JOURNAL OF SOLID STATE CHEMISTRY 67, 170–175 (1987)

Synthesis of a New Bismuth Oxide Fluoride with the γ-Bi_2O_3 Structure Type

HIROSHI KODAMA,* AKITERU WATANABE,
AND YOSHIYUKI YAJIMA

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

Received April 11, 1986; in revised form June 30, 1986

A new bismuth compound with the γ-Bi_2O_3 structure type has been synthesized by a hydrothermal method. The experimental results show that only the solution or starting materials which contain fluorine ions are effectual for the synthesis of the compound. Chemical analysis proved that the new compound contains a small amount of fluorine. We comment the stabilization of the γ-form by partial replacement of oxygen atoms with fluorine atoms and assume $Bi_{26}O_{38}F_2$ as its constitution. The measured dimension of the unit cell is 10.183(2) Å. Its thermal stability is also studied by differential thermal analysis. © 1987 Academic Press, Inc.

Introduction

The polymorphism of Bi_2O_3 has been investigated by many researchers, and four polymorphs have been reported (*1–8*). Two of them are known as thermodynamically stable phases: The monoclinic α phase is stable from room temperature to 729°C and the cubic δ phase is stable from 729°C up to its melting point at 824°C. On cooling of the δ phase, formation of intermediate metastable phases near 650°C has been reported. These are the tetragonal β phase at 650°C and the body-centered cubic (bcc) γ-phase (sillenite (*9*)) at 639°C (*8*). However, reported data on the behavior of metastable Bi_2O_3 polymorphs on cooling are inconsistent and incomplete.

Contaminated bcc Bi_2O_3 was first reported by Sillen (*1*) and pure γ-Bi_2O_3 was first prepared by Schumb and Rittner (*2*) by controlled cooling of β-Bi_2O_3 from 750–800°C. The existence of pure γ-Bi_2O_3 was later confirmed by Aurivillius and Sillen (*3*), Levin and Roth (*7*), and Harwig and Gerards (*8*). Moreover, a number of investigators have reported that the impure bcc phase formed by contamination with porcelain, Si, Fe, Al, or other impurities. In particular, Levin and Roth (*10*) have studied in detail the effect of small oxide additions on the polymorphism of Bi_2O_3.

In the present paper, we report the preparation of a new bismuth compound with the γ-Bi_2O_3 structure type. This compound was not prepared by cooling of δ-Bi_2O_3 or addition of extraneous cations but rather by replacement of some of the oxygen atoms in bismuth oxide with fluorine atoms. In addition, the thermal stability of this compound was studied by differential thermal analysis (DTA).

---

* To whom correspondence should be addressed.

0022-4596/87 $3.00

TABLE I

REACTION PRODUCTS OF α-Bi_2O_3 HEATED IN KF SOLUTIONS[a]

Concentration (moles dm^{-3})	Products
1.25	α-$Bi_2O_3 \gg \gamma$-Bi_2O_3[b]
1.5	γ-Bi_2O_3 + trace α-Bi_2O_3
1.5	γ-Bi_2O_3
1.75	α-$Bi_2O_3 > \gamma$-Bi_2O_3
2.5	α-Bi_2O_3 + trace γ-Bi_2O_3

[a] Temperature: 350°C, pressure: 600 kg cm^{-2}, heating time: 3 days.

[b] γ-Bi_2O_3 represents the compound with the γ-Bi_2O_3 structure type.

Experimental and Results

The compound was synthesized by a hydrothermal method. The apparatus used has been described in a previous paper *(11)*. The α form of Bi_2O_3 was used as a starting material. It was charged in a platinum capsule (4 or 5 mm outer diameter and 50 or 70 mm long) with a solvent. The platinum capsule was carefully sealed by welding and set in a reaction vessel. After the vessel had been sealed and pumped to the desired pressure, it was set within an electrically heated furnace. Temperatures were measured with a chromel-alumel thermocouple inserted into the vessel. The experimental error was a maximum of ±10°C. After a heating run, the reaction products were quenched by rapid immersion of the pressure vessel in water. The products were identified by their X-ray powder diffraction (XRPD) patterns.

