

THE NATURE OF THE DIELECTRIC AND MAGNETIC PROPERTIES OF  $\text{BiFeO}_3$ 

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Submitted to JETP editor August 17, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) 50, 69-75 (January, 1966)

The dielectric properties of  $\text{BiFeO}_3$  are investigated in the ultrahigh frequency range. High-temperature x-ray diffraction investigations of this compound and of a number of solid solutions of the system  $\text{BiFeO}_3\text{-PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  are carried out. All the available data on  $\text{BiFeO}_3$  are analyzed, and it is concluded that in  $\text{BiFeO}_3$  below the Néel point ( $370^\circ\text{C}$ ) compensated ferromagnetism is combined with ferroelectricity.

## INTRODUCTION

THERE are many papers on  $\text{BiFeO}_3$ , but there is so far, unfortunately, no unanimity on the nature of the properties of this compound. Thus, while in [1, 2] it is concluded that  $\text{BiFeO}_3$  is a ferroelectric, it is assumed in [3, 4] that it has no polarized state. At the same time [5, 6] subsequently admit the presence of special dielectric properties, but the conclusion is drawn that their nature is rather antiferroelectric than ferroelectric. And further, while the presence of magnetic ordering in  $\text{BiFeO}_3$  is no longer doubted, its nature (collinear or anti-collinear antiferromagnetism) cannot as yet be considered reliably established (see below).

In order to resolve these contradictions, we have in this paper, in addition to an analysis of the literature data, carried out the following:

1) An additional investigation of the dielectric properties and structure of  $\text{BiFeO}_3$  in a broad range of temperatures;

2) a new, careful investigation of solid solutions in the  $\text{BiFeO}_3\text{-PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  system from the side of  $\text{BiFeO}_3$ .

We present below the results of these investigations, and a conclusion is reached on the nature of the properties of  $\text{BiFeO}_3$ .

## EXPERIMENTAL DATA

1. An investigation of the frequency dependence of the dielectric permittivity and the tangent of the dielectric losses of  $\text{BiFeO}_3$  showed dispersion of  $\epsilon$  and a maximum of  $\tan \delta$  in the region of 200 Mcs (Fig. 1). These results are analogous to data on the frequency dependence of these dielectric parameters in ferroelectrics of the type  $\text{BaTiO}_3$ . [10] A special feature of  $\text{BiFeO}_3$  is the dispersion fre-

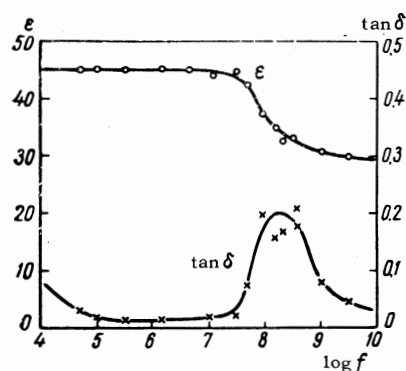


FIG. 1. The frequency dependence of the dielectric permittivity  $\epsilon$  and of the dielectric loss tangent  $\tan \delta$  in  $\text{BiFeO}_3$ .

quency which is smaller by an order of magnitude compared with the indicated ferroelectrics. Measurements of the reversible dielectric constant in bias fields up to 30 kV/cm in a weak ultrahigh-frequency field exhibited no nonlinearity of  $\epsilon$ .

2. In [11, 12] temperature investigations of the unit-cell parameters of  $\text{BiFeO}_3$  and also dielectric and magnetic measurements were carried out which made it possible to establish anomalous changes in the parameters, and a point of inflexion on the  $\epsilon(t)$  curve at the Néel point ( $T_N = 370^\circ\text{C}$ ). In a recent paper [5] a number of anomalies were observed in this curve in the region of  $420\text{--}500^\circ\text{C}$  both in pure  $\text{BiFeO}_3$  and in solid solutions  $\text{BiFeO}_3\text{-PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  on the side of  $\text{BiFeO}_3$ , where a sharper high-temperature maximum of  $\epsilon$  was observed in compositions containing from 10 to 40 mole % in addition to these anomalies. The origin of these anomalies remained unexplained. In this connection we have undertaken new dielectric and x-ray temperature investigations of  $\text{BiFeO}_3$ , more detailed than in [11, 12], (particularly

