are perpendicular to the b axis as is readily seen in Fig. 2. The layered structure of $BiSr_3O_3Cl_3$ is different from the known Sillén bismuth oxyhalides in several aspects. The structures of the Sillén phases consist of $[M_2O_2]$ layers (M = Pb, Bi, Cd, Ba, Sr) intermixed with either halogen or metal halogen layers. For example, in $PbBiO_2Cl$ (*17*), a single Cl layer is separated by $[M_2O_2]$ layers. In BiOCl (*18*), the layered structure is formed in sequence /Bi_2O_2/Cl/Cl/Bi_2O_2/. In $Ca_{1.25}Bi_{1.5}O_2Cl_3$ (*12*), $[M_2O_2]$ is separated by triple Cl layer with metal ions in the middle Cl layer. Although more complex structures with mixed single and double or triple halogen layers were found, no compound with mixed metal–oxygen–halogen layers has been reported. Such a feature is unique to $BiSr_3O_3Cl_3$ and $BiCa_3O_3Cl_3$. The Cl layer may be viewed as distorted close packed Cl(1) atoms (see Fig. 3). The two sets of Cl(1) atoms with coordinates (x, y, z) and ($-x$, $-y$, $-z$) are not exactly in the same plane, giving an effective thickness of the layer of 0.14 Å. Each Cl atom is surrounded by six neighboring Cl atoms. The intralayer Cl–Cl distance 3.530(5) Å is much shorter than the 3.88 Å observed in BiOCl (*18*) and the 3.956 Å in $PbBiO_2Cl$ (*17*). In fact, it is smaller than twice the Cl$^-$ crystal radius, 3.62 Å (*19*). As shown in Fig. 3, each Sr(1) atom above or under the layer is surrounded by four Cl$^-$ ions forming a C_1 symmetry MX_4 group. However, only three Sr(1)–Cl(1) distances are within the bonding

TABLE I

Indexed X-ray Powder Patterns for $BiSr_3O_3Cl_3$ and $BiCa_3O_3Cl_3$

			$BiSr_3O_3Cl_3$ Calcd.		Obsd.		$BiCa_3O_3Cl_3$			Obsd.	
h	*k*	*l*	*d*	*I*	*d*	*I*	*h*	*k*	*l*	*d*	*I*
0	1	1	8.141	19	8.140	11	0	1	1	7.852	34
1	0	1	5.789	52	5.787	47	1	0	1	5.582	25
0	0	2	5.783	17							
0	2	0	5.731	43	5.737	31	0	2	0	5.404	27
1	1	1	5.167	22	5.166	19	1	1	1	4.956	21
1	1	2	4.087	74	4.085	58	1	0	2	4.239	34
1	2	1	4.073	11			1	1	2	3.968	39
0	3	1	3.628	45	3.629	41	1	2	1	3.882	22
1	2	2	3.477	87	3.476	75	0	1	3	3.595	29
1	0	3	3.340	26	3.339	21	0	3	1	3.425	43
2	1	0	3.210	69	3.208	74	1	2	2	3.348	43
1	1	3	3.206	54							
1	3	1	3.189	15	3.190	18					
0	0	4	2.891	33	2.884	100	2	0	0	3.232	12
1	2	3	2.886	71			1	1	3	3.115	100
1	3	2	2.878	89			2	1	1	2.960	12
0	4	0	2.866	43	2.867	53	0	0	4	2.862	44
2	2	1	2.802	100	2.804	98					
0	3	3	2.714	34	2.713	27	1	2	3	2.801	55
2	0	3	2.526	11	2.524	16	1	3	2	2.755	69
2	1	3	2.467	14	2.466	15	0	4	0	2.705	31
1	4	2	2.397	43	2.398	53	2	2	1	2.675	65
2	2	3	2.311	19	2.311	17	0	3	3	2.619	27
0	1	5	2.267	19	2.265	16	0	2	4	2.529	10
1	0	5	2.186	11	2.184	12	2	3	0	2.390	16
1	4	3	2.175	14	2.175	14	1	2	4	2.347	23
2	1	4	2.148	30	2.147	39	1	4	2	2.283	17
1	1	5	2.147	17			2	0	4	2.131	19
2	4	1	2.138	11	2.133	10	3	0	1	2.092	18
1	5	1	2.131	10	2.133	13	2	4	1	2.031	16
3	0	2	2.080	20	2.081	19	0	3	5	1.932	34
3	2	1	2.045	10	2.045	13	1	3	5	1.852	10
0	3	5	1.979	28	1.978	31	2	3	4	1.833	18
0	6	0	1.910	20	1.912	16	2	5	0	1.793	17
3	1	3	1.903	15	1.903	20	2	2	5	1.760	14
2	5	0	1.891	27	1.892	29	1	6	1	1.714	11
1	5	3	1.890	16			2	0	6	1.635	35
3	3	2	1.827	24	1.827	12					
2	2	5	1.805	30	1.805	20					
3	4	2	1.683	25	1.684	12					
4	0	0	1.672	10	1.672	8					
1	3	6	1.667	15	1.666	14					
1	6	3	1.658	21	1.659	16					
2	5	4	1.582	15	1.583	19					
1	5	5	1.582	12							

