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The Hydrothermal Synthesis of Bismuth Oxide Chlorides

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The compounds, $Bi_4O_5Cl_2$, $Bi_{24}O_{31}Cl_{10}$, Bi_3O_4Cl, and $Bi_{12}O_{17}Cl_2$ have been synthesized under hydrothermal conditions. H_2O and mixtures of Bi_2O_3 and BiOCl have been used as solvent and starting materials. The crystallization field of these compounds have been revealed in the range 350 to 550°C. A structural image of $Bi_4O_5Cl_2$ has been observed by a high resolution transmission electron microscope and compared with the crystal structure model. The thermal stability region of $Bi_4O_5Cl_2$ has been reexamined. © 1988 Academic Press, Inc.

Introduction

The system Bi_2O_3–$BiCl_3$ shows five intermediate compounds such as BiOCl, $Bi_4O_5Cl_2$, $Bi_{24}O_{31}Cl_{10}$, Bi_3O_4Cl, and $Bi_{12}O_{17}Cl_2$ (*1–4*), but little is known about them except BiOCl.

The present study deals with the synthesis of $Bi_4O_5Cl_2$, $Bi_{24}O_{31}Cl_{10}$, Bi_3O_4Cl, and $Bi_{12}O_{17}Cl_2$ by a hydrothermal method. Since metal oxide chlorides are generally less stable at high temperatures, this method, which was carried out at comparatively low temperatures, is expected to be useful for the synthesis of these compounds.

The hydrothermal synthesis of bismuth oxide chlorides was first tried by Nurgaliev *et al.* (*5*). They used $Bi_{12}O_{17}Cl_2$ as a starting material and aqueous solutions of HCl, NH_4Cl, LiCl, and KCl as solvents, which were different from what we used in the present study. They explored the crystallization field of bismuth oxide chlorides at 400°C but could not detect $Bi_4O_5Cl_2$ under their conditions.

In the present study, besides the hydrothermal synthesis, the thermal stability of $Bi_4O_5Cl_2$ was reexamined. In the phase diagram reported by Nurgaliev *et al.* (*1*), this compound is drawn as a stable phase extending from room temperature to 915°C, but this feature is questionable.

The grown crystals of bismuth oxide chlorides were examined by means of a scanning electron microscope. Moreover, a structure image of $Bi_4O_5Cl_2$ was obtained by high resolution transmission electron microscopy to examine the crystal structure. This is the first extension of the technique to metal oxide halogenides, although it has been used successfully in the studies of many metal oxides.

Experimental Procedure

In the hydrothermal synthesis, we used appropriate amounts of Bi_2O_3 and BiOCl as

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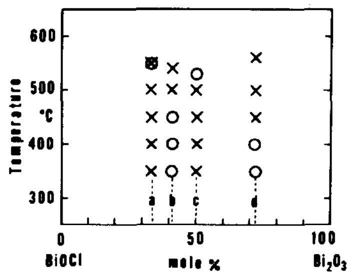

FIG. 1. Each position of the sign ○ or × represents experimental conditions; heating temperature and composition of starting material in each run. The signs, *a*, *b*, *c*, and *d* correspond to the composition of $Bi_4O_5Cl_2$, $Bi_{24}O_{31}Cl_{10}$, Bi_3O_4Cl, and $Bi_{12}O_{17}Cl_2$, respectively.

starting materials and pure water as a solvent to form $Bi_{12}O_{17}Cl_2$, Bi_3O_4Cl, $Bi_{24}O_{31}Cl_{10}$, and $Bi_4O_5Cl_2$. The mixture was placed in a platinum capsule (4 mm outer diameter and 50 mm long), and the capsule was carefully sealed by welding and then enclosed by another platinum capsule (5 mm outer diameter and 70 mm long). This doubly sealed capsule was placed in a hydrothermal synthesis apparatus (described in a previous paper (*6*)). After a heating run, the reaction products were quenched by rapid immersion of the pressure vessel in cold water.