careful investigations were carried out in the region of 400–500°C), as well as investigations of solid solutions of the system  $\text{BiFeO}_3$ – $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  which will hereafter be denoted by (Fe,Nb). The polycrystalline samples for the investigations were prepared by the usual ceramic techniques. The compositions differed in the  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  content by 1–2 mole %. Samples with a  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  content up to 5% and  $\text{BiFeO}_3$  were annealed for two hours in air at 750°C, the others—at 850°C. The x-ray investigations at 20°C were carried out with  $\text{CoK}\alpha$  radiation in RKU-114 cameras, and the high-temperature studies were carried out using  $\text{FeK}\alpha$  radiation. The accuracy of the parameter determination of the perovskite cells amounted to  $\pm 0.001$  Å and that of the angles to  $\pm 1'$ .

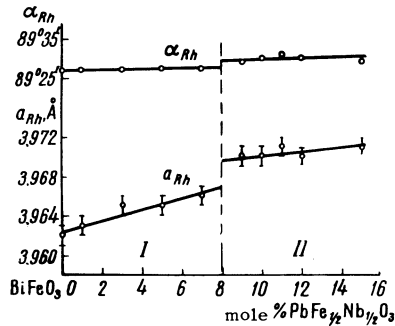


FIG. 2. Dependence of the angle and unit cell parameter of the solid solutions  $\text{BiFeO}_3$ – $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  on the composition.

Figure 2 shows the values of the lattice parameter and angle of the rhombohedral perovskite cell for various compositions of the investigated solid solutions. At 8 mole % of  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  a jump-like increase in the lattice parameters is observed, i.e., a morphotropic phase transition takes place in which the rhombohedral modification I which exists in the range of  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  concentrations from 0 to 8 mole % is replaced by another rhombohedral modification II.

High-temperature x-ray studies were carried out on a  $\text{BiFeO}_3$  sample and also on compositions containing 5 mole %  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  which belong to the rhombohedral modification I, and with 15 mole %  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  belonging to modification II (hereafter these are denoted by 5 and 15 respectively). The results of the investigation are presented on Figs. 3–5.

Figure 3 also shows data on the temperature dependence of  $\epsilon$  and  $\tan \delta$  measured at a frequency of 300 Mcs by the coaxial measuring line method,<sup>[22]</sup> and a curve of the temperature de-

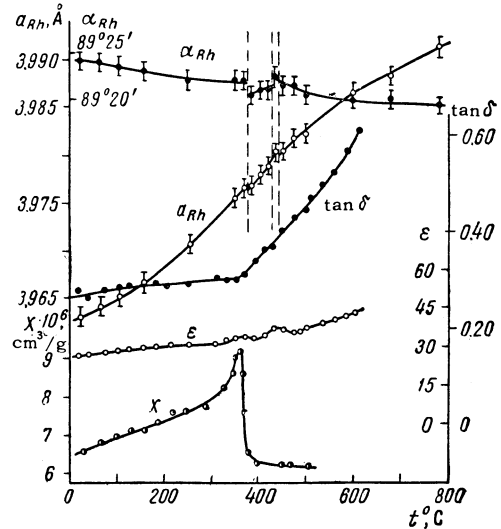


FIG. 3. Temperature dependence of the unit cell parameters in  $\text{BiFeO}_3$ .

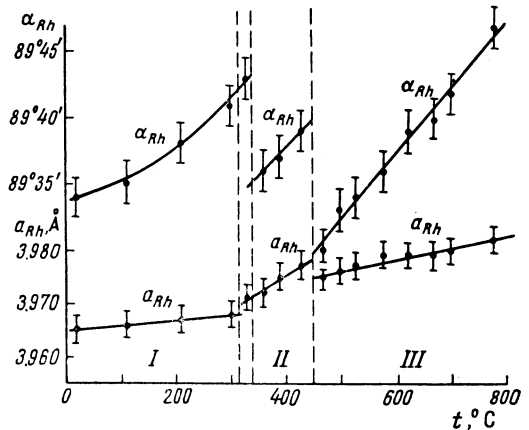


FIG. 4. Temperature dependence of the unit-cell parameters of the composition  $0.95\text{BiFeO}_3$ – $0.05\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ .

