JOURNAL OF SOLID STATE CHEMISTRY 36, 349–355 (1981)

New Members of a Family of Layered Bismuth Compounds

HIROSHI KODAMA,* FUJIO IZUMI, AND AKITERU WATANABE

National Institute for Researches in Inorganic Materials, 1-1 Namiki, Sakura-Mura, Niihari-Gun, Ibaraki-Ken, 305, Japan

Received June 6, 1980

Two new compounds, $Bi_3Ti_2O_8F$ and $PbBi_3Ti_3O_{11}F$, were prepared and identified by X-ray diffraction analysis. These compounds are members of the family called layered bismuth compounds. Thermal properties of the new compounds were also studied. Besides the preparation and identification of these new compounds, a new method for preparing already known members, Bi_2NbO_5F and $Bi_2TiO_4F_2$, was reported. Moreover, the possibility of the existence of other new members belonging to the family was discussed.

Introduction

A family of layered bismuth compounds is represented by the general formula

$$Bi_2A_{n-1}B_nO_{3n+3}, \qquad (1)$$

where A is K^+, Pb^{2+}, Bi^{3+}, etc.; B is Ti^{4+}, Nb^{5+}, W^{6+}, etc.; and n is an integer (*1, 2*). These compounds are constructed by regular intergrowth of $(Bi_2O_2)^{2+}$ layer and perovskite layer $(A_{n-1}B_nO_{3n+1})^{2-}$. Many compounds belonging to the family have been synthesized by various researchers (*3–6*).

Two new compounds, $Bi_3Ti_2O_8F$ and $PbBi_3Ti_3O_{11}F$, reported in this paper, cannot be described directly by the above-mentioned formula, but are characterized by a slightly modified formula:

$$Bi_2A_{n-1}B_nO_{3n+3-m}F_m, \qquad (2)$$

where F is a fluorine ion, m is an integer (usually 1 or 2), and A, B, and n are the same symbols as used in the original formula. Three members belonging to the family described by the modified formula have already been synthesized by another researcher (*7*). They are Bi_2NbO_5F, Bi_2TaO_5F ($n = 1, m = 1$), and $Bi_2TiO_4F_2$ ($n = 1, m = 2$), corresponding to the simplest case, $n = 1$ above. Thus, the existence of the members characterized by the modified formula suggests the possibility of the formation of other new members.

In the present paper, we report on the preparation and identification of two new compounds, $Bi_3Ti_2O_8F$ and $PbBi_3Ti_3O_{11}F$, and discuss the possibility of the existence of other new members belonging to the family of bismuth oxide fluoride compounds with layer-type structures. Moreover, a new method for preparing Bi_2NbO_5F and $Bi_2TiO_4F_2$ was studied.

Experimental

$Bi_2TiO_4F_2$

Aurivillius (*7*) synthesized this com-

---

* To whom correspondence is to be addressed.

0022-4596/81/030349-07$02.00/0

pound by heating a mixture of BiF_3 and TiO_2 in a molar ratio, 2: 1, in air at 640°C, but the powder photographs obtained from the produced compounds showed that they were not pure but contained BiOF and unknown compounds. In the present work, pure $Bi_2TiO_4F_2$ was prepared by hydrothermal synthesis. A mixture of Bi_2O_3, BiF_3 and TiO_2 in a molar ratio, 2 : 2 : 3, was used as a starting material. It was placed in a platinum capsule with NH_4F solutions and reacted under high temperature and high pressure. The sizes of the platinum capsules were: 4 mm in diameter, 40 mm long (for about 100 mg of starting material) and 5 mm in diameter, 65 mm long (for 600–800 mg of starting material). The experimental apparatus and procedure are reported in detail in another paper (*8*). The experimental conditions of the successful synthesis are given in Table I(a).

The X-ray diffraction data were obtained with a diffractometer using CuKα radiation and an internal standard of high-purity quartz.

The fluorine content of the produced sample was found to be 6.6 wt%, which is in good agreement with the value calculated for $Bi_2TiO_4F_2$ (6.7 wt%).

Methods for Fluorine Analysis

The sample was first decomposed by fusing with $Na_2CO_3 \cdot K_2CO_3$, and were then neutralized with H_2SO_4 solution. The neutralized solution was distilled with water vapor and the distillate was analyzed with absorptiometry by using La-Alizarin Complexone.