TABLE II

POSITIONAL PARAMETERS AND B_{eq} FOR $BiSr_3O_3Cl_3$

Atom	x	y	z	B_{eq}[a]
Bi 4*c*	0.09656(6)	3/4	0.36790(4)	1.03(2)
Sr(1) 8*d*	0.1675(1)	0.57073(7)	−0.39011(8)	1.23(3)
Sr(2) 4*c*	−0.3491(2)	3/4	0.5275(1)	1.48(5)
Cl(1) 8*d*	0.4035(3)	0.9941(2)	0.3581(2)	2.1(1)
Cl(2) 4*c*	0.4124(4)	3/4	0.7701(3)	1.5(1)
O(1) 8*d*	−0.0763(8)	0.8764(6)	0.4478(6)	1.4(3)
O(2) 4*c*	0.291(1)	3/4	0.5062(8)	1.2(3)

[a] $B_{eq} = (8\pi^2/3)\,\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

TABLE IV

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR $BiSr_3O_3Cl_3$

Sr(1)–O(1)	2.404(7)	Bi –O(1)	2.071(6) ×2
–O(1)	2.557(6)	–O(2)	2.062(8)
–O(2)	2.518(5)	–Cl(1)	3.472(3) ×2
–Cl(1)	3.039(3)		
–Cl(1)	3.394(3)	Cl(1)–O(1)	3.632(6)
–Cl(1)	3.023(3)	–O(1)	3.468(7)
–Cl(2)	3.010(2)	–O(2)	3.366(6)
–Cl(2)	3.215(3)		
Sr(2)–O(1)	2.505(6) ×2	Cl(2)–O(1)	3.571(7) ×2
–O(2)	2.419(8)	–O(2)	3.157(10)
–Cl(1)	3.238(3) ×2	–O(2)	3.620(9)
–Cl(1)	3.796(4) ×2		
–Cl(2)	3.227(4)		
–Cl(2)	2.922(3)		