In hydrothermal synthesis, the first problem is to find effectual solvents. In the present study, the effectiveness of various acidic or basic solutions was examined experimentally, and it was ascertained that only the solutions containing fluorine ions were useful for the synthesis of bcc Bi_2O_3. Among them, potassium fluoride and ammonium fluoride solutions gave good results.

Table I shows experimental conditions and results, where a potassium fluoride solution was used as a solvent. These results suggest that the concentration of the KF solution is one of the important factors in transforming the starting material (α-Bi_2O_3) into the compound with the γ-Bi_2O_3 structure. The 1.5-mole dm^{-3} KF solution gave the best results. At the concentrations lower than this, only a part of α-Bi_2O_3 changed into the sillenite-like phase. On the other hand, at the higher concentrations, single crystals of α-Bi_2O_3 formed.

Table II shows experimental conditions and results when ammonium fluoride solution was used as a solvent. In this case, 0.5–0.75 mole dm^{-3}, concentrations different from those used in the above experiments, were the best for synthesis of the sillenite-like phase. At the concentrations lower than this, only a part of α-Bi_2O_3 changed into the sillenite-like phase, and at the higher concentrations, the major product was BiOF.

These two results suggest that the synthetic compound with the sillenite structure

TABLE II

REACTION PRODUCTS OF α-Bi_2O_3 HEATED IN NH_4F SOLUTIONS[a]

Concentration (moles dm^{-3})	Products
0 (pure H_2O)	α-Bi_2O_3
0.1	α-$Bi_2O_3 > \gamma$-Bi_2O_3[b]
0.25	α-$Bi_2O_3 + \gamma$-Bi_2O_3
0.5	γ-Bi_2O_3
0.75	γ-Bi_2O_3
1	γ-$Bi_2O_3 > Bi_7O_9F_3$
2	BiOF $> \gamma$-Bi_2O_3
4	BiOF

[a] Temperature: 350°C, pressure: 600 kg cm^{-2}, heating time: 3 days.

[b] γ-Bi_2O_3 represents the compound with the γ-Bi_2O_3 structure type.

TABLE III

REACTION PRODUCTS OF THE MIXTURE $38Bi_2O_3$ + $2BiF_3$ HEATED IN NH_4F SOLUTIONS[a]

Concentration (moles dm^{-3})	Products
0 (pure H_2O)	γ-Bi_2O_3[b] $\gg$ unidentified phases
0.1	γ-Bi_2O_3 + trace unidentified phases
0.1	γ-Bi_2O_3
0.5	γ-Bi_2O_3 $\gg$ $Bi_7O_9O_3$
1.0	γ-Bi_2O_3 $\gg$ BiOF

[a] Temperature: 450°C, pressure: 1500 kg cm^{-2}, heating time: 3 days.

[b] γ-Bi_2O_3 represents the compound with the γ-Bi_2O_3 structure type.

is not pure bismuth oxide but contains F atoms as an essential constituent. To confirm this, a chemical analysis was performed, and the fluorine content was found to be 1.1 ± 0.1 wt%. The method of fluorine analysis is same as that described in a previous paper (*12*).

