# X-RAY STUDY OF PHASE TRANSITIONS IN BISMUTH FERRITE

CRYSTALLOGRAPHY

1966

SovietRxiv

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## Abstract

## Full Text

UDC 548.736

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# X-RAY STUDY OF PHASE TRANSITIONS IN BISMUTH FERRITE

*(Presented by Academician N. V. Belov, December 8, 1965)*

Bismuth ferrite $BiFeO_3$ is an antiferromagnet with weak ferromagnetism, with a Néel temperature of 370°, and is a ferroelectric or antiferroelectric ($^{1-5}$). Because of its high electrical conductivity, its Curie temperature $T_K$ has been estimated radiographically by extrapolating the $T_K$ of some of its solid solutions, and was found to be $T_K = 850°$ ($^2$). High-temperature X-ray investigation of $BiFeO_3$ carried out up to 700° ($^6$) revealed no phase transitions. In ($^7$), X-ray and dielectric studies found a transition near 370°. A more detailed X-ray study of bismuth ferrite up to 750° was carried out by us ($^8$). The high resolving power of the method we used made it possible to detect, in addition to the transition at $\sim 375°$, a second transition at about 575°. However, in the most important interval, 750–850°, $BiFeO_3$ had not been investigated. Therefore, up to the present time, the $T_K$ of this compound had not been directly established. The nature of the phase transition also remained unclear, as did the structural changes occurring in it, in particular changes in cell symmetry. The present work is devoted to these questions.

Ceramic $BiFeO_3$ was prepared at the Institute of Semiconductors of the Academy of Sciences of the USSR. The starting materials were $Bi_2O_3$ and $Fe_2O_3$ (chemically pure). Preliminary firing was carried out at 700° with a holding time of 4 hours, and final firing at 800° for 15 min. The high-temperature X-ray investigation was performed, as in previous works ($^9$,$^{10}$), by the ionization method on a URS-50I X-ray diffractometer using iron radiation ($\lambda K_{\alpha_1} = 1.93597$ Å). The reflections $200_{\alpha_1}$, $220_{\alpha_1}$, $\bar{2}20_{\alpha_1}$, and $\bar{2}22_{\alpha_1}$ were used as calculation maxima. The value of the rhombohedral angle $\alpha_{\text{Rh}}$ was calculated from the reflections $220_{\alpha_1}$ and $\bar{2}20_{\alpha_1}$, between which there is a considerable angular separation ($\Delta 2\theta \sim 66'$). The positions of the maxima up to 750° were determined by point-by-point tracing of the pulses; above this, by a lamp voltmeter. In the latter case, the time

**Fig. 1.** Temperature dependence of the cell parameters of $BiFeO_3$.

the recording of one maximum was 2-3 min, which made it possible, long before any substantial decomposition of $BiFeO_3$ occurred, to determine the cell parameters. The latter were found with an accuracy of $\Delta a_{Rh} = \pm 0.001$ Å, $\Delta \alpha_{Rh} = \pm 1'$, and $\Delta v = \pm 0.05$ Å$^3$. In the interval 20-850°, X-ray diffraction photographs were taken at 38 temperatures.

The temperature dependence of the cell parameters is presented in Fig. 1. In the same figure, for 825, 835, and 850°, the maxima $220_{\alpha_1}$ and $\bar{2}20_{\alpha_1}$ are shown. As is seen from the figure, in bismuth ferrite in the interval 20-850° there occur 7 phase transitions, of which only 2 had previously been known: at 370-375° ($^7$, $^8$) and at 575° ($^8$). Some structural changes also occur at $\sim 645$ and $\sim 750°$; they may also be connected with phase transitions. At 845° there is an abrupt change in the parameters, but the rhombohedral symmetry of the cell remains unchanged.