pendence of the magnetic susceptibility obtained in<sup>[9]</sup>. Comparison of the structure data with the results of the magnetic investigations of solid solutions of (Fe,Nb)<sup>[13]</sup> and  $\text{BiFeO}_3$  indicates that at the Néel point there occurs in all samples a jump-like change in the parameters of the perovskite cell within the same rhombohedral modification.

It is interesting to note that at the Néel point in  $\text{BiFeO}_3$  a small anomaly is observed on the  $\epsilon(t)$  and  $\tan \delta(t)$  curves which agrees with previous results.<sup>[12]</sup> A comparison of the temperature dependences of the parameters of  $\text{BiFeO}_3$  and the 5 and 15 compositions with the data of the dielectric investigations at frequencies of 1–59 Mcs<sup>[5]</sup> and our results on  $\text{BiFeO}_3$  at 300 Mcs indicates that in the region of the diffuse maxima on the  $\epsilon(t)$  curve in  $\text{BiFeO}_3$  and in the sample with the 5 composition, as well as in the region of the step on the

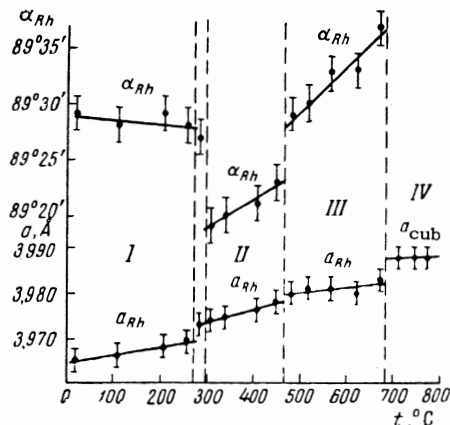


FIG. 5. Temperature dependence of the unit-cell parameters of the composition  $0.85\text{BiFeO}_3 - 0.15\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ . I, II, III – various rhombohedral modifications, IV – cubic modification.

$\epsilon(t)$  curve in the sample with the 15 composition, jumps are observed in the magnitude of the rhombohedral distortion angle, as well as certain anomalies in the change of the parameters of the perovskite unit cells. In principle there is obviously no difference between these phase transitions and they probably all are the result of a jump-like change in the ion displacements within the same rhombohedral symmetry of the unit cell. A certain difference between these phase transitions [the diffuse maximum on the  $\epsilon(t)$  curve of  $\text{BiFeO}_3$  and of the sample with the 5 composition, the step in the sample with the 15 composition, and the different behavior of  $\alpha_{\text{Rh}}$ ] can moreover be explained by the fact that according to Fig. 2 the  $\text{BiFeO}_3$  and the sample with the 5 composition belong to the rhombohedral modification I, whereas the sample with the 15 composition belongs to modification II. The unit cells of  $\text{BiFeO}_3$  and of the sample with the 5 composition remain rhombohedral up to their decomposition which commences at  $760\text{--}780^\circ\text{C}$ ; in the 15 composition a transition is observed of the rhombohedral modification to the cubic at  $680^\circ$ .

3. The determination of the atomic structure of  $\text{BiFeO}_3$  (the determination of the atomic displacements) was carried out in <sup>[14]</sup> by means of electron microdiffraction. According to these electron-diffraction data  $\text{BiFeO}_3$  has the noncentrosymmetric space group  $R3m$  typical of pyroelectrics and ferroelectrics.

At the same time, a superstructure cell of the type of  $\text{LaAlO}_3$  with two formula units  $\text{ABO}_3$  was proposed for  $\text{BiFeO}_3$  in <sup>[15]</sup> on the basis of three additional neutron-diffraction reflections of  $\text{BiFeO}_3$  treated as the result of antiparallel displacement of the oxygen atoms, and a conclusion was drawn

about the presence of antiferroelectric properties in bismuth ferrite.

