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Synthesis of New Layered-Type and New Mixed-Layered-Type Bismuth Compounds

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Four new compounds, $PbBi_2TiTaO_8F$, $PbBi_2TiNbO_8F$, $Bi_5Ti_2WO_{14}F$, and $Bi_7Ti_5O_{20}F$, were prepared and identified by X-ray diffraction analysis. Two of them are new members of a family called layered bismuth compounds. The other two are new members of a family called mixed-layered bismuth compounds. Thermal properties of the new compounds were studied. Moreover, the possibility of the existence of other new members belonging to the family called mixed-layered bismuth compounds is discussed.

Introduction

Many compounds called layered bismuth compounds have been synthesized by various researchers (*1–4*). They are members of the family 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 from 1 to 6 (*5–7*).

Later, similar compounds called mixed-layered-type bismuth compounds were synthesized (*8, 9*). They are members of the family represented by the general formula

$$Bi_4A_{2n-1}B_{2n+1}O_{6n+9}, \qquad (2)$$

where A and B are the same symbols as used in formula (1) and n is an integer from 1 to 3.

Recently, two new compounds, $Bi_3Ti_2O_8F$ and $PbBi_3Ti_3O_{11}F$, were reported (*10*) which belonged structurally to the family represented by formula (1). However, they cannot be described directly by formula (1), but are characterized by a slightly modified formula,

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

where F is a fluorine ion, m is an integer, 1 or 2, and all the other symbols are the same as those used in formula (1).

In the present paper, we report the preparation and identification of four new compounds, $PbBi_2TiTaO_8F$, $PbBi_2TiNbO_8F$, $Bi_5Ti_2WO_{14}F$, and $Bi_7Ti_5O_{20}F$. The first two are new members belonging to the family represented by formula (3). The other two compounds have the mixed-layered-type structure with partial substitution of oxygen atoms with fluorine atoms. However, these phases cannot be described directly by formula (2), but are characterized by a slightly modified formula,

$$Bi_4A_{2n-1}B_{2n+1}O_{6n+9-m}F_m, \qquad (4)$$

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where all the symbols are the same as those used in formula (3). That is, $Bi_5Ti_2WO_{14}F$ ($n = 1, m = 1$) and $Bi_7Ti_5O_{20}F$ ($n = 2, m = 1$) are the first compounds synthesized as members belonging to the family represented by formula (4).

Experimental

$PbBi_2TiNbO_8F$. A mixture of Bi_2O_3, BiF_3, PbO, TiO_2, and Nb_2O_5 was used as a starting material. About 200 mg of starting material was charged in a platinum capsule (4 mm o.d., about 50 mm long). Sometimes about 600 mg of starting material was charged in a platinum capsule (5 mm o.d., about 70 mm long). After the air in the dead space was displaced, the platinum capsule was sealed in a quartz capsule. The double capsule was heated for 16–40 hr at 750°C after being preheated for 2 hr at 650°C. This experimental procedure is similar to that described before (*10*).

A mixture of Bi_2O_3, BiF_3, PbO, TiO_2, and Nb_2O_5 in a molar ratio, 5:2:6:6:3, was first used as the starting materials. The following balanced equation might be written:

$$5Bi_2O_5 + 2BiF_3 + 6PbO + 6TiO_2 + 3Nb_2O_5 \rightarrow 6PbBi_2TiNbO_8F.$$

However, the product was not pure. The formation of impure products may be caused by volatilization of BiF_3, or by a reaction with oxygen remaining in the platinum capsule. This was prevented by the addition of excess BiF_3. About 0.9 wt% of excess BiF_3 mixed with the starting material promoted the formation of a pure product.

$PbBi_2TiTaO_8F$. A mixture of Bi_2O_3, BiF_3, PbO, TiO_2, and Ta_2O_5 in a molar ratio, 5:2.1:6:6:3, was used as the starting material. For the same reason as mentioned above, the mixture contained excess BiF_3 (about 0.4 wt%). The reactants charged in a platinum capsule was heated for 20–48 hr at 750°C after being preheated for 2 hr at 650°C.

$Bi_5Ti_2WO_{14}F$. A mixture of Bi_2O_3, BiF_3, TiO_2, and WO_3 in a molar ratio, 7:1:6:3, was used as the starting material. The following equation might be written:

$$7Bi_2O_3 + BiF_3 + 6TiO_2 + 3WO_3 \rightarrow 3Bi_5Ti_2WO_{14}F.$$

The mixture, charged in a platinum capsule, was heated for 20–60 hr at 800°C, sometimes after being preheated for 10 hr at 700°C. The reaction products were almost pure $Bi_5Ti_2WO_{14}F$, although they contained a trace of impurity. Addition of excess BiF_3 did not improve the result, in contrast to the other procedures.

