The Crystal Structure of Bismuth Oxide Fluoride

II. A Refinement of the Previously Published Structure *

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The crystal structure of bismuth oxide fluoride reported earlier [1] has been reexamined using a newly collected X-ray single-crystal intensity material. The intensities were corrected for absorption and a least-squares refinement was made. The investigation gave as result that the previously given structure is essentially correct. The influence of introducing the anomalous scattering of the bismuth atoms in the calculations has been studied.

An X-ray investigation was made on synthetic bismuth oxide fluoride in 1948 by the present author.[1] Quite recently a mineral, *zavaritskite*, essentially containing BiOF has been reported.[2] The symmetry and the cell edges of this mineral agree with those of the above-mentioned synthetic material. Bismuth oxide fluoride is isotypic with the other bismuth oxide halides, *viz.* BiOCl, BiOBr and BiOI.[1] Only the positions of the bismuth atoms could be determined at that time from the intensity data. The positions of the oxygen and fluorine atoms were mainly deduced from geometrical considerations. Using modern methods, such as absorption corrections and least-squares refinements, it seemed probable that at least the structure type should be obtained solely by the aid of the observed intensity data.

For this study the same crystalline sample was used as investigated earlier.[1] The cell edges were redetermined using a Guinier focusing camera with $CuK\alpha_1$ radiation and potassium chloride as an internal standard. The following values of the edges of the tetragonal unit cell were obtained:

$a = 3.7469 \pm 0.0005$ Å, $c = 6.226 \pm 0.001$ Å.

The values of the cell edges of the mineral *zavaritskite* [2] are:

$a = 3.75$ Å, $c = 6.23$ Å.

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* Part I, *cf.* Ref.[1]

Table 1. Powder diagram of tetragonal BiOF. Guinier focusing camera of 80 mm diameter with CuKα₁ radiation and potassium chloride as internal standard (a(KCl) = 6.2930 Å).

h k l	$10^4 \sin^2 \Theta$ obs	$10^4 \sin^2 \Theta$ calc	I obs
0 0 1	0155	0153	vw
0 0 2	0615	0612	w
1 1 0	0848	0845	st
1 1 1	1000	0998	vvw
1 0 2	1036	1035	w
0 0 3	1378	1378	vvw
1 1 2	1458	1457	m
2 0 0	1691	1690	st
2 0 1	1845	1844	w
1 1 3	2223	2223	vw
2 1 1	2266	2266	st
2 0 2	2302	2303	w
2 1 2	2725	2725	w
1 0 4	2871	2872	vw
2 0 3	3067	3068	vvw
2 2 0	3380	3381	m

The powder pattern of the synthetic bismuth oxide fluoride discussed in this paper is given in Table 1. The cell content is two formula units BiOF (*cf.* Ref.[1]).

THE INTENSITIES

The single crystal used for the investigation was a nearly quadratic plate with the edges 0.08 and 0.09 mm and the thickness 0.014 mm. The directions [110] are parallel to the square edges and the [001] direction perpendicular to the plate. The single-crystal intensities were registered by means of a Buerger precession camera and MoK radiation. The following photographs were taken:

Projection axis	Registered layer lines
[001]	0—3
[100]	0—2
[110]	0—2

For each zone a number of photographs were taken using different exposure times. The intensities of the reflections were estimated visually, comparing them to a calibrated scale. The Lorentz-polarization factors were calculated by means of a program developed by Werner.[3] All programs cited in this paper are written for the digital computer FACIT EDB of the *The Computer Division of the National Swedish Rationalization Agency*, which has been used throughout this work.

The intensities registered with [001] as a projection axis need no correction for absorption, since due to the geometry of the Buerger precession camera the absorption is constant for each photograph with respect to all spots observed there. The intensities of the reflections in the other photographs around

the axes [100] and [110] were corrected by means of an absorption program developed by Werner.[4] A detailed discussion of the calculations of these absorption corrections and their influence on the final result will be reported elsewhere.[5]

There was nothing in the photographs that indicated a Laue symmetry lower than 4/*mmm* or another space group than *P4/nmm* (No. 129 in the *International Tables* [6]), which was also assumed earlier.[1] When putting the intensities, corrected for absorption, on a common scale and taking mean values of them, use was therefore made of the Laue symmetry given above.