O(1)–Bi–O(1)	88.8(3)	O(1)–Bi–O(2)	90.3(2)
Cl(1)–Bi–Cl(1)	107.4(1)	O(1)–Bi–Cl(1)	77.3(2)
O(1)–Bi–Cl(1)	155.3(2)	O(2)–Bi–Cl(1)	69.7(1)
Cl(1)–Sr(1)–Cl(1)	145.05(3)	Cl(1)–Sr(1)–Cl(1)	87.1(1)
Cl(1)–Sr(1)–Cl(2)	70.9(1)	Cl(1)–Sr(1)–Cl(2)	73.7(1)
Cl(1)–Sr(1)–O(1)	87.4(2)	Cl(1)–Sr(1)–O(1)	131.4(1)
Cl(1)–Sr(1)–O(2)	137.4(2)	Cl(1)–Sr(1)–Cl(1)	66.4(1)
Cl(1)–Sr(1)–Cl(2)	144.0(1)	Cl(1)–Sr(1)–Cl(2)	113.4(1)
Cl(1)–Sr(1)–O(1)	71.1(2)	Cl(1)–Sr(1)–O(1)	73.7(1)
Cl(1)–Sr(1)–O(2)	67.5(2)	Cl(1)–Sr(1)–Cl(2)	132.8(1)
Cl(1)–Sr(1)–Cl(2)	68.4(1)	Cl(1)–Sr(1)–O(1)	90.3(1)
Cl(1)–Sr(1)–O(1)	139.8(1)	Cl(1)–Sr(1)–O(2)	89.1(2)
Cl(2)–Sr(1)–Cl(2)	65.58(3)	Cl(2)–Sr(1)–O(1)	128.1(1)
Cl(2)–Sr(1)–O(1)	79.3(2)	Cl(2)–Sr(1)–O(2)	81.3(2)
Cl(2)–Sr(1)–O(1)	151.8(2)	Cl(2)–Sr(1)–O(1)	126.6(2)
Cl(2)–Sr(1)–O(2)	65.5(2)	O(1)–Sr(1)–O(1)	81.6(2)
O(1)–Sr(1)–O(2)	135.0(2)	O(1)–Sr(1)–O(2)	70.5(2)
Cl(1)–Sr(2)–Cl(1)	129.9(1)	Cl(1)–Sr(2)–Cl(2)	65.76(5)
Cl(1)–Sr(2)–Cl(2)	74.9(1)	Cl(1)–Sr(2)–O(1)	139.1(1)
Cl(1)–Sr(2)–O(1)	73.0(2)	Cl(1)–Sr(2)–O(2)	86.0(1)
Cl(1)–Sr(2)–Cl(2)	65.76(5)	Cl(2)–Sr(2)–Cl(2)	66.38(4)
Cl(1)–Sr(2)–O(1)	132.8(2)	Cl(2)–Sr(2)–O(2)	66.2(2)
Cl(2)–Sr(2)–O(1)	81.9(2)	Cl(2)–Sr(2)–O(2)	132.6(2)
O(1)–Sr(2)–O(1)	70.7(3)	O(1)–Sr(2)–O(2)	133.4(2)

range, the fourth Sr(1)–Cl(1) distance being longer than 3.7 Å. This is very different from the C_{4v} symmetry of the MX_4 group in Sillén's compounds.

The Sr–O layer is formed from the layers of Sr(1) and O(1) atoms with a separation between the Sr(1) layer and the O(1) layer of 0.61 Å. Figure 4 gives the perspective view of this layer. The O(1) atoms in the layer form a close packed arrangement, each O(1) atom being surrounded by six other O(1) atoms generating an irregular hexagon where the shortest O(1)–O(1) distance is 2.90(1) Å. Each Sr(1) atom sits above or under a triangle formed from three O(1) atoms but only bonds to one of them with a Sr(1)–O(1) bond length 2.404(7) Å. Again, this is very different from the $C_{4v}MO_4$ group in Sillén's compounds. Another O(1) atom from the next Sr–O layer, one O(2) atom and two Cl(2) atoms from the mixed Bi–Sr–O–Cl layer, and three Cl(1) atoms from the Cl layer are also coordinated to Sr(1), resulting in an irregular octacoordination polyhedron. The repulsion between $Sr(1)^{2+}$–$Sr(1)^{2+}$ in this layer causes the longer O(1)–O(1) distance [3.24(1) Å] in the O(1) close packed sheet.