In connection with these two mutually exclusive results, we carried out additional work investigating the possibility of the existence of an atomic superstructure in  $\text{BiFeO}_3$  by using electron and x-ray diffraction data. The latter were obtained with  $\text{BiFeO}_3$  single crystals grown by V. M. Skorikov. <sup>[16]</sup>

From an analysis of several variants of the superstructure model corresponding to displacement of the heavy atoms (bismuth and iron), as well as the displacement of only the light (oxygen) atoms it was possible to conclude that there can be no antiparallel displacement of the atoms (in antiparallel displacement a sharp discrepancy is observed with the experimental data). Further investigations in this direction, presented in detail in <sup>[16]</sup>, also showed the equivalence of the displacements of the same types of atoms in the perovskite subcells constituting the superstructure. The latter leads automatically to a simple perovskite unit cell with the previously established displacements of the atoms. <sup>[14]</sup>

Thus our x-ray and electron-diffraction data indicate the absence of atomic superstructure in  $\text{BiFeO}_3$ . As regards the three additional lines on the neutron polycrystalline  $\text{BiFeO}_3$  patterns and a series of "superfluous" reflections observed on x-ray patterns of solid solutions (Fe, Nb) from the  $\text{BiFeO}_3$  side, which have been taken in <sup>[15, 17]</sup> to be due to superstructure, our analysis <sup>[18]</sup> showed that these lines are due to the presence of a second phase of the composition  $\text{Bi}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3$ .

## DISCUSSION OF RESULTS

1. The nature of the dielectric properties of  $\text{BiFeO}_3$ . The specific properties of  $\text{BiFeO}_3$  (as shown in a calculation in <sup>[19]</sup>, the spontaneous electric polarization is very high) excluded the possibility of obtaining dielectric hysteresis loops, whereas the lack of sufficiently large single crystals makes it difficult to establish the domain structure. In view of this, conclusions about the dielectric properties of  $\text{BiFeO}_3$  have to be drawn from the aggregate of other experimental facts.

In our opinion, the following previously known facts and data obtained in this work may provide evidence indicating the presence of ferroelectric properties in  $\text{BiFeO}_3$ :

a) The presence of a continuous series of solid solutions in the  $\text{PbTiO}_3\text{--BiFeO}_3$  system and the increase in the Curie temperature of this system practically up to pure  $\text{BiFeO}_3$ ; <sup>[2]</sup>

b) the presence of maxima on the temperature dependences of the dielectric permittivity  $\epsilon$  in some solid solutions based on  $\text{BiFeO}_3$  (for example, in the system  $\text{BiFeO}_3\text{-PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ );<sup>[5]</sup>

c) structure data on the noncentrosymmetric space group of  $\text{BiFeO}_3$  and the lack of atomic superstructure; the rhombohedral cell distortion ( $\alpha_{\text{Rh}} < 90^\circ$ ) typical of ferroelectrics;

d) data on the resonance absorption of gamma quanta in  $\text{BiFeO}_3$ <sup>[20]</sup> indicating the absence of structurally nonequivalent positions of the iron atoms (which should occur in the case of anti-ferroelectricity);

e) the frequency dispersion of the dielectric permittivity  $\epsilon$  and the maximum of the dielectric losses in the dispersion region which as a rule does not appear in antiferroelectrics.<sup>[10]</sup>

The specific properties of  $\text{BiFeO}_3$ —the large values of the internal electrical fields and of the spontaneous polarization,<sup>[19]</sup> the high Curie temperature ( $850^\circ\text{C}$ ), the absence of nonlinear properties at room temperature—show that this compound, just as  $\text{PbTiO}_3$ , is a hard ferroelectric.