Bi_2NbO_5F

This compound was also synthesized by Aurivillius (*7*) by the same method as $Bi_2TiO_4F_2$, but X-ray diffraction data obtained from the compound showed it was not pure. Pure Bi_2NbO_5F was prepared here by the hydrothermal method. A mixture of Bi_2O_3, BiF_3 and Nb_2O_5 in a molar ratio, 5 : 2 : 3, was used as a starting material. Experimental apparatus and procedure were the same as in the synthesis of $Bi_2TiO_4F_2$. The successful experimental conditions are given in Table I(b).

The fluorine content of the obtained sample was found to be 3.1 wt%. This value agrees very well with the calculated one for Bi_2NbO_5F (3.2 wt%).

$Bi_3Ti_2O_8F$

A mixture of Bi_2O_3, BiF_3, and TiO_2 was used as a starting material. It was placed in a platinum capsule. After the air in the dead space had been removed as much as possible, the capsule was sealed and placed in a quartz capsule. After it had

TABLE I

THE SUCCESSFUL EXPERIMENTAL CONDITIONS OF THE SYNTHESIS OF $Bi_2TiO_4F_2$ (a) AND Bi_2NbO_5F (b)

	Concentration mole cm^{-3}	Temperature (°C)	Pressure (kg cm^{-2})	Duration (days)	Weight of sample (mg) / Volume of solution (cm^3)
a	1	396	560	3	802/0.5
	2	400	500	3	601/0.5
	1	500	750	3	104/0.1
	2	500	750	6	807/0.5
b	0.5	402	500	3	102/0.1
	1	400	500	3	605/0.5
	1	402	500	3	802/0.5
	2	402	500	3	108/0.1

been sealed, the double capsule was heated in an electric furnace. The quartz capsule was used for detecting any leak of fluorine or fluoride gas from the platinum capsule, if it occurred, and for decreasing the pressure difference produced by the heating between the interior and exterior of the platinum capsule.

When a mixture of Bi_2O_3, BiF_3, and TiO_2 in a molar ratio, 4 : 1 : 6, was heated, the reaction product was not pure but slightly decomposed $Bi_3Ti_2O_8F$. The formation of the impure compound may be caused by volatilization of BiF_3 and by a reaction with oxygen left in the platinum capsule. The decomposition was prevented by the presence of the excess BiF_3 contained in the starting material. The starting mixture which contained 0.9–3.9 wt% of excess BiF_3 gave good results. That is, the mixture of Bi_2O_3, BiF_3, and TiO_2 in the molar ratio, 4: 1.1–1.4 : 6, was used as starting material. The suitable amount of excess BiF_3 depended on the dead space in the charged platinum capsule. When 200 mg of starting material was charged in the capsule (4 mm o.d., about 50 mm long), it contained 0.9 wt% excess BiF_3, and when about 600 mg of starting material was placed in a platinum capsule (5 mm o.d., about 65 mm long), the mixed excess amount of BiF_3 was 3.9 wt%. The mixture was heated for 8–42 hr at 750°C, after being preheated for 2 hr at 650°C.

X-ray powder diffraction data were obtained by using CuKα radiation and internal standards of high-purity Si and quartz.

$PbBi_3Ti_3O_{11}F$

A mixture of PbO, Bi_2O_3, TiO_2, and BiF_3 in a molar ratio, 3 : 4 : 9 : 1.2–1.4, was used as a starting material. For the same reason as mentioned above, it contained excess BiF_3 (1.5–3 wt%). The experimental procedure was almost the same as for $Bi_3Ti_2O_8F$. The mixture was heated for 6–48 hr at 800°C, after being preheated for 2 hr at 650°C.

Results and Discussion

$Bi_2TiO_4F_2$ and Bi_2NbO_5F

The X-ray diffraction data of these compounds are given in Table II and III, respectively. The dimensions of tetragonal unit cells of the two compounds are given below:

$Bi_2TiO_4F_2$ $a = 3.802$ Å, $c = 16.35$ Å.

Bi_2NbO_5F $a = 3.834$ Å, $c = 16.63$ Å.

These values are almost equal to the results reported by Aurivillius (*7*).

