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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

PHYSICS

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DETERMINATION OF THE CURIE TEMPERATURE OF THE FERROELECTRIC $BiFeO_3$

(Presented by Academician A. V. Shubnikov, 17 V 1961)

In works ([1,2]), on the basis of an X-ray study of solid solutions in the $PbTiO_3$–$BiFeO_3$ system, the conclusion was drawn that there exists a new ferroelectric –bismuth ferrite–with a Curie temperature higher than that of lead titanate.

As X-ray analysis has shown ([2]), bismuth ferrite at room temperature has a rhombohedrally distorted perovskite-type cell with parameters $a = 3.963$ Å and $\alpha = 89°24'$, which is confirmed by the data ([3,4]).

Fig. 1. Temperature dependence of the lattice parameters of bismuth ferrite

Fig. 2. Phase diagram of the $PbTiO_3$–$BiFeO_3$ system

Determination of the Curie points of bismuth ferrite and of solid solutions $(Pb, Bi)(Ti, Fe)O_3$ could not be carried out by dielectric measurements because of the high electrical conductivity of these materials (the forbidden band for bismuth ferrite has a small width, ~ 0.80 eV). The dielectric constant of the indicated materials could be measured only up to 500°, and up to this temperature no maxima were observed on the curves $\varepsilon = f(T)$ (except for lead titanate). From the form of these curves (from the way ε increased with temperature), it was possible to conclude only that the maxima lie in the temperature region above 500°.

In order to determine the Curie temperature of bismuth ferrite, high-temperature X-ray studies of this compound were undertaken; the results are presented in Fig. 1. With increasing temperature up to 800°, the period a increases, while the angle of rhombohedral distortion practically does not change. At a temperature of 700°, bismuth ferrite begins to decompose and a second crystalline phase appears. At a temperature of 800°, the sample is already dissociated to a considerable degree; the second phase is already present in a larger amount. However, up to a temperature of 800°, the principal phase is the perovskite phase with a rhombohedrally distorted cell.

Thus, high-temperature X-ray photographs of $BiFeO_3$, owing to its decomposition during long exposures, did not give a definitive answer concerning the Curie temperature of this compound.

Additional information on the Curie temperature of bismuth ferrite was obtained as a result of studying the system $PbTiO_3$—$BiFeO_3$, whose phase diagram is presented in Fig. 2. In this case, account was taken of the fact that in this system, with increasing concentration of lead titanate, the Curie temperature should decrease, while the stability of the samples should increase. The Curie points of samples with 30 and 80 wt.% $BiFeO_3$, respectively $\sim 540°$ and $\sim 750°$, were determined as a result of high-temperature X-ray measurements. The Curie temperature of the sample with 60 wt.% $BiFeO_3$ was found by extrapolating the data on the Curie temperatures of samples of the ternary system (40 wt.% $PbTiO_3$–60 wt.% $BiFeO_3$)–$LaAlO_3$, in which, with increasing lanthanum aluminate content, the Curie temperature shifts appreciably toward lower temperatures.

From the behavior of the Curie temperature in the $PbTiO_3$—$BiFeO_3$ system, the Curie temperature of bismuth ferrite may be estimated as approximately 850°. It should also be noted that earlier we established [5] that the onset of incongruent melting of bismuth ferrite occurs precisely at a temperature of $\sim 850°$. Thus, the spontaneous polarization of bismuth ferrite is retained up to the melting temperature of this compound.

The Curie temperature established for bismuth ferrite, $\sim 850°$, is very high in comparison with the Curie temperatures of other known ferroelectrics. This fact makes it possible to obtain, on the basis of bismuth ferrite, ferroelectric and piezoelectric materials with high Curie temperatures, as indicated in [6] and as is now being confirmed in practice.

In addition, owing to the presence of the iron ion in bismuth ferrite, it is possible on the basis of $BiFeO_3$ to obtain materials possessing both ferroelectric and magnetic properties, which is of great scientific and practical interest.

In conclusion, I express my gratitude to Prof. G. S. Zhdanov and Yu. N. Venevtsev for scientific guidance of the work.

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