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A. I. ZASLAVSKII and A. G. TUTOV

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Abstract

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PHYSICS

A. I. ZASLAVSKII and A. G. TUTOV

STRUCTURE OF THE NEW ANTIFERROMAGNET $BiFeO_3$

(Presented by Academician A. F. Ioffe, 20 VI 1960)

In connection with the work on the search for new ferromagnetic semiconductors being carried out in the ferrites and ferroelectrics laboratory of the Institute of Semiconductors of the Academy of Sciences of the USSR, a compound of composition $BiFeO_3$, which is an antiferromagnet, was synthesized.

Polycrystalline samples of $BiFeO_3$ were prepared by the usual ceramic technology. The temperature of the preliminary firing was 750°, and of the final firing 800°. The fact that the sample was available only in powder form determined the course of the X-ray structural investigation. The powder pattern of $BiFeO_3$ was obtained in a VRS-3 camera of diameter 143 mm using Cu $K\alpha$ radiation. The interplanar spacings were corrected according to a correction curve constructed for this camera and this radiation. NH_4Br was used as the standard substance ($a = 4.051$ kX).

From the X-ray pattern it could be concluded that $BiFeO_3$ has a unit cell close to cubic, with a small rhombohedral distortion.

Using the hexagonal curves of T. B. Buerger (^{1}), a reliable indexing of the first 13 lines was carried out. All subsequent work on the analysis of the structure was performed in hexagonal coordinates. Complete indexing of all 54 reflections of the powder pattern was carried out with the aid of de Wolff' s scheme of Q values in the reciprocal lattice (^{2}).

From the calculated parameters of the hexagonal cell ($a = 5.569 \pm 0.002$ kX; $c = 6.920 \pm 0.004$ kX) and the pycnometric density $\delta_{\text{op}} = 8.31$ g/cm^3, the number of "molecules" of $BiFeO_3$ for the hexagonal cell was determined to be $Z = 3$. Hence the X-ray density is $\delta_X = 8.39$ g/cm^3. The systematic absences of reflections corresponded to the rhombohedral condition$-H + K + L = 3n$.

From the extinctions the possible space groups were established (^{3}): 146. $R3$; 148. $R\bar{3}$; 155. $R32$; 160. $R3m$ and 166. $R\bar{3}m$.

By constructing the Patterson–Harker interatomic-vector function $P(00z)$ along the direction (0001), the vector $\mathbf{u} = 1/2$, corresponding to the Bi—Fe distance, was determined. In the present case this conclusion and simple crystal-chemical considerations made it possible to choose space group 166. $R\bar{3}m$. The coordinates of the ions Bi^{3+}, Fe^{3+}, and O^{2-} were determined by trial and error. The experimental intensities were obtained on a URS-50I diffractometer using Cu $K\alpha$ radiation. Because of the rapid decrease of intensity with increasing diffraction angle, the intensities of only the first 26 reflections were measured. The diffractogram was recalculated with allowance for counter losses according to the formula

$$N = N_0/(1 - \tau N_0),$$

where N is the corrected number of pulses; N_0 is the measured number of pulses; τ is the time constant, equal to $2 \cdot 10^{-4}$ sec.

In view of the presence of groups of closely spaced reflections, their total integral intensity was determined by the weighing method. The division of the group into separate values was carried out proportionally

calculated values I_{HKL}, which were calculated by the formula $I_{HKL} = LPF^2$.

Table 1

Interplanar spacings and intensities of the $BiFeO_3$ powder pattern

hkl *	d_{obs}	d_{calc}	I_{obs}	I_{calc}	hkl	d_{obs}	d_{calc}
100	3.946	3.957	140	120	400	0.9889	0.9892
110	2.809	2.812	171	192	322	0.9685	0.9685
$10\bar{3}$	2.782	2.785	161	182	410	0.9621	0.9620
111	2.308	2.307	23	23	$40\bar{1}$	0.9580	0.9575
$10\bar{1}$	2.273	2.278	65	65	411	0.9375	0.9372
200	1.976	1.978	100	100	$\bar{4}11$	0.9319	0.9322
210	1.775	1.776	72	60	$30\bar{3}$	0.9289	0.9282
$20\bar{1}$	1.761	1.763	37	31	331	0.9149	0.9148
211	1.626	1.629	45	40	$33\bar{1}$	0.9088	0.9092
$21\bar{1}$	1.613	1.613	83	75	$31\bar{3}$	0.9041	0.9037
$11\bar{2}$	1.607	1.608	42	38	420	0.8885	0.8882
220	1.405	1.406	24	33	$40\bar{2}$	0.8813	0.8815
$20\bar{2}$	1.390	1.392	23	32	421	0.8693	0.8691
221	1.330	1.330	7	8	$42\bar{1}$	0.8644	0.8643
300	1.319	1.319	6	7	$41\bar{2}$	0.8618	0.8611
$21\bar{2}$	1.314	1.313	36	39	332	0.8518	0.8515
310	1.254	1.255	29	34	$33\bar{2}$	0.8427	0.8425
$30\bar{1}$	1.248	1.248	28	33	323	0.8403	0.8404
311	1.200	1.200	9	5	422	0.8147	0.8143