The mixed Bi, Sr(2), O(2), and Cl(2) layer is located at $y = 1/4$ and $y = 3/4$. The perspective view of this layer is given in Fig. 5. Within this layer, each Sr(2) atom bonds to two Cl(2) atoms with Sr–Cl distances of 3.227(3) and 2.922(3) Å, as well as one O(2) atom with a Sr–O distance of 2.419(6) Å. This Sr(2) also bonds to two pairs of Cl(1)

TABLE III

ANISOTROPIC THERMAL PARAMETERS ($\times 10^{-3}$ Å^2) FOR THE ATOMS OF $BiSr_3O_3Cl_3$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	12.6(2)	13.2(2)	13.2(2)	0	0.3(2)	0
Sr(1)	16.9(4)	12.8(5)	17.1(4)	−1.6(3)	−2.4(3)	0.7(3)
Sr(2)	10.6(4)	22.5(7)	23.0(7)	0	0.9(4)	0
Cl(1)	28(1)	28(1)	25(1)	−10(1)	−1(1)	5(1)
Cl(2)	16(1)	21(2)	21(2)	0	−2(1)	0
O(1)	15(3)	16(4)	23(4)	0(2)	2(2)	3(3)
O(2)	23(4)	6(5)	18(5)	0	−5(4)	0

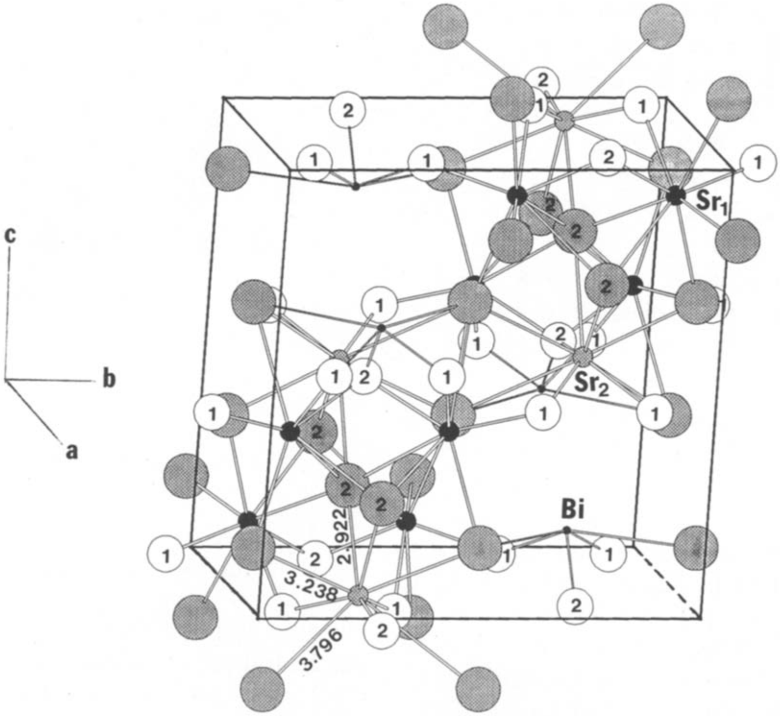

FIG. 1. Unit cell of $BiSr_3O_3Cl_3$. The open circles with numbers are oxygen atoms. The shaded circles without numbers are Cl(1) atoms.

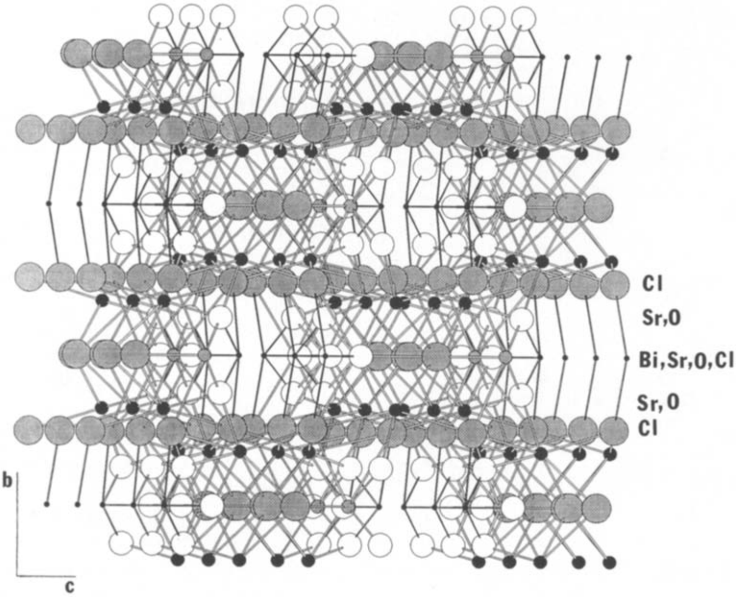

FIG. 2. Perspective view along the *a* axis showing the layered structure.