The starting materials are another potential source of fluorine. Therefore, formation of the sillenite-like phase is to be expected when fluorine is contained in the starting materials, and not in the solvent. To confirm this, additional hydrothermal experiments were carried out. The experimental results are shown in Table III, where a mixture of α-Bi_2O_3 and BiF_3 in a 38:2 molar ratio was used as a starting material. The reason for choosing this particular ratio will be explained in the next section. In the first experiment, pure water was used as a solvent. The result shows that the major reaction product was the compound with the γ-Bi_2O_3 structure type. This suggests that the sillenite-like phase is stabilized by the fluorine atoms present in starting material. Moreover, when this starting material was reacted in 0.1-mole dm^{-3} NH_4F solution, the yield of the sillenite-like phase was increased. This suggests that a small amount of excess fluorine is necessary to compensate for its loss into solution. Therefore, The experiments for determining the optimum ratio were carried out, where H_2O was used as the solvent. Table IV shows the results, where, in all the experiments, the reaction product was the pure sillenite-like phase. These experimental conditions are the best for synthesizing comparatively large amounts of the pure sillenite-like phase with good reproducibility.

An XRPD pattern was obtained from a specimen synthesized under the conditions shown in Table IV. The data (Table V) were

TABLE IV

SUCCESSFUL EXPERIMENTAL CONDITIONS FOR THE HYDROTHERMAL SYNTHESIS OF THE COMPOUND WITH THE γ-Bi_2O_3-TYPE STRUCTURE

Starting materials	Temperature (°C)	Pressure (kg/cm^2)	Weight of sample (mg)/volume of solution (cm^3)
$17Bi_2O_3$ + $2BiF_3$	454	1000	200/0.2
$17Bi_2O_3$ + $2BiF_3$	450	1000	400/0.2
$17Bi_2O_3$ + $2BiF_3$	448	1000	1000/0.5
$17Bi_2O_3$ + $2BiF_3$	350	700	206/0.1
$17Bi_2O_3$ + $2BiF_3$	350	600	808/0.4
$17Bi_2O_3$ + $2BiF_3$	250	540	201/0.1
$17Bi_2O_3$ + $2BiF_3$	150	300	201/0.1
$11Bi_2O_3$ + $2BiF_3$	447	1000	200/0.2
$11Bi_2O_3$ + $2BiF_3$	450	1000	602/0.6

TABLE V

X-RAY POWDER DIFFRACTION DATA FOR $Bi_{26}O_{38}F_2$

d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\ k\ l$
7.18	7.20	3	1 1 0	1.502	1.501	11	6 3 1
5.09	5.09	5	2 0 0	1.469	1.470	2	4 4 4
4.15	4.16	6	2 1 1	1.440	1.440	5	5 5 0
3.60	3.60	26	2 2 0				5 4 3
3.218	3.220	100	3 1 0	1.412	1.412	1	6 4 0
2.940	2.940	20	2 2 2	1.386	1.386	4	5 5 2
2.720	2.722	60	3 2 1				7 2 1
2.543	2.546	2	4 0 0	1.361	1.361	3	6 4 2
2.401	2.400	8	3 3 0	1.336	1.337	1	7 3 0
			4 1 1	1.293	1.293	3	6 5 1
2.277	2.277	10	4 2 0				7 3 2
2.171	2.171	12	3 3 2	1.273	1.273	1	8 0 0
2.080	2.079	5	4 2 2	1.253	1.253	2	8 1 1
1.997	1.997	14	5 1 0				7 4 1
1.860	1.859	7	5 2 1	1.234	1.235	1	6 4 4
1.799	1.800	1	4 4 0				8 2 0
1.746	1.746	29	5 3 0	1.217	1.217	7	6 5 3
			4 3 3	1.200	1.200	6	8 2 2
1.697	1.697	12	6 0 0				6 6 0
			4 4 2	1.184	1.184	6	8 3 1
1.652	1.652	18	5 3 2				7 5 0
			6 1 1				7 4 3
1.572	1.571	3	5 4 1	1.153	1.153	2	7 5 2
1.534	1.535	3	6 2 2	1.138	1.138	1	8 4 0

obtained by using Cu$K\alpha$ radiation and a silicon internal standard. The dimension of bcc unit cell is 10.183 ± 0.002 Å and all the observed peaks are extremely well indexed on this cell.