$Bi_7Ti_5O_{20}F$. A mixture of Bi_2O_3, TiO_2, and BiF_3 in a molar ratio, 10:15:1, was used as the starting material. The following equation might be written:

$$10Bi_2O_3 + 15TiO_2 + BiF_3 \rightarrow 3Bi_7Ti_5O_{20}F. \quad (5)$$

However, the reaction product was not $Bi_7Ti_5O_{20}F$ but $Bi_4Ti_3O_{12}$. As already described, the presence of excess BiF_3 in the starting material can prevent the formation of impure products. In the present case, about 2 wt% of excess BiF_3 mixed in the starting material promoted the formation of $Bi_7Ti_5O_{20}F$, which was nearly pure.

In addition to the chemical equation (5), we can write

$$Bi_4Ti_3O_{12} + Bi_3Ti_2O_8F \rightarrow Bi_7Ti_5O_{20}F, \quad (6)$$

$$2Bi_4Ti_3O_{12} + BiF_3 \rightarrow 3Bi_3Ti_2O_8F. \quad (7)$$

From the above equations, the following reaction can be proposed:

$$5Bi_4Ti_3O_{12} + BiF_3 \rightarrow 3Bi_7Ti_5O_{20}F. \quad (8)$$

Therefore, a deficiency of BiF_3 could promote the formation of $Bi_4Ti_3O_{12}$.

A small excess of Bi_2O_3, in addition to a 2 wt% of excess BiF_3, was placed in the starting material. When the starting mixture, charge in a platinum capsule, was heated for about 20 hr at 800°C after being preheated for 2 hr at 650°C, the reaction product was pure $Bi_7Ti_5O_{20}F$. The optimum amount of excess Bi_2O_3 was 2–3 wt% of the starting material. This may be explained by the reaction

$$BiF_3 + Bi_2O_3 \rightarrow 3BiOF. \qquad (9)$$

That is, the shift of a composition of a starting mixture from a stoichiometric composition may be caused not only by the volatilization of BiF_3 but also by the removal of BiOF.

The X-ray diffraction data for $PbBi_2TiNbO_8F$ and $PbBi_2TiTaO_8F$ were obtained with a diffractometer using Cu*K*α radiation and an internal standard of high-purity quartz, whereas with $Bi_5Ti_2WO_{14}F$ and $Bi_7Ti_5O_{20}F$ high-purity silicon was used as the internal standard.

The thermal properties of these compounds were studied by differential thermal analysis (DTA). The temperature accuracy of the apparatus was ±2°C.

Results and Discussion

$PbBi_2TiNbO_8F$ and $PbBi_2TiTaO_8F$

The X-ray diffraction data for these compounds are given in Tables I and II, respectively. These compounds are expected to be isostructural with $PbBi_2Nb_2O_9$ or $PbBi_2Ta_2O_9$ (*2, 4*). Therefore, the diffraction peaks of $PbBi_2TiNbO_8F$ and $PbBi_2TiTaO_8F$ were indexed on the basis of the previously reported pseudotetragonal cells. Their unit cell parameters are as follows:

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR $PbBi_2TiNbO_8F$

d_{obs} (Å)	d_{calc} (Å)	I_{obs}	*h k l*	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	*h k l*
12.66	12.76	5	0 0 2	2.119	2.126	1	0 0 12
7.03	—	1	—	1.928	1.928	1	2 0 0
6.35	6.38	63	0 0 4	1.860	1.863	1	1 1 10
4.235	4.252	8	0 0 6	1.745	1.749	1	1 0 13
3.815	3.812	1	1 0 1	1.633	1.634	1	1 2 5
3.518	3.512	1	1 0 3	1.590	1.594	1	0 0 16
3.178	3.189	15	0 0 8	1.552	1.556	2	1 0 15
3.075	3.076	9	1 0 5	1.537	1.538	1	2 0 10
2.727	2.727	1	1 1 0	1.272	1.271	6	3 0 3
2.648	2.649	1	1 0 7	1.247	1.246	1	3 0 5
2.550	2.551	100	0 0 10	1.209	1.211	1	2 1 15
2.295	2.295	1	1 1 6	1.155	1.155	1	1 1 20
2.281	2.284	1	1 0 9	1.100	1.100	1	1 3 10

