

X-Ray Studies on the System  $\text{BiF}_3\text{-Bi}_2\text{O}_3$ I. Preliminary Phase Analysis and a Note on the Structure of  $\text{BiF}_3$ 

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The fluorine content of bismuth fluoride gradually decreases on heating it in air, the end product being bismuth oxide. A preliminary phase analysis of the system  $\text{BiF}_3\text{-Bi}_2\text{O}_3$  has been made. The structure of bismuth fluoride as found by Zachariassen from studies of powder photographs has been confirmed by single crystal methods.

On heating bismuth fluoride in air it is found that the fluorine content gradually decreases at 600—800° C. The reaction is probably  $\text{BiF}_3 + x\text{H}_2\text{O} = \text{BiO}_x\text{F}_{3-2x} + 2x\text{HF}$  or, for low values of  $x$ , possibly  $\text{BiF}_3 + x\text{H}_2\text{O} = \text{Bi}(\text{OH})_x\text{F}_{3-x} + x\text{HF}$ . Samples of about 2 g bismuth fluoride were heated in small platinum crucibles for various periods of time (up to 60 h) in an electrical oven at 670° C. This temperature was chosen because it gave a suitable reaction velocity. The fluorine content of the samples was determined and powder photographs were taken in focusing cameras using Cr -  $K$  or Cu -  $K\alpha$  radiation. The result of the phase analyses is summarized in Table 1. The actual heating times are not related to the progress of the reaction since the humidity of the atmosphere was not controlled.

## METHODS OF SYNTHESIS

To prepare  $\text{BiF}_3$ , we first tried the method of precipitating the compound from a bismuth nitrate-mannitose solution with a potassium or sodium fluoride solution as described by Hassel and Nilssen <sup>4</sup> and by Hund and Fricke <sup>5</sup>. However, the products obtained in this way always contained potassium or sodium and attempts to remove the alkali metal lead to preparations considerably poorer in fluorine (18 %) than the theoretical value calculated for  $\text{BiF}_3$  (21.4 %). We therefore tried the simple method of digesting bismuth oxide with dilute (1:1) hydrofluoric acid in a platinum dish. This method lead to samples with  $21.1 \pm 0.2$  % F and  $77.4 \pm 0.2$  % Bi (theoretical 21.4 % F and 78.6 % Bi).

## METHODS OF ANALYSES

*Fluorine.* The samples were distilled with perchloric acid as described by Willard and Winter <sup>6</sup>. The distillate was titrated with thorium nitrate solution, using sodium-alizarin sulphionate as an indicator.

Table 1. Results of phase analyses of various samples obtained by heating bismuth fluoride at  $670^\circ\text{C}$  in air.

Heating time (h)	Fluorine content obs., % by weight	Phases (main constituents)
0	21.1	$\text{BiF}_3^*$
	20.0	$\text{BiF}_3 + \alpha$
	19.7	$\alpha$
	17.3	$\alpha + \beta$
	14.8	$\beta$
	12.5	$\beta$
	6.7	$\text{BiOF}^{**} + \gamma$
	5.2	$\gamma$
	4.5	$\delta$
	2.7	$\delta$
60	0	$\text{Bi}_2\text{O}_3^{***}$

\* Orthorhombic  $\text{BiF}_3$ , Ref.<sup>1</sup>

\*\*  $\text{BiOCl}$  type, Ref.<sup>2</sup>

\*\*\* Monoclinic  $\text{Bi}_2\text{O}_3$ , Ref.<sup>3</sup>

$\alpha$ . Approximate composition is  $\text{BiO}_{0.1}\text{F}_{2.8}$ . Hexagonal structure of tysonite type with the cell dimensions  $a = 4.08 \text{ \AA}$  and  $c = 7.32 \text{ \AA}$ . A report of a determination of the crystal structure will appear shortly.

$\beta$  Face-centered cubic cell with  $a = 5.84 \text{ \AA}$  (sample with 14 % F). The composition is probably variable.

$\gamma$  Seemingly a deformed face-centered cubic lattice.

$\delta$  Monoclinic needles with  $a = 19.7 \text{ \AA}$ ,  $b = 7.5 \text{ \AA}$ ,  $c = 21.3 \text{ \AA}$  and  $\beta = 107^\circ$ .

*Bismuth.* The samples were heated with conc. nitric acid and repeatedly evaporated to dryness in a platinum dish to expel the hydrofluoric acid. The residue was then dissolved in dilute nitric acid and the bismuth precipitated with ammonia and finally weighed as  $\text{Bi}_2\text{O}_3$ .

#### SINGLE CRYSTAL INVESTIGATION OF BISMUTH FLUORIDE

Since the powder photographs of bismuth fluoride, prepared in the way described above, differed completely from those of the cubic compounds described by Hassel and Nilssen<sup>4</sup> and Hund and Fricke<sup>5</sup> and because the paper by Zachariassen (*l. c.* in Ref.<sup>1</sup>) was not known to us at that time we started an investigation of single crystals of our compound by means of rotation and Weissenberg photographs ( $0kl$ ,  $1kl$ ,  $h0l$ , and  $h1l$ ). We found the Laue symmetry to be  $Pmmm$  and the unit cell dimensions  $a = 6.56 \text{ \AA}$ ,  $b = 7.04 \text{ \AA}$  and  $c = 4.83 \text{ \AA}$ , which is in good agreement with Zachariassen's values  $a = 6.56 \text{ \AA}$ ,  $b = 7.03 \text{ \AA}$  and  $c = 4.86 \text{ \AA}$ . The observed density was 7.92 and the calculated value for 4 formula units per unit cell 7.90. The systematically absent spectra were those characteristic of the space-groups  $Pnma$  (No. 62) and  $Pna2_1$  (No. 33). The positions of the bismuth atoms were found to be in agreement with the former symmetry, occupying the position  $4(c)$ :  $\pm(x, \frac{1}{4}, z)$ ,  $\pm(\frac{1}{2}-x, \frac{3}{4}, \frac{1}{2}+z)$  with  $x = 0.35_3$  and  $z = 0.038$ . Our observations thus agree with the statements of Zachariassen<sup>1</sup> and of Zalkin and Templeton<sup>1</sup> that  $\text{BiF}_3$  is iso-

morphous with  $\text{YF}_3$ , the coordinates of the yttrium atoms according to the latter being  $x = 0.367$  and  $z = 0.058$ . Reasonable Bi—F distances are also obtained when assuming the same F parameters for  $\text{BiF}_3$  as those given for  $\text{YF}_3$ .

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