In connection with the conclusions reached above concerning the ferroelectric properties of  $\text{BiFeO}_3$ , the following explanation can be offered for the high-temperature phase transitions in  $\text{BiFeO}_3$  and in samples of the (Fe, Nb) system. The transition in the sample with the 15 composition, accompanied by a change from the rhombohedral modification to cubic and by a sharp maximum in  $\epsilon(t)$ , is the ferroelectric Curie point; on the other hand, in the range of  $430\text{--}500^\circ\text{C}$  a transformation takes place both in  $\text{BiFeO}_3$  and in the 5 and 15 compositions from one ferroelectric modification to another. The phase transition from the ferroelectric modification into the paraelectric would occur both in  $\text{BiFeO}_3$  and in the sample with the 5 composition if there were no dissociation of these compositions at  $t > 700^\circ\text{C}$ . Ismailzade<sup>[21]</sup> holds an analogous opinion concerning the nature of the phase transitions in  $\text{BiFeO}_3$ . However, unlike our results, he indicates another phase transition in  $\text{BiFeO}_3$  in the region of  $575^\circ\text{C}$ .

2. The nature of the magnetic properties of  $\text{BiFeO}_3$ . As is well known, neutron diffraction investigations<sup>[7]</sup> showed the presence of a G-type antiferromagnetic structure of  $\text{BiFeO}_3$ . The presence of antiferromagnetic ordering was also established in<sup>[8, 9]</sup> by means of magnetic measurements. At the same time, although no spontaneous magnetic moment was observed in  $\text{BiFeO}_3$  either in<sup>[8]</sup> or in<sup>[9]</sup>, it was concluded, in<sup>[8]</sup> on the basis of an analysis of the character of the temperature dependence of its magnetic susceptibility

(a sharp maximum at the Néel point) and in<sup>[9]</sup> from the presence of a small spontaneous magnetic moment in solid solutions of the rhombohedral modification of the  $\text{BiFeO}_3\text{-LaFeO}_3$  system, that  $\text{BiFeO}_3$  is an antiferromagnet with weak ferromagnetism. However, as was correctly noted in<sup>[13]</sup>, by virtue of the symmetry laws ferroelectricity cannot be combined in  $\text{BiFeO}_3$  with weak ferromagnetism. The latter is only possible in structures in which the chemical and magnetic unit cells coincide.<sup>[23]</sup> On the basis of results obtained in<sup>[15]</sup> and also of data on the superstructure cell of  $\text{BiFeO}_3$  in solid solutions (Fe, Nb),<sup>[17]</sup> the small spontaneous magnetic moment present in the solid solutions (Fe, Nb) is considered in<sup>[13]</sup> to be an indication of weak ferromagnetism. This conclusion extends also to  $\text{BiFeO}_3$  in which a spontaneous moment of  $0.035\text{ G-cm}^3/\text{g}$  was determined by extrapolation of the dependence of  $m_s$  on the composition of the solid solutions. However, because at  $\sim 10\%$   $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  a maximum is observed in the dependence of  $m_s$  on the composition, and according to the results of this paper a phase transition takes place in this region from the rhombohedral modification I to modification II, the indicated extrapolation is not justified.

The sharp maximum on the curve of the temperature dependence of the specific magnetic susceptibility  $\chi(t)$  obtained with a polycrystalline sample of  $\text{BiFeO}_3$  is also not sufficient proof of the presence in this compound of weak antiferromagnetism. Only the presence of a sharp maximum in  $\chi_{\perp}(t)$  at the Néel point and its absence in  $\chi_{\parallel}(t)$  (the spontaneous moment in antiferromagnets appears in the basal plane<sup>[24]</sup>) could serve as such sufficient proof. Basing oneself on data of magnetic measurements which exhibit no spontaneous moment in  $\text{BiFeO}_3$  and on results of this paper on the lack of a superstructure cell in this compound, it must be concluded that  $\text{BiFeO}_3$  is a compensated antiferromagnet. The spontaneous moment of solid solutions of (Fe, Nb), on the other hand, is apparently due to a certain ordering of the ions in the octahedral interstices, and in the rhombohedral region of the  $\text{BiFeO}_3\text{-LaFeO}_3$  system it is apparently due to the possible presence of a small amount of the weakly ferromagnetic, pseudo-monoclinic phase I.

Thus, below  $T_N = 370^\circ\text{C}$  compensated antiferromagnetism is combined in  $\text{BiFeO}_3$  with ferroelectricity.

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Translated by Z. Barnea