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR $PbBi_2TiTaO_8F$

d_{obs} (Å)	d_{calc} (Å)	I_{obs}	*h k l*	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	*h k l*
12.64	12.64	3	0 0 2	2.617	2.634	15	1 0 7
9.48	—	5	—	2.529	2.529	100	0 0 10
7.00	—	2	—	2.403	—	2	—
6.32	6.32	69	0 0 4	2.287	2.286	3	1 1 6
6.04	—	2	—	2.270	2.270	6	1 0 9
4.21	4.21	2	0 0 6	2.109	2.108	4	0 0 12
3.803	3.805	2	1 0 1	2.062	2.063	2	1 1 8
3.498	3.501	2	1 0 3	1.924	1.925	7	2 0 0
3.422	—	3	—	1.853	1.853	24	1 1 10
3.269	—	2	—	1.806	1.806	7	0 0 14
3.236	—	3	—	1.735	1.736	5	1 0 13
3.160	3.161	21	0 0 8	1.644	1.644	1	2 0 8
3.063	3.063	62	1 0 5	1.629	1.630	10	1 2 5
3.022	—	44	—	1.578	1.581	13	0 0 16
2.800	—	2	—	1.544	1.544	13	1 0 15
2.721	2.722	12	1 1 0	1.531	1.531	5	2 0 10
2.668	2.661	2	1 1 2	1.511	1.505	5	1 1 14

$$PbBi_2TiNbO_8F \quad a = 3.856, \quad c = 25.51 \text{ Å},$$

$$PbBi_2TiTaO_8F \quad a = 3.849, \quad c = 25.29 \text{ Å}.$$

The errors in these figures are estimated to be ±0.1%.

As shown in Table I, almost all the observed peaks are indexed based on the unit cell for $PbBi_2TiNbO_8F$, which indicates that the product is nearly pure.

However, Table II shows that some observed peaks are not indexed based on the unit cell for $PbBi_2TiTaO_8F$, indicating that the product may not be pure. Identification of these unindexed lines was not possible.

No variation in the size of the unit cells with fluorine content was found. The positions of O and F atoms cannot be distinguished from the diffraction data because of the similarity in the reflection power and ionic radii of O^{2-} and F^-.

DTA plots for $PbBi_2TiTaO_8F$ are shown in Fig. 1. When it was heated in dry argon (10°C min^{-1}) to about 700°C, an endothermic peak was observed at 530°C. In the cooling process, an exothermic peak was observed at 528°C. No structural changes were observed on the sample after the DTA experiment. This suggests that $PbBi_2TiTaO_8F$ transforms reversibly at about 529°C.

When $PbBi_2TiTaO_8F$ was heated in air, it decomposed quite easily below 580°C. The decomposition products were not oxides with layered-type structures.

DTA for $PbBi_2TiNbO_8F$ was carried out from room temperature to 700°C in dry argon, but no thermal effects were observed. When the DTA was carried out in air, $PbBi_2TiNbO_8F$ decomposed below 700°C.

$Bi_5Ti_2WO_{14}F$ and $Bi_7Ti_5O_{20}F$

The X-ray diffraction data for these compounds are given in Tables III and IV. $Bi_5Ti_2WO_{14}F$ and $Bi_7Ti_5O_{20}F$ are expected to be isostructural with $Bi_5TiNbWO_{15}$ and $Bi_7Ti_4NbO_{21}$, respectively (9). The diffraction peaks of $Bi_5Ti_2WO_{14}F$ and $Bi_7Ti_5O_{20}F$ were therefore indexed on the basis of published pseudotetragonal cells, the dimensions of which are as follows:

$Bi_5Ti_2WO_{14}F$ $a = 3.809$, $c = 20.69$ Å,

$Bi_7Ti_5O_{20}F$ $a = 3.828$, $c = 28,91$ Å.

The errors in these figures are estimated to be ±0.1%.

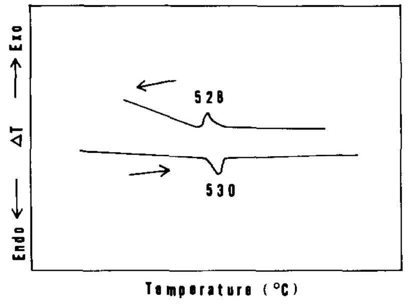

FIG. 1. Differential heating and cooling plots for $PbBi_2TiTaO_8F$ in dry argon.

TABLE III

X-RAY POWDER DIFFRACTION DATA FOR $Bi_5Ti_2WO_{14}F$

d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\ k\ l$
10.30	10.35	6	0 0 2	2.336	2.335	1	1 0 7
6.90	6.90	47	0 0 3	2.299	2.299	5	0 0 9
6.22	—	2	—	2.258	2.257	2	1 1 5
5.17	5.17	16	0 0 4	2.139	2.140	1	1 0 8
4.14	4.14	6	0 0 5	2.071	2.069	1	0 0 10
3.807	3.809	1	1 0 0	1.989	1.991	1	1 1 7
3.760	3.746	1	1 0 1	1.970	1.968	1	1 0 9
3.333	3.334	1	1 0 3	1.905	1.905	5	2 0 0
3.233	—	1	—	1.881	1.881	2	0 0 11
3.068	3.067	7	1 0 4	1.866	1.865	5	1 1 8
3.027	—	4	—	1.828	—	1	—
2.956	2.956	31	0 0 7	1.749	1.749	1	1 1 9
2.867	—	1	—	1.724	1.724	2	0 0 12
2.797	2.802	1	1 0 5	1.685	1.686	5	1 0 11
2.694	2.693	8	1 1 0	1.616	1.618	5	1 2 4
2.589	2.586	100	0 0 8	1.571	1.571	5	1 0 12
2.487	—	2	—	1.534	1.534	2	2 0 8

As shown in Tables III and IV, almost all the observed peaks are indexed on the above cells, which indicates that the products are quite pure. No variation in the size of unit cells with fluorine content was found.

