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Abstract

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ELECTRON-DIFFRACTION STUDY OF THE CRYSTAL STRUCTURE OF $BiFeO_3$

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Among materials possessing simultaneously special magnetic and electrical properties, an important place is occupied by the ferroelectric antiferromagnet $BiFeO_3$. This compound has a very high Curie point $T_K \sim 850°$ (^{1,2}) and a sufficiently high Néel point $T_N \sim 370°$ ($^{3-5}$), which is favorable for obtaining, on its basis, practically important materials with a desired combination of special magnetic and electrical properties.

To explain the special properties of this compound, structural data on the directions and magnitudes of displacements of atoms from their positions in the cell above T_K are important. According to (^{1,6,7}), $BiFeO_3$ has a perovskite-type structure with a rhombohedral distortion. In (^{7}) an attempt was made to establish the structure of this substance from powder-pattern data. According to (^{7}), the $BiFeO_3$ cell has the centrosymmetric space group $R\bar{3}m$. The authors found no displacements of atoms from their positions in the ideal perovskite cell. These results contradict the conclusions of (^{1,2}) on the presence of ferroelectric properties in $BiFeO_3$. Thus, the structure of the compound could not be considered solved.

In the present work the structure of $BiFeO_3$ was investigated by the method of electron diffraction. This method was chosen in order to overcome the difficulties associated with the absence of sufficiently large single crystals required for X-ray and neutron-diffraction investigations.

As the diffraction instrument, a UEMB-100 electron microscope with an accelerating voltage of 75 kV was used. The microdiffraction system made it possible to obtain a diffraction pattern from a region of the order of several microns. To obtain the objects for investigation, $BiFeO_3$ ceramics were used, prepared from Bi_2O_3 and Fe_2O_3 oxides (of, respectively, chemically pure and analytically pure grades) by a single firing at 780° for 1 hour.

X-ray analysis showed, first, the practical single-phase character of this ceramic, and, second, confirmed the perovskite structure of $BiFeO_3$ with rhombohedral distortion ($a = 3.962$ Å$, \alpha = 89°31'$). The ceramic obtained was thoroughly ground in an agate mortar for several hours; then a suspension was prepared in a solution of 50% ethyl alcohol and 50% water. After settling, the finest dispersed part of the suspension was taken with a pipette and deposited on the collodion substrate of the specimen grid of the microscope. During grinding of the ceramic and formation of the suspension, its cleavage occurs down to monocrystalline plates with a thickness of hundreds of ångströms, which are suitable for obtaining diffraction in the electron microscope. These micro-single-crystals were examined in the electron microscope, and electron-diffraction patterns were obtained from the best of them; these were subsequently used for structural analysis. The intensities of the reflections were estimated microphotometrically with an accuracy of about 20%. From the electron-diffraction data, a Fourier synthesis was carried out in the form of a projection of the potential onto the coordinate plane ($hk0$). The work on summing the series was carried out on the "Strela" computer.

From $BiFeO_3$ microcrystals, spot electron-diffraction patterns were obtained in the electron microscope, representing a section of the reciprocal lattice of the crystal by the coordinate plane. Analysis of the electron-diffraction patterns showed that the unit-cell period of $BiFeO_3$ is $a = 3.9$ Å, and the angle is $\sim 90^\circ$. An important stage of the investigation was determination of the character of scattering by $\cdots$

according to the method described in (⁀8). The scattering proved to be close to kinematical; the transition to structural amplitudes was carried out by the formula $|\Phi| \sim \sqrt{I}$, where I is the integral intensity. To determine the phases of the structural amplitudes, non-centrosymmetric models were used in which the interatomic distance between Bi and Fe was varied. In these first syntheses, the positions of the oxygen atoms were specified without displacement from their sites at the face centers of the perovskite cell. The criteria for the correctness of the structure were the following features: absence of "extra" peaks in the synthesis pattern, an approximately correct ratio of the potential values at the atomic centers, reasonable interatomic distances, and the minimum value of the reliability coefficient R (⁀8).

As a result of the synthesis, displacements of oxygen atoms were automatically revealed, although these had not been specified beforehand. The direction and magnitude of the oxygen-atom displacements were confirmed by difference synthesis (with Bi and Fe subtracted). By successively carrying out syntheses using refined data until the atomic coordinates ceased to change, it was possible to reduce R to 0.17. The final results of the synthesis show that the Bi and Fe atoms in the $BiFeO_3$ cell are displaced along the body diagonal, while the oxygen framework is appreciably distorted (see Tables 1 and 2).

Table 1

Coordinates of atoms in the $BiFeO_3$ cell
(the cell is fixed by the position of the Fe atom 0.500; 0.500; 0.500)

	x/a	y/a	z/a
Bi	0.0337	0.0337	0.0337
Fe	0.500	0.500	0.500
O_I	−0.025	0.500	0.500
O_{II}	0.500	−0.025	−0.500
O_{III}	0.500	0.500	0.025

Table 2

Interatomic distances in $BiFeO_3$ (in Å)

	Displacement $\delta = 0$	Displacement $\delta \neq 0$
Bi–Fe	3.43	3.66
Bi–Fe	3.43	3.20
$(Fe—O)_I$	1.98	2.08
$(Fe—O)_{II}$	1.98	1.88
$(Bi—O)_I$	2.79	2.62
$(Bi—O)_{II}$	2.79	3.00

From the synthesis pattern it may be concluded that, within the error of determining the atomic coordinates, the projection of the atoms of the $BiFeO_3$ cell onto the coordinate plane has a line of symmetry passing through the Bi and Fe atoms, which makes it possible to assign to this compound the non-centrosymmetric space group $R3m$.

Thus, as a result of the electron-diffraction analysis, independent structural data have been obtained which indicate that $BiFeO_3$ belongs to one of the pyroelectric space groups that do not exclude the existence of ferroelectric properties in this compound, the conclusion as to the presence of which was made in (^1). Judging from the established magnitudes of the displacements, $BiFeO_3$ may be assigned to "ferroelectric-rigid" materials, as had already been indicated in (^2).

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