THE REFINEMENT OF THE STRUCTURE

Three differently prepared intensity materials were used for the final refinements by the method of least-squares, *viz.* (*A*) made up of the reflections registered with [001] as the projection axis, (*B*) made up of the reflections registered with [100] and [110] as the projection axes, and (*C*) made up of all observed reflections.

The intensity data *A* was given double weight with respect to the data *B* as it had a constant absorption, *vide supra*. All observed structure factors of the intensity material *B* and *C* had at first each one scale factor. Using the method of least-squares seven separate scale factors were introduced, *viz.* six for the zones *hk*0-*hk*5 and one for the zones *hk*6-*hk*8. Thus the intensity data was redivided in separate zones along [001], applying one scale factor for each zone.

The refinements of the various intensity materials were performed with the aid of a program developed by Åsbrink and Brändén.[7] Cruickshank's scheme was used for the weighting of the reflections. For these refinements the atoms of the unit cell were considered to be bismuth, oxygen, and fluorine atoms and not the corresponding ions. The appropriate scattering factors were taken from the *International Tables*.[8] The anomalous scattering of the bismuth atoms was introduced when treating the intensity material *C*. At first only the real part was considered, then also the imaginary part was introduced. The appropriate values of $\Delta f_{\text{Bi}}'$ and $\Delta f_{\text{Bi}}''$ were taken from the *International Tables*.[8]

The atomic parameters obtained earlier [1] were used as a starting point for the least-squares refinement. The second setting of the space group *P4/nmm* (No. 129) was used, however. With this setting the positions of the atoms arrived at earlier are:

2 Bi in $\pm$ ($\frac{1}{4}$,$\frac{1}{4}$,z); $z = 0.208$,
2 F in $\pm$ ($\frac{1}{4}$,$\frac{1}{4}$,z); $z = 0.65$,
2 O in $\pm$ ($\frac{1}{4}$,$\frac{3}{4}$,0).

As the x and y parameters given above were fixed during the least-squares calculations, a transformation of the tetragonal space group to an orthorhombic equivalent, which is usually necessary when applying the above-mentioned program,[7] could be avoided. It was thus sufficient to consider the independent reflections. All refinements were carried to a stage for which the shifts in the

Table 2. The structure of BiOF. Final weight analysis for the refinement of the intensity material C, using scattering factors not corrected for the anomalous dispersion of bismuth. w is the weighting factor. $\Delta = ||F_o|-|F_c||$.

Interval $\sin\Theta$	Number of independent reflections	$\overline{w\Delta^2}$	Interval $|F_o|$	Number of independent reflections	$\overline{w\Delta^2}$
0.00 — 0.36	40	1.21	11 — 32	32	0.45
0.36 — 0.45	31	0.77	32 — 43	20	1.06
0.45 — 0.48	14	1.00	43 — 54	23	1.08
0.48 — 0.54	20	0.49	54 — 75	21	0.92
0.54 — 0.61	10	1.91	75 — 107	19	1.86

scale factors, the positional parameters and the isotropic, individual temperature factors were only fractions of percents of the corresponding standard deviations. The final weight analysis for the intensity material C with non-corrected scattering factor of bismuth is given in Table 2. The deviations from unity of the separate $\overline{w\Delta^2}$ values given there may be ascribed to the fact that only a limited number of independent reflections were used. The results of the various refinements are given in Table 3 together with the number of independent reflections used in the different cases.