The thermal stability of $Bi_4O_5Cl_2$ was studied by isothermal heating in a triply sealed capsule; the inner two were platinum and the outer one was quartz. As much air as possible was removed from the capsule by minimizing the dead space before sealing. A mixture of Bi_2O_3 and BiOCl (molar ratio 1 : 2) was heated isothermally in the same manner. From these results, we determined the relative stability of these compounds.

The products were identified by their X-ray powder diffraction (XRPD) patterns. These were obtained with a conventional diffractometer using Cu*Kα* radiation from a curved graphite monochromator.

The scanning electron micrographs were obtained by means of a Akashi-130 type electron microscope.

Transmission electron micrographs were obtained with a Hitachi-1250 type electron microscope operated at 1 MV, the optical operating conditions of which were the same as those reported previously (*7*). The specimen was stable against the electron irradiation so that we could apply the many-beam lattice image technique. In order to analyze the observed images, a computer simulation of the image contrast was carried out, taking the dynamical scattering of electrons into consideration (*8*).

Results and Discussion

The experimental results are shown in Fig. 1. The successful results are indicated by the symbol ○; the symbol × represents the unsatisfactory results.

Pure $Bi_{12}O_{17}Cl_2$ crystallized in the range from 350 to 400°C. The grown crystals are yellow and very thin platelets and are shown in Fig. 2. On heating over 450°C, a small amount of Bi_3O_4Cl crystallized with this compound.

Pure Bi_3O_4Cl crystallized only at 530°C. At lower temperatures $Bi_{24}O_{31}Cl_{10}$ also crystallized out. The grown crystals are yellow and form thick platelets as shown in Fig. 3.

Pure crystals of $Bi_{24}O_{31}Cl_{10}$ were obtained in the temperature range 350–450°C. At higher temperatures $Bi_4O_5Cl_2$ or an unidentified phase was obtained along with $Bi_{24}O_{31}Cl_{10}$. The grown crystals form yellow platelets as shown in Fig. 4.

Pure $Bi_4O_5Cl_2$ was not readily synthesized. When a molar ratio (1 : 2) of Bi_2O_3 and BiOCl was used, no pure $Bi_4O_5Cl_2$ was obtained at any temperature. Below 450°C, the major reaction products were mixtures of $Bi_{24}O_{31}Cl_{10}$ and $Bi_4O_5Cl_2$. With increasing reaction temperatures, the ratio of $Bi_4O_5Cl_2$ increased but even at 530°C, the reaction products contained $Bi_{24}O_{31}Cl_{10}$.

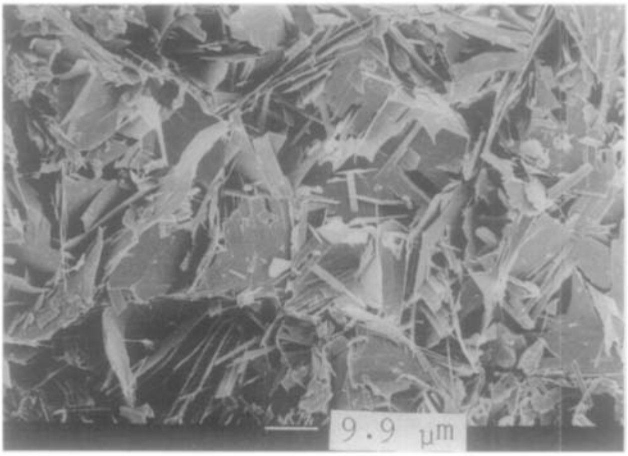

FIG. 2. Scanning electron micrograph of $Bi_{12}O_{17}Cl_2$.