Recently V. V. Zhdanova carried out a dilatometric study of $BiFeO_3$ and found 7 phase transitions, in good agreement with those established by us: at 124; 200; 278; 370-380; 485-490; 580; and 835-845°. The transition found by us at $\sim 845°$ had earlier been established indirectly at a temperature of 850°, taken as the Curie temperature of $BiFeO_3$ ($^{1-3}$). However, in solid solutions of the system $BiFeO_3{-}Pb(Fe_{0.5}Nb_{0.5})O_3$, where the second component also has a rhombohedral cell, the transition from the ferroelectric or antiferroelectric state to the paraelectric one is accompanied by a transition of the rhombohedral cell into a cubic one ($^8$). It is natural that the same change in cell symmetry will occur at the Curie point of $BiFeO_3$ itself. Therefore 845-850° is not the Curie point of bismuth ferrite. In ($^8$), extrapolation of the Curie point of solid solutions in the direction of $BiFeO_3$ gave $T_K \sim 900°$. In the present work, the course of convergence of $220_{\alpha_1}$ and $\bar{2}20_{\alpha_1}$ at $800 \to 825 \to 835 \to 850°$ gives for $BiFeO_3$ an approximate value $T_K \cong 875$-880°. The question whether bismuth ferrite is a ferroelectric or an antiferroelectric has not yet been decided unambiguously. A neutron-diffraction study by G. S. Zhdanov and co-workers ($^{11}$) showed that the period of the magnetic elementary cell of $BiFeO_3$, in comparison with the simple perovskite cell, is doubled. On the other hand, it has been established that $BiFeO_3$ is an antiferromagnet possessing weak ferromagnetism ($^{2-5}$), and this requires the obligatory coincidence of the magnetic and crystallographic elementary cells ($^{12}$). Therefore, if the results of ($^{11}$) are correct (of which there can be no doubt), then the true crystallographic cell of $BiFeO_3$ must also be a multiple of the simple perovskite cell with $a = 2a_p$.

It turned out that this is indeed the case: on Debye photographs taken in an RKU-114M camera with Fe radiation, we found 9 lines that cannot be indexed in the simple $BiFeO_3$ cell and do not belong to $Bi_2O_3$, $Fe_2O_3$, or $Bi_2O$(_3 )$2Fe_2O_3$. They are well indexed when the period of the simple cell is doubled, $a = 2 \cdot 3.963$ Å:

| $hkl$ | 211 | 221 | 731 | $7\bar{3}1$ | $\bar{7}31$ | 732 | $7\bar{3}2$ | $\bar{7}32$ | $\bar{8}10$ |
|---|---|---|---|---|---|---|---|---|---|
| $d_{hkl}$, Å | 3.186 | 2.705 | 1.034 | 1.029 | 1.025 | 1.010 | 1.004 | 0.998 | 0.996 |
| Intensity | v. weak | v. weak | med.-weak | med.-weak | med.-weak | med.-weak | weak | weak | med.-weak |

Thus, our X-ray data, in agreement with the magnetic data, indicate the presence in the $BiFeO_3$ elementary cell of a superstructure, caused in the present case by antiparallel displacements of the ions in the cell. Consequently, bismuth ferrite is an antiferroelectric–antiferromagnet with a transition temperature from the antipolarized state (rhombohedral phase) to the paraelectric one (cubic phase) $T_K \sim 875°$. Apparently, the phase transitions existing below $\sim 875°$, or some of them, are also antiferroelectric transitions. The presence of a large number of transitions in $BiFeO_3$ (similar to the antiferroelectric $NaNbO_3$, in which in the interval 20–650°

the discovery of 6 phase transitions (13) indicates a more complex picture of ion displacements in its cell than has been established up to the present. Therefore it is necessary to carry out a detailed neutron-diffraction investigation of the atomic structure of bismuth ferrite on single crystals.

I express my deep gratitude to Prof. G. S. Zhdanov and Prof. G. A. Smolenskii for useful advice, to N. N. Krainik for providing the $BiFeO_3$ specimen, and to V. V. Zhdanova for kindly communicating the dilatometric-measurement data.

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Received
3 XII 1965

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