Various dimensions, such as 10.245 Å (*2*), 10.268(1) Å (*7*, *8*), and 10.184 Å (*13*), have been previously reported for the bcc unit cell of pure γ-Bi_2O_3. The present dimension is almost same as these values.

DTA curves observed for the new phase are shown in Fig. 1. The temperature accuracy of the apparatus was ±2°C. When heated below 700°C in N_2, two endothermic peaks were observed at 529 and 637°C. In the cooling process, two exothermic peaks were observed at 603 and 495°C. The same peaks were observed at the same temperatures in the repeated heating and cooling processes. In the heating and cooling below 600°C in air, only the first peak was observed at the same temperatures (529 and 495°C), as observed in N_2. In both cases, the specimens showed XRPD patterns different from that of the sillenite-like phase after the DTA experiments. The new XRPD patterns showed that the latter had decomposed into a mixture of α-Bi_2O_3 and a bismuth oxide fluoride. The DTA curves did not show the peak corresponding to the decomposition. Only a gentle change of the base line was observed between 400 and 500°C. By isothermal heating, it was ascertained that the decomposition of the sillenite-like phase proceeded quickly and perfectly below (and near) 500°C.

Discussion

Metastable γ-Bi_2O_3 is usually stabilized by the presence of small amounts of other cations. For example, ternary bismuth oxides such as $Bi_{24}Si_2O_{40}$ and $Bi_{24}Ge_2O_{40}$ are known to adopt the same bcc structure as

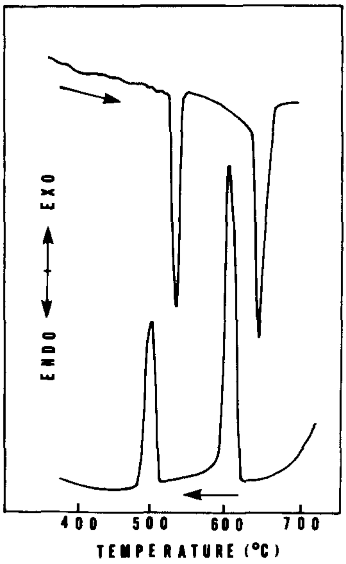

FIG. 1. DTA curves for $Bi_{26}O_{38}F_2$ measured at a rate of 10°C min^{-1} in N_2.

pure γ-Bi_2O_3 (*1, 3, 5, 14*) and it has been proposed that one of the most important ways to stabilize the γ-Bi_2O_3 structure is to create the compound stoichiometry $Bi_{24}M_2O_{40}$, where M represents tetravalent cations.

The unit cell contents, $Bi_{26}O_{39}$, of pure γ-Bi_2O_3 are inconsistent with the structural unit of $A_{26}O_{40}$ per cell in $Bi_{24}Si_2O_{40}$. Two explanations have been proposed (*3, 15*). One is a statistical distribution of oxygen atoms on the available sites. The occupancy factor of the oxygen sites in the pure γ-phase would then be 39/40. The other is a higher oxidation state of some of the bismuth ions and the incorporation of an extra oxygen in the structure, e.g., $Bi_{24}\{Bi^{3+}, Bi^{5+}\}O_{40}$.

In the present experiments, the situation is different from the above cases. As shown by chemical analysis, hydrothermally synthesized γ-Bi_2O_3 contains a small number of fluorine. This suggests that the metastable γ-Bi_2O_3 structure may be stabilized by the presence of a small number of anion impurities. When one oxygen atom in $Bi_{26}O_{39}$ is replaced by two fluorine atoms, the composition changes to $Bi_{26}O_{38}F_2$, which can be regarded as a member of a family of bismuth compounds with the formula $A_{26}O_{40}$. This assumption is consistent with the present experimental results that only the solutions or starting materials which contained fluorine ions were effectual in the synthesis of the compound with the γ-Bi_2O_3 structure.