Loss of chlorine into solution may disturb the crystallization of $Bi_4O_5Cl_2$ and excess chlorine might be necessary to compensate for the loss. Therefore, various molar ratios (1 : 2–1 : 4) of Bi_2O_3 and BiOCl were tried as starting materials; the best molar ratio was found to be 1 : 2.025. When the mixture in this molar ratio was heated to 540°C, the reaction products were pure $Bi_4O_5Cl_2$ crystals. However, below 500°C, no pure $Bi_4O_5Cl_2$ could be produced with this starting material. When the mixture in a molar ratio $1 : x$ ($x > 2.025$) was heated in the range from 350 to 550°C, the products were mixtures of BiOCl and $Bi_4O_5Cl_2$, or BiOCl, $Bi_4O_5Cl_2$ and $Bi_{24}O_{31}Cl_{10}$. These experimental results show that $Bi_4O_5Cl_2$ is stable only in a very narrow range of temperatures and of Cl concentrations.

Crystals of $Bi_4O_5Cl_2$ are white and pillar-shaped, as shown in Fig. 5. The XRPD data of $Bi_4O_5Cl_2$ are given in Table I. These are the first experimental data; they almost agree with the calculated ones of the

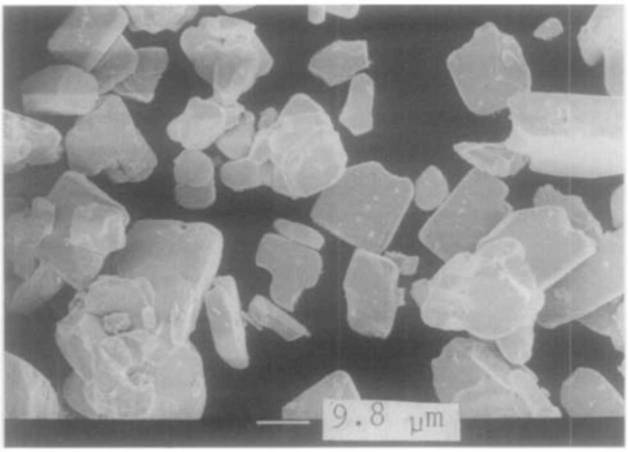

FIG. 3. Scanning electron micrograph of Bi_3O_4Cl.

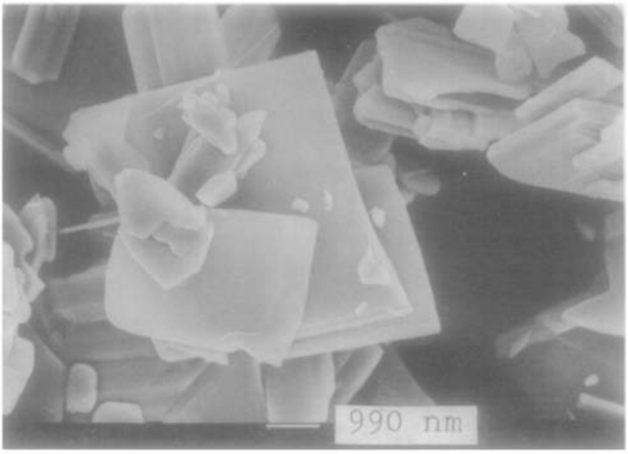

FIG. 4. Scanning electron micrograph of $Bi_{24}O_{31}Cl_{10}$.

JCPDS card (*9*), which are based on the structure model by Hopfgarten (Orthorhombic, *Pnma*, $a = 40.532$, $b = 3.8688$, and $c = 15.487$ Å) except for the intensity. The reasons for the intensity difference are not clear, but one possible explanation involves the effect of the preferential orientation in the XRPD specimen, since it is noted from the electron diffraction that the elongated axis of the crystal is parallel to the *b* axis.

The pillar-shaped crystals of $Bi_4O_5Cl_2$ were cut as thin as possible normal to the elongated axis by a razor. Figure 6 is a high resolution electron microscope image of a fragment. Electrons are incident along the *b* axis. The corresponding diffraction pattern indicates that the lattice parameters are $a = 40.5$ and $c = 15.5$ Å. These are almost identical with those described above.