Those refinements, for which the anomalous scattering of bismuth was taken into account, may need some comments. When only the real part $\Delta f_{Bi}'$ was considered, $(f_{Bi} + \Delta f_{Bi}')$ was used instead of f_{Bi} in the calculations. In the case where also $\Delta f_{Bi}''$ was introduced, the initial values of F_o were substituted by F_o' which, following Zachariasen and Plettinger,[9] was defined by the following equation:

$$(F_o')^2 = F_o^2 - (\Delta f_{Bi}'')^2 \cos^2 2\pi(hx_{Bi} + ky_{Bi} + lz_{Bi}) \exp\ [-2B_{Bi}(\sin\Theta/\lambda)^2]$$

The values of z_{Bi} and B_{Bi} were taken from the refinement of the intensity data C with non-corrected f_{Bi} values. As mentioned above $\Delta f_{Bi}''$ was taken from the *International Tables*. The F_o' values were calculated by hand. On making the refinement of the F_o' values so obtained, $(f_{Bi} + \Delta f_{Bi}')$ was used instead of f_{Bi}. For careful calculations this procedure must be reiterated (Ref.[10]) until nearly constant values are obtained for z_{Bi} and B_{Bi}. In the present case the difference between the parameters obtained, when the anomalous scattering of bismuth was considered and was not considered, was so small that a reiteration seemed to be unnecessary (*cf.* Table 3).

In one refinement of the intensity data C the positions of the oxygen and fluorine atoms were interchanged to see if it was possible to distinguish between them using only the observed intensity material. That distinction between the atomic species was not revealed by the calculations, however (*cf.* Table 3).

As seen from Table 3 the coordinates of the atoms and their standard deviations agree closely for the intensity materials B and C. As mentioned above the parameter values were not changed, when account was taken to the anomalous scattering of bismuth. Nor did the *positional* parameters

Table 3. The structure of BiOF. The discrepancy factors (R %), the atomic parameters, the isotropic individual temperature factors and the estimated standard deviations for the various refinements. The number of independent reflections are for material A 52, for B 109 and for C 115. The coordinates obtained earlier [1] are given in italics.

Notation	R (%)	$z_{Bi} \pm \sigma z_{Bi}$	$B_{Bi} \pm \sigma B_{Bi}$ Å²	$B_O \pm \sigma B_O$ Å²	$z_F \pm \sigma z_F$	$B_F \pm \sigma B_F$ Å²
Material A	4.5	0.2067 ± 0.0005	0.58 ± 0.02	1.3 ± 0.5	0.696 ± 0.010	1.4 ± 0.5
Material B	10.1	0.2068 ± 0.0003	1.41 ± 0.03	0.5 ± 0.5	0.671 ± 0.009	2.9 ± 0.9
Material C	8.1	0.2068 ± 0.0003	1.02 ± 0.03	0.7 ± 0.5	0.676 ± 0.009	2.3 ± 0.9
Material C $\Delta f'$ considered	8.1	0.2068 ± 0.0003	0.91 ± 0.03	0.9 ± 0.5	0.677 ± 0.009	2.5 ± 0.9
Material C $\Delta f'$ and $\Delta f''$ considered	8.6	0.2068 ± 0.0004	0.97 ± 0.03	0.7 ± 0.5	0.676 ± 0.009	2.4 ± 0.9
Material C F and O interchanged	8.1	0.2068 ± 0.0003	1.02 ± 0.03	1.2 ± 0.6	0.674 ± 0.011	2.2 ± 1.0
Ref.[1]		*0.208*			*0.65*	

obtained with the intensity material A show any significant differences from those of B and C. The temperature factors obtained for the three cases do, however, differ, especially for the bismuth atoms. This is probably due to the fact that the "temperature factors" calculated here will contain correction factors for errors in the photographic method, the visual estimation of the intensities of the spots and for errors in the absorption correction factors. In the following the parameter values and temperature factors obtained for the material C with non-corrected scattering factor for the bismuth atoms will be used. As seen from Table 3, the parameter values arrived at agree well with those reported earlier.[1] Observed and calculated structure factors are given in Table 4.