hkl *	d_{obs}	d_{calc}	I_{obs}	I_{calc}	*hkl*	d_{obs}	d_{calc}
$31\bar{1}$	1.191	1.192	18	11	$42\bar{2}$	0.8065	0.8065
222	1.138	1.139	44	48	$22\bar{4}$	0.8041	0.8043
320	1.102	1.102	13	9	430	0.7952	0.7951
$30\bar{2}$	1.092	1.092	13	8	500	0.7914	0.7914
321	1.066	1.066	22	22	$40\bar{3}$	0.7878	0.7878
$32\bar{1}$	1.058	1.058	22	22	431	0.7817	0.7815
$31\bar{2}$	1.053	1.054	22	22	$43\bar{1}$	0.7776	0.7775
					$50\bar{1}$	0.7745	0.7746
					$31\bar{4}$	0.7728	0.7729

* *hkl*—rhombohedral indices.

Table 2

Ion	Neighbors	Number of neighbors	Distance in kX	Sum of ionic radii * in kX
Bi^{3+}	O^{2-}	6	2.785 (in the layer)2.812 (between layers)	2.70
Fe^{3+}	O^{2-}	6	1.978	2.03
O^{2-}	O^{2-}	4	2.785 (in the layer)2.812 (between layers)	2.72

* Ionic radii were taken according to N. V. Belov and G. B. Bokii (5), with allowance for the correction for coordination number.

In view of the comparison of intensities for relatively small values $s = \sin\vartheta/\lambda \leqslant 0.475$, no temperature correction was introduced. Nor was a dispersion correction introduced for Fe^{3+} because of the large atomic

bismuth numbers. All intensities were reduced to the 200 reflection, taken as 100. Table 1 shows good agreement between the experimental and calculated intensities. The “reliability factor” [4]

$$R = \sum ||F_{\text{exp}}| - |F_{\text{calc}}|| / \sum |F_{\text{exp}}| = 0.09.$$

Passing from the hexagonal cell to the rhombohedral one, we obtain the following characteristics:

Fig. 1

Figure 1: Fig. 1

$$a_{rh} = 3.952 \pm 0.001 \text{ kX}; \qquad \alpha_{rh} = 89°36' \pm 3'; \qquad Z = 1.$$

The coordinates of the atoms in the rhombohedral cell are:

$$\begin{aligned} \text{Bi}^{3+}: &\quad (1a),\ 000. \\ \text{Fe}^{3+}: &\quad (1b),\ \tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2}. \\ \text{O}^{2-}: &\quad (3e),\ 0\,\tfrac{1}{2}\,\tfrac{1}{2};\ \tfrac{1}{2}\,0\,\tfrac{1}{2};\ \tfrac{1}{2}\,\tfrac{1}{2}\,0. \end{aligned}$$

Figure 1 shows the hexagonal cell of $BiFeO_3$ with the rhombohedral cell singled out. Directly from the arrangement of the ions it is seen that the structure of $BiFeO_3$ belongs to the perovskite type. The oxygen and bismuth ions together form an almost complete cubic close-packed arrangement. The coordination polyhedra are an "oxygen" cuboctahedron for bismuth and an "oxygen" octahedron for iron. The polyhedra are only slightly distorted. The most important interatomic distances in the structure are compared with the ionic radii and presented in Table 2.

Fig. 1

It is known that the geometrical criterion

$$t = (r_A + r_O)/\sqrt{2}(r_B + r_O),$$

where r_A is the radius of ion A, r_B is the radius of ion B, and r_O is the radius of the oxygen ion, for compounds crystallizing in a structure of the perovskite type lies in the range from 0.8 to 1.05. In our case $t_{\text{BiFeO}_3} = 0.89$.

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Institute of Semiconductors
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.