The $Bi_4O_5Cl_2$ image was calculated on the basis of Hophgarten's model, and the result is presented in the photograph with the same magnification. It fits well with the real image. The arrangement of dark dots coincides with the projected position of Bi atoms. The calculation was done for the crystal thickness of about 31 Å with a spherical aberration of the objective lens of

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR $Bi_4O_5Cl_2$

h k l	d_{cal}(Å)	d_{obs}(Å)	I_{obs}	I_{cal}
2 0 1	12.30	12.26	10	3
4 0 0, 3 0 1	10.13	10.10	10	9
2 0 2, 5 0 1	7.233	7.225	11	4
6 0 1	6.192	6.171	12	9
8 0 0, 6 0 2	5.066	5.052	7	11
4 0 3	4.600	4.59	10	3
2 1 1	3.691	3.704	19	2
4 1 0, 8 0 3	3.614	3.607	9	1
12 0 0	3.378	3.365	62	100
6 0 4	3.359	3.345	100	55
12 0 1	3.300	3.290	4	5
4 1 2, 6 1 1	3.275	3.273	6	2
8 1 0, 13 0 1	3.075	3.078	3	4
4 1 3, 4 0 5	2.961	2.962	84	13
8 1 2, 14 0 1	2.858	2.855	11	3
12 0 3	2.826	2.837	9	8
6 1 3	2.814	2.818	8	8
10 0 4	2.800	2.792	8	5
10 1 1	2.754	2.756	43	7
2 1 4, 14 0 2	2.712	2.716	24	5
8 1 3	2.642	2.643	17	4
1 0 6, 0 0 6	2.576	2.571	4	1
2 0 6	2.560	2.553	5	2
6 1 4, 3 0 6	2.536	2.526	8	4
14 0 4	2.319	2.313	5	3
8 0 6	2.300	2.291	3	1
10 1 4	2.268	2.268	2	1
14 1 2	2.221	2.223	3	2
2 0 9	2.199	2.194	4	1

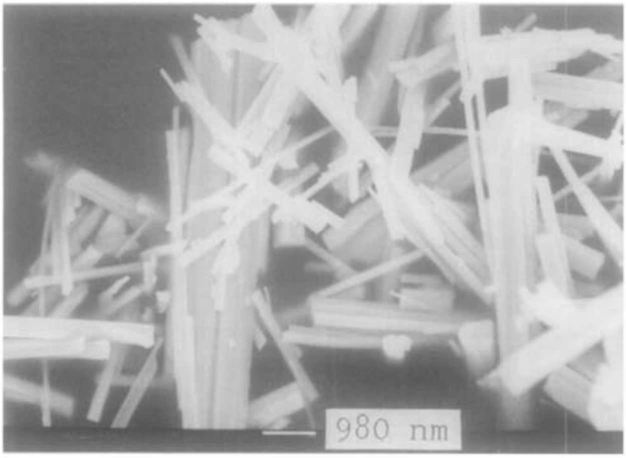

FIG. 5. Scanning electron micrograph of $Bi_4O_5Cl_2$.

5 mm, a defocus of 600 Å underfocus, a mean focal fluctuation of 150 Å due to the instability in the accelerating voltage and the lens current, an angle of beam convergence of 8×10^{-4} rad, and an objective aperture of 0.63 $Å^{-1}$. Similar calculations