Moreover, if the above assumption is true, we can expect the synthesis of $Bi_{26}O_{38}F_2$ based on the following chemical reaction, $38Bi_2O_3 + 2BiF_3 \rightarrow 3Bi_{26}O_{38}F_2$, and this is the reason why the mixture of Bi_2O_3 and BiF_3 in a 38 : 2 molar ratio was used as a starting material.

The calculated fluorine content for $Bi_{26}O_{38}F_2$ is about 0.6 wt%, which is a little smaller than the experimentally obtained value. Two explanations may be given for this disagreement. One is the replacement of more than one oxygen atom with fluorine atoms in $Bi_{26}O_{39}$. In this case, cation vacancies must be introduced to preserve electrical neutrality because the number of available anion sites is 40. The other is the coexistence of some other bismuth oxide fluorides with $Bi_{26}O_{38}F_2$, examples being $Bi_7O_9F_3$ or BiOF (*16*). They have a fluorine content higher than 0.6 wt%, but are not detectable by XRPD analysis because of the insensitivity of this method to trace constituents. We believe the latter to be the case because a few noncubic crystals were observed in the reaction products by means of a polarizing microscope, even though not detected by XRPD analysis.

The experimental DTA results suggest that the observed two peaks correspond to phase transformations in the bismuth oxide fluoride formed by thermal decomposition of $Bi_{26}O_{38}F_2$. The presence of this compound was ascertained in our preliminary phase research. However, according to the phase diagram of the BiF_3–Bi_2O_3 system reported by Nurgaliev *et al.* (*16*), the decomposition products to be expected are a mixture of α-Bi_2O_3 and $Bi_7O_9F_3$, and the latter has transformation temperatures at 505 and 585°C. These are in disagreement with the present results. Although further discussion of this matter is necessary, it is not the purpose of the present study and will be discussed in another paper.

References

1. L. G. SILLEN, *Ark. Kem. Mineral. Geol.* **12A[18]**, 1 (1937).
2. W. C. SCHUMB AND E. S. RITTNER, *J. Am. Chem. Soc.* **65**, 1055 (1943).
3. B. AURIVILLIUS AND L. G. SILLEN, *Nature (London)* **155**, 305 (1945).
4. L. P. FOMCHENKOV, A. A. MAIER, AND N. A. GRACHEVA, *Inorg. Mater. (Engl. Transl.)* **10**, 1733 (1974).
5. G. GATTOW UND H. SCHRODER, *Z. Anorg. Allg. Chem.* **318**, 176 (1962).

6. J. W. Medernack and R. L. Snyder, *J. Am. Ceram. Soc.* **61,** 494 (1978).
7. E. M. Levin and R. S. Roth, *J. Res. Natl. Bur. Stand.* **68A,** 189 (1964).
8. H. A. Harwig and A. G. Gerards, *Thermochim. Acta* **28,** 121 (1979).
9. C. Frondel, *Am. Mineral.* **28,** 521 (1943).
10. E. M. Levin and R. S. Roth. *J. Res. Natl. Bur. Stand.* **68A,** 197 (1964).
11. H. Kodama and A. Watanabe, *J. Solid State Chem.* **56,** 225 (1985).
12. H. Kodama, F. Izumi, and A. Watanabe, *J. Solid State Chem.* **36,** 349 (1981).
13. J. Correia Neves, J. E. Lopes Nunes, Th.G. Sahama, M. Lehtinen, and O. von Knorring, *Rev. Cien. Geol. Ser. A* **7,** 1 (1974).
14. H. A. Harwig, *Z. Anorg. Allg. Chem.* **444,** 151 (1978).
15. H. A. Harwig and J. W. Weenk, *Z. Anorg. Allg. Chem.* **444,** 167 (1978).
16. B. Z. Nurgaliev, T. F. Vasekina, A. E. Baron, B. A. Popovkin, and A. V. Novoselova, *Russ. J. Inorg. Chem.* **28,** 415 (1983).