As shown in Table II and III, all the observed peaks are well indexed on the above cells, so the produced compounds are pure in both cases.

$Bi_3Ti_2O_8F$

The X-ray diffraction data are given in Table IV. This compounds is expected to be isostructural with Bi_3TiNbO_9 or Bi_3TiTaO_9 (*4*). Therefore, with the reference of the X-ray diffraction data on Bi_3TiNbO_9, the diffraction peaks of $Bi_3Ti_2O_8F$ were indexed on the basis of a pseudotetragonal cell of $a = 3.818$ Å and $c = 24.97$ Å.

No variation in the size of the unit cell with fluorine content was found, and it therefore seems probable that the composition of the phase is constant and the variation of the F content is due to the presence of small impurities which are not visible in the X-ray diffraction pattern.

The cell parameter and the chemical composition of $Bi_3Ti_2O_8F$ may suggest a structural model similar to that of Bi_3TiNbO_9, as shown in Fig. 1a, where

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR $Bi_2TiO_4F_2$

d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\ k\ l$
8.16	8.18	40	0 0 2	1.624	1.627	24	1 1 8
4.082	4.088	2	0 0 4	1.559	1.559	10	0 2 6
3.708	3.703	11	0 1 1	1.509	1.509	4	2 1 5
3.118	3.118	100	0 1 3	1.391	1.392	1	0 2 8
2.719	2.725	25	0 0 6	1.382	1.382	3	0 1 11
2.691	2.684	28	1 1 0	1.360	1.363	2	0 0 12
2.555	2.554	8	1 1 2	1.345	1.344	3	2 2 0
2.478	2.479	18	0 1 5	1.327	1.326	1	2 2 2
2.247	2.246	9	1 1 4	1.240	1.241	7	1 2 9
2.041	2.044	1	0 0 8	1.236	1.234	3	0 3 3
1.912	1.914	24	1 1 6	1.214	1.215	3	1 1 12
1.903	1.901	16	0 2 0	1.206	1.206	3	2 2 6
1.852	1.852	3	0 2 2	1.204	1.202	3	1 3 0
1.693	1.691	2	1 2 1	1.191	1.190	1	1 3 2
1.636	1.639	17	0 1 9	1.182	1.182	1	0 3 5

Nb is replaced with Ti and a part of O with F. The position of O and F atoms will not be distinguishable from the diffraction data because of the similarity in the reflection power and ionic radii of O^{2-} and F^-.

The replacement of oxygen atoms with fluorine atoms, and of niobium atoms with titanium atoms was correlated with DTA data. When the new phase was heated in air, it decomposed at about 630°C. The compound produced by the

TABLE III

X-RAY POWDER DIFFRACTION DATA FOR Bi_2NbO_5F

d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\ k\ l$
8.34	8.32	26	0 0 2	1.638	1.638	18	2 1 3
3.739	3.736	3	0 1 1	1.576	1.577	11	2 0 6
3.155	3.153	100	1 0 3	1.525	1.524	2	2 1 5
2.774	2.772	36	0 0 6	1.407	1.406 1.409		1 0 11 2 0 8
2.712	2.711	25	1 1 0	1.387	1.386	3	0 0 12
2.578	2.578	4	1 1 2	1.356	1.356	2	2 2 0
2.513	2.512	12	1 0 5	1.339	1.338	<1	2 2 2
2.272	2.271	3	1 1 4	1.257	1.256 1.257	7	2 0 10 2 1 9
2.080	2.079	1	0 0 8	1.246	1.245	3	3 0 3
1.940	1.938	22	1 1 6	1.234	1.234	2	1 1 12
1.918	1.917	16	2 0 0	1.218	1.218	3	2 2 6
1.868	1.868	2	2 0 2	1.215	1.213	2	1 0 13
1.706	1.706	<1	1 2 1	1.213	1.212	3	3 1 0
1.665	1.665	16	1 0 9 0 0 10	1.134	1.135	2	2 2 8
1.649	1.650	3	1 1 8				