The result of the refinement was controlled on making three-dimensional electron density difference sections at successive z values, differing from each other by 0.02 z from z = 0 to z = 0.5, covering the asymmetric part of the unit cell. The contributions of both the bismuth and the oxygen atoms were subtracted from the observed Fourier sections. The background in these difference sections was smooth and no extra peaks or pits were found. The calculations of the sections were performed by the aid of programs developed by Liminga and Olovsson.[11]

DISCUSSION OF THE STRUCTURE

Thus it seems that the structure type of BiOF reported earlier [1] is confirmed, if the reasonable assumption is made that layers $Bi_2O_2^{2+}$ exist in the structure as in a number of other bismuth oxide compounds and not layers $Bi_2F_2^{4+}$

Table 4. Observed and calculated structure factors for BiOF.

h	k	l	$|F_{obs}|$	$|F_{calc}|$	h	k	l	$|F_{obs}|$	$|F_{calc}|$
1	1	0	142.0	137.0	4	0	3	40.5	40.1
2	0	0	124.2	136.9	3	3	3	39.5	43.5
2	2	0	111.4	108.1	4	1	3	34.9	41.0
3	1	0	87.2	88.1	4	2	3	33.0	35.3
4	0	0	72.7	76.4	4	3	3	29.7	31.8
3	3	0	66.4	64.2	5	0	3	33.7	31.8
4	2	0	65.1	65.8	5	1	3	33.3	34.2
5	1	0	57.6	48.9	5	2	3	28.7	28.2
					6	0	3	26.4	22.1
1	0	1	113.1	125.0					
1	1	1	19.3	19.3	0	0	4	59.5	55.0
2	0	1	37.9	35.5	1	0	4	107.5	96.8
2	1	1	101.5	99.0	1	1	4	36.0	37.7
2	2	1	33.2	28.6	2	0	4	43.9	45.2
3	0	1	75.6	83.0	2	1	4	74.5	79.9
3	1	1	16.2	16.4	2	2	4	43.9	38.3
3	2	1	72.6	71.2	3	0	4	60.6	67.6
4	0	1	20.0	20.9	3	1	4	24.0	28.4
4	1	1	58.3	62.1	3	2	4	64.5	58.2
3	3	1	13.4	13.0	4	0	4	35.4	29.0
4	2	1	19.3	18.2	4	1	4	50.0	50.6
4	3	1	50.6	47.9	3	3	4	17.9	21.8
5	0	1	45.0	47.9	4	2	4	26.5	25.6
5	2	1	46.4	42.5	4	3	4	35.4	39.2
6	1	1	44.4	33.8	5	1	4	19.0	17.0
0	0	2	139.9	117.4	0	0	5	97.7	91.6
1	0	2	93.7	77.3	1	0	5	26.0	21.8
1	1	2	139.9	120.5	1	1	5	77.4	75.0
2	0	2	75.5	90.9	2	0	5	69.1	77.9
2	1	2	56.4	59.3	2	1	5	21.8	18.1
2	2	2	76.2	75.2	2	2	5	66.1	67.6
3	0	2	46.0	48.4	3	0	5	12.5	15.3
3	1	2	72.1	78.3	3	1	5	47.9	56.6
3	2	2	41.6	40.8	3	2	5	12.2	13.2
3	3	2	55.3	57.4	4	0	5	63.5	51.9
4	0	2	52.6	55.0	4	1	5	11.8	11.5
4	1	2	31.3	35.0	3	3	5	45.0	43.9
4	2	2	49.8	47.7	4	2	5	43.6	46.1
4	3	2	24.8	26.6	5	1	5	38.6	34.6
5	0	2	25.1	26.6					
5	1	2	42.0	44.1	1	0	6	76.3	76.1
5	2	2	23.8	23.4	2	0	6	11.4	9.8
6	0	2	31.7	29.0	2	1	6	69.1	65.8
6	1	2	19.3	18.5	3	0	6	53.1	57.3
					3	2	6	50.7	50.3
0	0	3	82.2	70.5	4	1	6	35.5	44.5
1	0	3	86.7	78.7	4	3	6	48.0	35.2
1	1	3	88.7	80.2					
2	0	3	61.1	60.4	0	0	7	67.6	59.2
2	1	3	66.4	64.4	1	0	7	16.9	18.4
2	2	3	51.3	52.4	1	1	7	58.7	61.3
3	0	3	51.9	54.6	2	0	7	46.6	51.5
					2	1	7	14.8	16.4
3	1	3	52.3	57.0	2	2	7	48.0	45.3
3	2	3	43.5	47.2	3	1	7	48.6	47.4

