

X-Ray Studies on the System  $\text{BiF}_3\text{-Bi}_2\text{O}_3$ 

## II. A Bismuth Oxide Fluoride of Defective Tysonite Type

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A bismuth oxide fluoride of approximate composition  $\text{BiO}_{0.1}\text{F}_{2.8}$  has been prepared. From single crystal investigations the crystal structure was found to be closely related to that of tysonite.

By heating orthorhombic bismuth fluoride in air at  $670^\circ\text{C}$ , various bismuth oxide fluoride phases have been obtained as reported in a previous communication<sup>1</sup>. The first phase observed in this series was also prepared by carrying out the heat treatment at  $850^\circ\text{C}$  for a period of a few minutes. When similarly heating bismuth fluoride in a closed crucible no change of the substance occurred. The new phase evidently was not a new modification of bismuth fluoride, as was also confirmed by chemical analysis.

The fluorine content of various samples containing the new phase was found to lie between 19 and 21 %, while the theoretical value for bismuth fluoride is 21.4 %. Assuming the new phase to be a bismuth oxide fluoride this will correspond to the approximate composition  $\text{BiO}_{0.1}\text{F}_{2.8}$ .

The substance was colourless and could be obtained as crystal plates of up to about 1 mm length and 0.3 mm thickness. X-ray photographs were taken in a Guinier focusing powder camera using  $\text{Cu-K}\alpha$  radiation (*cf.* Table 1) and in a Weissenberg camera with  $\text{Cu-K}$  radiation.

## UNIT CELL AND SPACE GROUP

In the single crystal photographs, the reflexions  $0kl$ ,  $1kl$ ,  $hhl$ , and  $h,h+1,l$  were registered. The Laue symmetry proved to be  $6/mmm$ . Systematically missing spectra were  $hhl$  with  $l = \text{odd}$ , which is characteristic of the space-groups  $P6_3/mmc$  (No. 194),  $P6_3mc$  (No. 186) and  $P6_3c$  (No. 190). Powder photographs of a sample prepared at  $850^\circ\text{C}$  (20.3 % F) gave the unit cell dimensions  $a = 4.08_3 \text{ \AA}$  and  $c = 7.32_3 \text{ \AA}$ .

Preparations of lower fluorine content seemed to show minor alterations in the positions of the reflexions. Some of the lines in the photographs of these

Table 1. Powder photograph of  $\text{BiO}_x\text{F}_{3-2x}$ . Cu-K $\alpha$  radiation. Sample with 20.3 % F prepared at 840° C. The value of  $x$  is 0.09.

$I$ obs	$10^4\sin^2\Theta$ obs	$10^4\sin^2\Theta$ calc	$hkl$	$I$ obs	$10^4\sin^2\Theta$ obs	$10^4\sin^2\Theta$ calc	$hkl$
m	442	443	002	m	2 895	2 888	203
m	468	475	100	m	3 197	3 199	114
vst	580	586	101	m	3 249	3 245	105
m	914	918	102	vw	3 320	3 327	210
broad m	1 418	1 426	110	m	3 435	3 438	211
m	1 471	1 472	103	w	3 671	3 674	204
vw	1 776	1 773	004	w	3 773	3 770	212
m	1 869	1 869	112	vw	3 999	3 999	006
vw	1 893	1 901	200	w	4 278	4 278	300
m	2 002	2 012	201	m	4 328	4 324	213
w	2 251	2 248	104	vw	4 464	4 474	106
w	2 340	2 344	202	m	4 677	4 671	205
				m	4 714	4 721	302

samples were obviously split up into doublets while others were broadened. This effect and the result of the chemical analyses seem to indicate a distortion of the structure and a variable composition of the phase. For a sample prepared at 840° C with 19.6 % F,  $a$  was found to be 4.09<sub>8</sub> Å and  $c$  7.27<sub>7</sub> Å for the pseudo-cell. So far the nature of the slight distortion has not been elucidated and thus, when discussing the structure, the non-deformed atomic arrangement has been considered.

### Cell content

For the cell content the three following possibilities must be taken into consideration:

1. The composition of the phase may be represented by the expression  $\text{Bi}(\text{O}, \text{F})_3 \cdot x\text{Bi}$ , the extra bismuth atoms being inserted in interstices in a  $\text{Bi}(\text{O}, \text{F})_3$  array.

2. The formula of the compound is  $\text{Bi}(\text{OH}, \text{F})_3$  corresponding to a possible uptake of water during the heat treatment (cf. Ref.<sup>1</sup>).

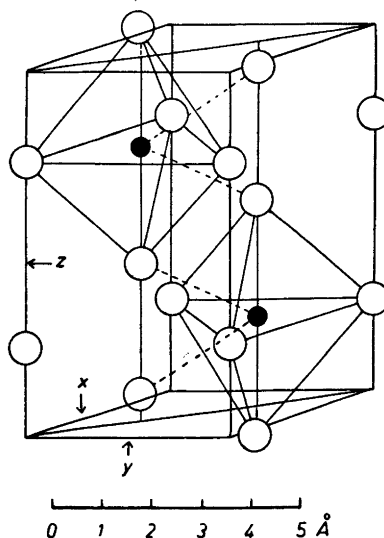
3. The composition of the phase is  $\text{BiO}_x\text{F}_{3-2x}$ .

Table 2. Cell dimensions and observed and calculated densities.