TABLE IV

X-RAY POWDER DIFFRACTION DATA FOR $Bi_3Ti_2O_8F$

d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\,k\,l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\,k\,l$
12.52	12.49	22	0 0 2	2.265	2.265	15	1 1 6
6.23	6.24	58	0 0 4	2.242	2.244	4	0 1 9
4.15	4.16	11	0 0 6	2.083	2.081	<1	0 0 12
3.776	3.774	15	0 1 1	2.040	2.042	3	1 1 8
3.464	3.470	4	0 1 3	1.910	1.909	9	0 2 0
3.359	—	7	—	1.831	1.833	18	1 1 10
3.120	3.121	14	0 0 8	1.782	1.784	<1	0 0 14
3.033	3.033	100	0 1 5	1.715	1.716	8	0 1 13
2.702	2.700	39	1 1 0	1.649	1.648	2	1 1 12
2.609	2.606	7	0 1 7	1.615	1.616	17	2 1 5
2.497	2.497	31	0 0 10				

decomposition was mainly $Bi_4Ti_3O_{12}$ ($n = 3$). When the heating was carried out in dry Ar gas, decomposition temperature rose to about 850°C. These results indicate that the former decomposition might proceed with the replacement of fluorine atoms with oxygen atoms, and the latter decomposition with the volatilization of bismuth or titanium fluoride. In both cases, the decomposed compounds consisted only of bismuth and titanium oxides. From formula (1), it is clear that $Bi_4Ti_3O_{12}$ is the only layered bismuth compound which consists of these two oxides.

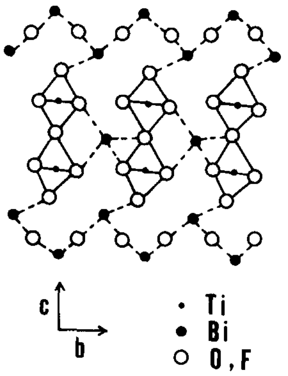

FIG. 1a. A section of the proposed structure of $Bi_3Ti_2O_8F$.

$PbBi_3Ti_3O_{11}F$

The X-ray diffraction data are given in Table V. This compound is expected to be isostructural with $PbBi_3Ti_2NbO_{12}$ (*9*). As the X-ray diffraction data already reported on it are not enough, the data on $PbBi_3Ti_2NbO_{12}$ were obtained here. With the help of the data, the diffraction peaks of $PbBi_3Ti_3O_{11}F$ were indexed on the basis of a pseudotetragonal cell of $a = 3.833$ Å and $c = 33.62$ Å. The cell parameters and the chemical composition of the new com-

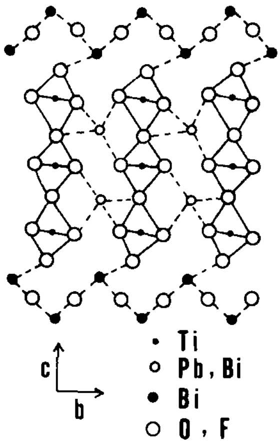

FIG. 1b. A section of the proposed structure of $PbBi_3Ti_3O_{11}F$.

TABLE V

X-RAY POWDER DIFFRACTION DATA FOR $PbBi_3Ti_3O_{11}F$

d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\ k\ l$
16.91	16.81	4	0 0 2	1.936	1.935	4	0 1 15
8.40	8.41	21	0 0 4	1.920	1.917	6	2 0 0
5.59	5.60	100	0 0 6	1.868	1.869 1.868	4	2 0 4 0 0 18
4.197	4.203	62	0 0 8	1.813	1.813	0	2 0 6
3.812	3.808	7	0 1 1	1.797	1.797	24	1 1 14
3.629	3.627	1	0 1 3	1.758	1.758	8	1 0 17
3.367	3.362	12	0 0 10	1.744	1.744	2	2 0 8
2.331	2.330	2	1 0 5	1.712	1.712	2	1 2 1
2.994	2.996	46	1 0 7	1.681	1.681	3	0 0 20
2.803	2.802	11	0 0 12	1.614	1.614	8	1 2 7
2.713	2.710	12	1 1 0	1.528	1.528	5	0 0 22
2.441	2.440	2	1 1 6	1.498	1.498	3	2 0 14
2.402	2.401	66	0 0 14	1.495	1.495	6	1 2 11
2.279	2.278	9	1 1 8	1.477	1.477	14	1 0 21
2.146	2.144	4	1 0 13	1.429	1.429	2	1 2 13 1 1 20
2.103	2.101	7	0 0 16	1.401	1.401	6	0 0 24
1.949	1.948	<1	1 1 12	1.356	1.355	3	2 2 0

pound suggest a structural model similar to $PbBi_3Ti_2NbO_{12}$, as shown in Fig. 1b.