h k l	$|F_{obs}|$	$|F_{calc}|$	h k l	$|F_{obs}|$	$|F_{calc}|$
3 2 7	12.3	13.0	2 1 8	35.5	37.9
4 1 7	13.3	11.7	2 2 8	20.7	22.8
0 0 8	37.2	29.6	3 1 8	24.8	25.8
1 0 8	42.5	42.8	3 2 8	27.2	30.0
1 1 8	33.4	32.9	4 1 8	32.4	26.9
2 0 8	25.1	25.9			

which hitherto have not been found in any structure. The arrangement with $Bi_2O_2^{2+}$ and F_2^{2-} layers seems also to be electrostatically more favourable than an arrangement with $Bi_2F_2^{4+}$ and O_2^{4-} layers. A similar though less pronounced case, namely the coordination of Y by O and F in the compound YOF has been discussed recently by Templeton.[12] It might be remarked that the structure type thus found for BiOF is somewhat astonishing. One would for BiOF rather have expected a structure based on a CaF_2 lattice or a deformed CaF_2 lattice as exists for YOF and related compounds (cf. Wells [13]) than a structure isotypic with BiOCl.

The interatomic distances Bi—Bi, Bi—O, Bi—F, O—O, F—F, and O—F are given in Table 5 and compared there with the corresponding distances

Table 5. Interatomic distances (in Å) in the structure of BiOF compared to the corresponding distances in the structure of BiOCl.[14] X denotes F or Cl. The distances in BiOF as obtained earlier [1] are given within brackets.

Distances	BiOF			BiOCl	
Bi—4 Bi	3.694	$\pm$ 0.003	(3.71)	3.71	$\pm$ 0.01
Bi—4 Bi	3.7469	$\pm$ 0.0005	(3.748)	3.883	
Bi—4 O	2.273	$\pm$ 0.002	(2.27)	2.309	$\pm$ 0.004
Bi— X	2.92	$\pm$ 0.06	(2.74)	3.49	$\pm$ 0.04
Bi—4 X	2.75	$\pm$ 0.02	(2.77)	3.07	$\pm$ 0.02
O —4 O	2.6494	$\pm$ 0.0004	(2.64)	2.7457	
O —4 X	2.75	$\pm$ 0.05	(2.86)	3.25	$\pm$ 0.03
X —4 X	3.44	$\pm$ 0.08	(3.22)	3.48	$\pm$ 0.05

in the isotypic compound BiOCl. The distances for BiOCl are those given in Ref.[14] It is seen from this table that the differences in all corresponding distances in the structures of BiOF and BiOCl can be explained from the fact that the F^- ion is smaller than the Cl^- ion. The Bi—O distances 2.273 $\pm$ 0.002 Å agree well with those found in other structures containing layers $Bi_2O_2^{2+}$, *e.g.* BiOCl (2.309 $\pm$ 0.004 Å) and $Bi_4Ti_3O_{12}$ (2.29 Å).[15]

The metal atoms are nine-coordinated in BiOF as in PbFCl and BiOCl. Four oxygen atoms and four fluorine atoms together form a square antiprism deformed along its fourfold axis and one fluorine atom is situated outside the largest square face of this polyhedron. Though the standard deviations inherent in the Bi-F distances are large it seems probable that the anion lying outside the square antiprism has a larger distance to the central metal ion than have the anions belonging to the antiprism, which indeed can be

proved for the structure of BiOCl, *cf.* Table 5. Conclusively it might be stated that the structure of BiOF fits well in the series of structures of the compounds BiOCl, BiOBr and BiOI.

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