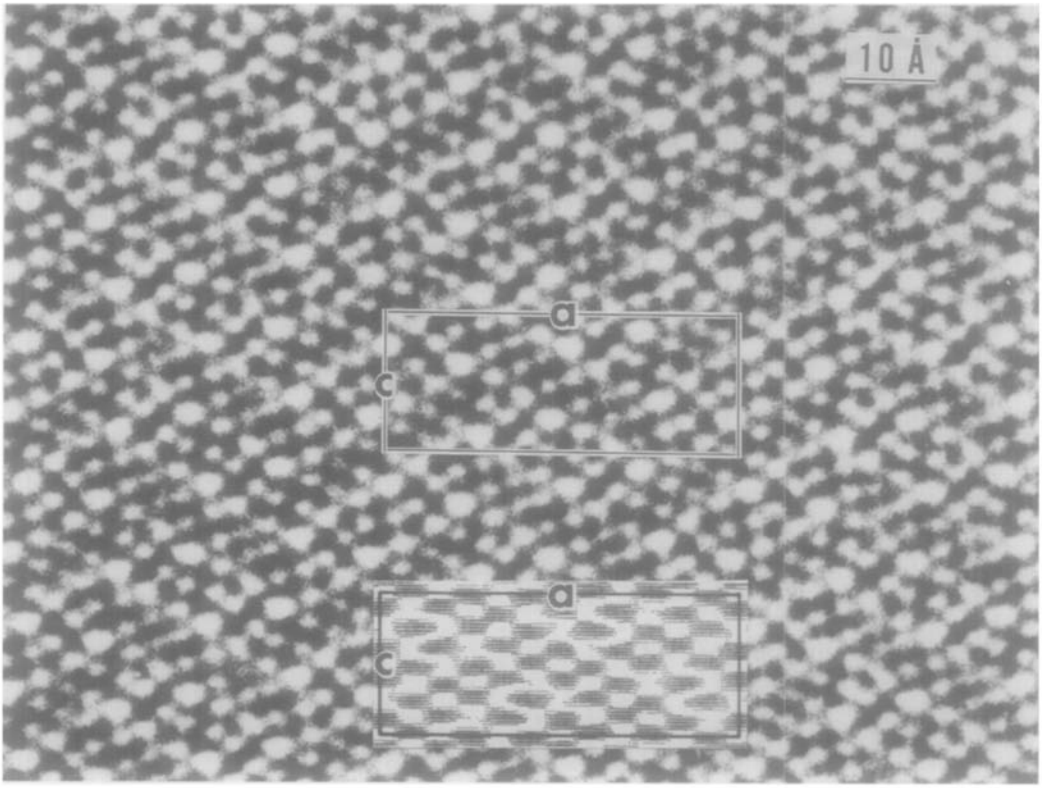

FIG. 6. High resolution electron microscope image and simulated image of $Bi_4O_5Cl_2$.

TABLE II

ISOTHERMAL HEATING OF $Bi_4O_5Cl_2$ AND MIXTURE OF Bi_2O_3 AND BiOCl

Starting material	Temperature (°C)	Reaction products
(a) $Bi_4O_5Cl_2$	800	$Bi_4O_5Cl_2$
	840	$Bi_4O_5Cl_2$ + BiOCl + $Bi_{24}O_{31}Cl_{10}$
	860	$Bi_4O_5Cl_2$ + BiOCl + $Bi_{24}O_{31}Cl_{10}$
(b) Bi_2O_3 + 2BiOCl	700	$Bi_{24}O_{31}Cl_{10}$ + BiOCl
	840	$Bi_{24}O_{31}Cl_{10}$ + BiOCl
	860	$Bi_{24}O_{31}Cl_{10}$ + BiOCl + $Bi_4O_5Cl_2$

were obtained with any thickness less than roughly 60 Å. Moreover, it has been noted in the calculation that Cl atoms affect the image contrast for the thickness range between 31 and 50 Å. This must be related to the variation in the dynamical diffraction amplitude. Oxygen affects the contrast only slightly. A detailed analysis of the image intensity will be reported elsewhere.

Table IIa shows the results of isothermal heating of $Bi_4O_5Cl_2$. Above 840°C, a part of the sample was decomposed into $Bi_{24}O_{31}Cl_{10}$ and BiOCl. Below 800°C, no decomposition occurred. Table IIb shows the results of isothermal heating of Bi_2O_3 and BiOCl mixtures. Below 840°C, the starting material changed not into $Bi_4O_5Cl_2$ but into a mixture of $Bi_{24}O_{31}Cl_{10}$ and BiOCl. Above 860°C, the starting material changed into mixtures of $Bi_{24}O_{31}Cl_{10}$, BiOCl, and $Bi_4O_5Cl_2$. These results suggest that we cannot conclude that $Bi_4O_5Cl_2$ is a stable phase from room temperature to 915°C, as reported by Nurgaliev *et al.* (*1*).

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