When this new compound was heated in air at 900°C, it decomposed into a mixture mostly of $PbBi_4Ti_4O_{15}$ ($n = 4$) and $Pb_2Bi_4Ti_5O_{18}$ ($n = 5$). This is consistent with the results of the X-ray diffraction analysis that the composition of the new phase is $PbBi_3Ti_3O_{11}F$; because the compounds produced by the decomposition of it consist of lead, bismuth, and titanium oxides. Only $PbBi_4Ti_4O_{15}$ and $Pb_2Bi_4Ti_5O_{18}$ are known as the preparable layered bismuth oxide compounds from them. It was confirmed by chemical analysis that the fluroine content of the decomposed compounds was negligible (0.015 wt%).

Two types of substitution are possible in the layered bismuth oxide compounds: (1) replacement of cations, (2) replacement of anions. While the cation substitution in perovskite-like layers or bismuth oxide layers has been investigated by various researchers (*10–15*), anion substitution has not been discussed.

From the similarity of ionic radii and cation coordination, the most probable anion substitution will be fluorine for oxygen. The present successful experiments to synthesize $Bi_3Ti_2O_8F$ and $PbBi_3Ti_3O_{11}F$ proved that this substitution could be carried out easily. These compounds are members of the family represented by formula (2), so the synthesis of many other members of the family will be probable: e.g., $CaBi_2TiNbO_8F$ ($n = 2$, $m = 1$), $CaBi_2Ti_2O_7F_2$ ($n = 2$, $m = 2$), $BaBi_3Ti_3O_{11}F$ ($n = 3$, $m = 1$), $SrBi_3Ti_3O_{11}F$ ($n = 3$, $m = 1$).

In the discussion of cation substitution, the concepts of the tolerance factor in the perovskite-like layer (*5, 6, 12*) and dimensional mismatch between the perovskite-like layer and bismuth oxide layer (*13, 15*) were introduced. Anion radii are used in the calculation of the parameters in the tolerance factor. The values of the tolerance factor of layered bismuth oxide fluoride will be different from those of the layered bismuth oxides, and new cation substitutions, not tolerated in the layered bismuth oxides, may occur in the layered bismuth oxide fluorides.

References

1. B. Aurivillius, *Ark. Kemi* **2,** 519 (1950).
2. E. C. Subbarao, *J. Phys. Chem. Solids* **23,** 665 (1962).
3. B. Aurivillius, *Ark. Kemi* **1,** 499 (1949).
4. B. Aurivillius, *Ark. Kemi* **1,** 463 (1949).
5. G. A. Smolenskii, V. A. Isupov, and A. I. Agranovskaya, *Fiz. Tverd. Tela,* **3,** 895 (1961) [*Sov. Phys. Solid State* **3,** 651 (1961)].
6. E. C. Subbarao, *J. Amer. Ceram. Soc.* **45,** 166 (1962).
7. B. Aurivillius, *Ark. Kemi,* **5,** 39 (1952).
8. H. Kodama and F. Izumi, *J. Cryst. Growth* **50,** 515 (1980).
9. L. E. Cross, "Ferroelectricity and conduction in ferroelectric crystals," Technical Report AFAL-TR72-146 (1972).
10. T. Kikuchi, *J. Less-Common Met.* **48,** 319 (1976).
11. T. Kikuchi, A. Watanabe, and K. Uchida, *Mater. Res. Bull.* **12,** 299 (1977).
12. I. G. Izumailzale, V. I. Nesterenko, F. A. Mirishi, and P. G. Rustamov, *Sov. Phys. Crystallogr.* **12,** 400 (1967).
13. R. A. Armstrong and R. E. Newnham, *Mater. Res. Bull.* **7,** 1025 (1972).
14. R. W. Wolfe and R. E. Newnham, J. Electrochem. Soc. **116,** 832 (1969).
15. T. Kikuchi, *Mater. Res. Bull.* **14,** 1561 (1979).