The pattern for $Bi_7Ti_5O_{20}F$ (Table IV) contains many strong (001) reflections. Even though the sample was ground well prior to the X-ray experiment, the pattern had the same tendency. This is caused by the preferred orientation of (001) planes.

DTA plots observed for $Bi_7Ti_5O_{20}F$ are

TABLE IV

X-RAY POWDER DIFFRACTION DATA FOR $Bi_7Ti_5O_{20}F$

d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\ k\ l$
14.39	14.46	10	0 0 2	3.213	3.212	15	0 0 9
9.62	9.64	11	0 0 3	2.999	2.997	15	1 0 6
7.22	7.23	20	0 0 4	2.892	2.891	6	0 0 10
6.39	—	1	—	2.709	2.707	3	1 1 0
5.78	5.78	100	0 0 5	2.628	2.628	10	0 0 11 1 0 8
4.817	4.818	7	0 0 6	2.410	2.409	51	0 0 12
4.571	—	1	—	2.264	2.264	2	1 1 7
4.129	4.130	62	0 0 7	2.225	2.224	6	0 0 13
3.800	3.795	2	1 0 1	2.064	2.065	3	0 0 14
3.333	—	2	—				

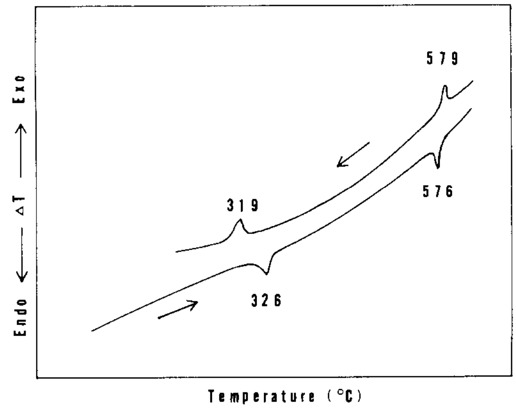

FIG. 2. Differential heating and cooling plots for $Bi_7Ti_5O_{20}F$ in dry argon.

shown in Fig. 2. When heated in dry argon or in air below 700°C, two endothermic peaks were observed at 326 and 576°C. In the cooling process, two exothermic peaks were observed at 579 and 319°C. After the DTA experiments, an X-ray powder diffraction pattern on the materials did not show any structural changes. This suggests that $Bi_7Ti_5O_{20}F$ transforms reversibly at about 322 and 577°C.

Even if starting materials are left in the products without reacting, there will not be the possibility in the DTA experiments that the observed endotherms cannot be caused by the impurities. This is because, judging from the reported data (*11–14*), the compounds such as PbO, Bi_2O_3, Ta_2O_5, and TiO_2 do not have their transformation temperatures near 322, 529, and 577°C. Besides, BiF_3 does not show an endothermic change in the heating process to 700°C, which was confirmed by the present authors.

While heating in air at 900°C for 12 hr, $Bi_7Ti_5O_{20}F$ decomposed into $Bi_4Ti_3O_{12}$ and α-Bi_2O_3.

In the case of $Bi_5Ti_2WO_{14}F$, no transformations were observed by the DTA experiments, which was carried out from room temperature to 700°C in dry argon and in air.

As previously reported (*10*), two types of substitutions are possible for the layered bismuth oxide compounds: One is the substitution of cations, the other is the substitution of anions. The latter has been shown by the successful synthesis of $Bi_3Ti_2O_8F$, $PbBi_3Ti_3O_{11}F$ (*10*), $PbBi_2TiNbO_8F$, $PbBi_2TiTaO_8F$, $Bi_5Ti_2WO_{14}F$, and $Bi_7Ti_5O_{20}F$. The last two compounds are noteworthy because they are new members of the family which have mixed-layered-type structure with the substitution of some of the oxygen atoms with fluorine atoms. With the successful synthesis of $Bi_5Ti_2WO_{14}F$ and $Bi_7Ti_5O_{20}F$, we can expect many other new compounds which may have the mixed-layered-type structure: e.g., $Bi_5TiNb_2O_{14}F$, $SrBi_6Ti_4NbO_{20}F$, and $BaBi_6Ti_4NbO_{20}F$.

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