Temp. °C	F % by weight	Density obs.	Density 1	Density 2	Density 3	$a$	$c$
840	21.1	8.3 <sub>1</sub> ± 0.06	8.43	8.36	8.34	4.08 <sub>0</sub>	7.32 <sub>3</sub>
840	20.3	8.1 <sub>9</sub>	8.55	8.34	8.29	4.08 <sub>3</sub>	7.32 <sub>3</sub>
840	20.1 *	8.2 <sub>6</sub>	8.63	8.38	8.32	4.07 <sub>2</sub>	7.32 <sub>9</sub>
670	19.6 *	8.2 <sub>1</sub>	8.70	8.37	8.29	4.07 <sub>7</sub>	7.31 <sub>9</sub>
840	19.6					4.09 <sub>8</sub>	7.27 <sub>7</sub>

\* On calculating the cell dimensions the weak extra line in the vicinity of 110 was neglected.

Fig. 1. Unit cell of the  $\text{BiO}_x\text{F}_{3-2x}$  phase, showing the coordination of the Bi atoms (full circles). The dashed lines connect the Bi atoms with (O, F) atoms (open circles, interatomic distances 2.7 Å), the latter belonging to a trigonal prismatic arrangement of non-metal atoms encompassing the  $\text{Bi}(\text{O,F})_6$  trigonal bipyramids, indicated by full lines.



The observed densities for samples of various compositions are given in Table 2 together with those calculated for the alternatives 1—3 assuming the elementary cell or pseudo-cell to contain two formula units. While 1 obviously is in disagreement with the observed data the density measurements do not allow a decision to be made between 2 and 3. However, the high temperature of formation makes it rather improbable that the structure contains hydrogen, while several examples are previously known of bismuth-oxygen compounds possessing vacancies in the oxygen framework. This suggests alternative 3 to be the more probable one.

### Crystal structure

(Notation according to International Tables for X-Ray Crystallography, I, Birmingham 1952.)

Since the reflexions  $03l$  with  $l = \text{odd}$  are absent in the photographs, the only possible positions for the two Bi atoms of the unit cell are  $2(d)$  and  $2(c)$  in space-group  $P6_3/mmc$ ,  $2(b)$  in  $P6_3mc$  or  $2(c)$  and  $2(d)$  in  $P\bar{6}2c$ , the point position of the two latter space groups, however, actually possessing the symmetry  $P6_3/mmc$ . Intensities calculated for this arrangement of the bismuth atoms are in fair agreement with the observed data. The positions of the light atoms were determined from space considerations, the distance (O, F)—(O, F) being initially assumed to be  $\geq 2.50$  Å and the distances  $\text{Bi}-(\text{O, F}) \geq 2.20$  Å. The former condition is only consistent with the space group  $P6_3/mmc$  and the point positions  $2(a)$ ,  $2(b)$ ,  $2(c)$ ,  $2(d)$ , and  $4(f)$  if the symmetry of the light atoms is assumed to be that revealed in the X-ray photographs. The only combination of 6(O, F) atoms on these point positions which is in agreement with the assumed restrictions of the interatomic distances is  $2(b)$  and  $4(f)$ , if the position

2(c) is arbitrarily adopted for the bismuth atoms. The  $z$ -parameter of the latter (O, F) position was finally chosen so as to give Bi—(O, F) distances  $\geq 2.3$  Å and (O, F)—(O, F) distances  $\geq 2.6$  Å. In this way the value  $z = 0.57$  was arrived at.

Thus the following structure is proposed:

Space-group  $P6_3/mmc$  (No. 194)

4 (O, F)<sub>2</sub> in 4( $f$ ):  $\frac{1}{3}, \frac{2}{3}, z; \frac{2}{3}, \frac{1}{3}, \bar{z}; \frac{2}{3}, \frac{1}{3}, \frac{1}{2} + z; \frac{1}{3}, \frac{2}{3}, \frac{1}{2} - z$       $z = 0.57$   
 2 (O, F)<sub>1</sub> in 2( $b$ ):  $0, 0, \frac{1}{4}; 0, 0, \frac{3}{4}$   
 2 Bi in 2( $c$ ):  $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}; \frac{2}{3}, \frac{1}{3}, \frac{3}{4}$

The corresponding interatomic distances and coordinations will be:

Bi—3 (O, F) <sub>1</sub> ; (O, F) <sub>1</sub> —3 Bi	2.36 Å
Bi—2 (O, F) <sub>2</sub> ; (O, F) <sub>2</sub> —Bi	2.35 Å
Bi—6 (O, F) <sub>2</sub> ; (O, F) <sub>2</sub> —3 Bi	2.70 Å
(O, F) <sub>1</sub> —6(O, F) <sub>2</sub> ; (O, F) <sub>2</sub> —3(O, F) <sub>1</sub>	2.70 Å
(O, F) <sub>1</sub> —6(O, F) <sub>2</sub> ; (O, F) <sub>2</sub> —3(O, F) <sub>1</sub>	3.32 Å
(O, F) <sub>2</sub> —(O, F) <sub>2</sub>	2.63 Å
(O, F) <sub>2</sub> —3(O, F) <sub>2</sub>	2.70 Å

#### DISCUSSION

The atomic arrangement thus arrived at is obviously closely related to that of several trifluorides of lanthanides and actinides described by Zachariasen<sup>2</sup> and of the mineral tysonite  $\text{RF}_3$  ( $\text{R} = \text{Ce, La etc.}$ ) studied by Schlyter<sup>3</sup>. It must, however, be emphasized that the present bismuth compound very probably does not exist at the composition  $\text{BiF}_3$  but is stabilized by the occurrence of vacancies in the non-metal framework accompanying the substitution of oxygen atoms for a small fraction of the fluorine atoms.

The investigation is continued by studying the cubic bismuth oxide fluoride phase<sup>1</sup> ( $a = 5.84$  Å) which is likely to be structurally related to the cubic bismuth fluoride phase described by Hassel and Nilssen<sup>4</sup>.

These studies form part of a research program on metal oxides and related compounds financially supported by the *Swedish Natural Science Research Council*.

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Received May 7, 1955.