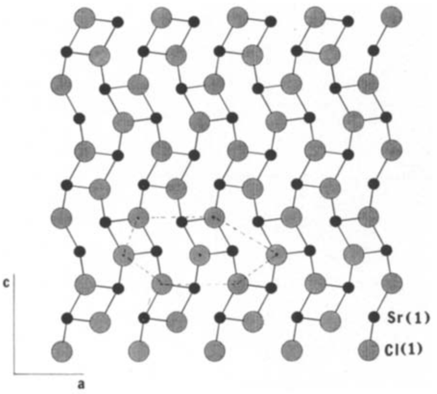

FIG. 3. Distorted close packed Cl layer with Sr(1) atoms from above or beneath this layer.

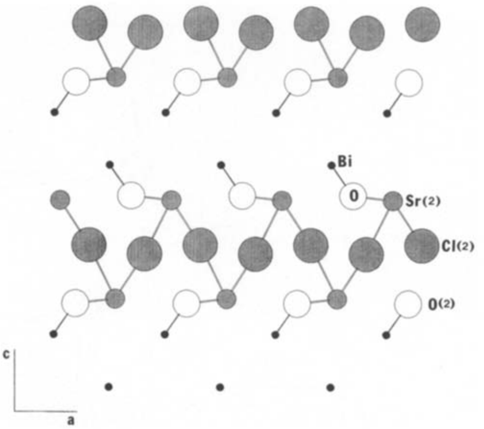

FIG. 5. /Bi–Sr–O–Cl/ mixed layer.

atoms in the two neighboring Cl(1) layers with bond lengths 3.227(4) and 3.796(4) Å, as well as one pair of O(1) atoms in the adjacent Sr–O layers with bond lengths of 2.505(6) Å. Thus, an irregular nonacoordinated polyhedron is formed around Sr(2). Similar to the Sr(2) atom, the Bi atom also bonds to one pair of O(1) atoms and one pair of Cl(1) atoms located in the neighboring layers, but only bonds to one O(2) atom in the layer with Bi–O(2) bond length 2.062(8) Å and finally forms an irregular pentacoordinated polyhedron. A typical lone pair environment for Bi^{III} is readily apparent in Fig. 1.

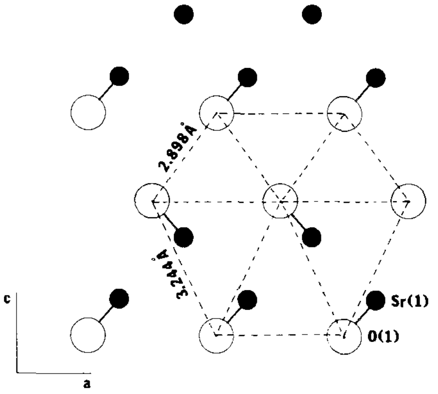

FIG. 4. Sr–O layer showing close packed nature of oxygen.

Both Cl(1) and Cl(2) are in approximate octahedral coordination to the cations. For Cl(1), there are three bonds to Sr(1) of the Sr–O layer, two to Sr(2) of the mixed layer, and one to Bi. For Cl(2), there are two bonds to Sr(1) of the Sr–O layer and four to Sr(2) of the mixed layer. The coordination of both oxygens is approximately tetrahedral: one bond to Bi, one bond to Sr(2), and two bonds to Sr(1).

Acknowledgment

We are grateful to Teledyne Wah Chang, Albany, for support of this work.

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