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### SYNTHESIS OF $\text{BiFeO}_3$ MULTIFERROIC FROM $\text{Bi}_{25}\text{FeO}_{39}$ PRECURSOR AND $\text{Fe}_2\text{O}_3$ OXIDE

The ceramic method of synthesis of  $\text{BiFeO}_3$  multiferroic from  $\text{Bi}_{25}\text{FeO}_{39}$  precursor and  $\text{Fe}_2\text{O}_3$  oxide was developed. Influence of various modes of heat treatment on crystal structure of  $\text{BiFeO}_3$  is studied and the optimum conditions of synthesis are chosen. The method offered allows to reduce synthesis temperature and time in comparison with ceramic method of  $\text{BiFeO}_3$  synthesis from  $\text{Bi}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  oxides, and also allows to reduce the quantity of impurity phases from 5 to 3%.

**Introduction.** Bismuth ferrite  $\text{BiFeO}_3$  is one of the most promising compounds on the basis of which new magnetoelectric materials with high values of the electric polarization and magnetization at room temperature are developed. The connection between the magnetic and electric subsystems in multiferroics, manifested in the form of magnetoelectric effects, provides the possibility using an electric field to control the magnetic properties of the material and, vice versa, the modulation of electrical properties with the magnetic field. This allows on the basis of these compounds to develop fundamentally new magnetic storage devices and spintronics, magnetic field sensors, recording and reading information et cetera [1–4]. Although the synthesis and properties of bismuth ferrite  $\text{BiFeO}_3$  are widely studied, obtaining of single-phase sample  $\text{BiFeO}_3$  is still a serious problem.

Numerous literature data show the impossibility of obtaining  $\text{BiFeO}_3$  without impurity compounds of paramagnetic and antiferromagnetic  $\text{Bi}_{25}\text{FeO}_{39}$   $\text{Bi}_2\text{Fe}_4\text{O}_9$  during the interaction of oxides of bismuth (III) and iron (III) [5–8]. According to some authors, the formation of impurities and byproducts  $\text{Bi}_{25}\text{FeO}_{39}$   $\text{Bi}_2\text{Fe}_4\text{O}_9$  occurs not only in solid-phase synthesis method, but also in the preparation of bismuth ferrite by sol-gel technology. At a temperature of  $600^\circ\text{C}$  obtained by sol-gel method bismuth ferrite exhibits thermodynamic instability and prolonged heat treatment leads to the decomposition of  $\text{BiFeO}_3$  on  $\text{Bi}_2\text{Fe}_4\text{O}_9$  and  $\text{Bi}_{25}\text{FeO}_{39}$  according to the reaction  $49\text{BiFeO}_3 \rightarrow 12\text{Bi}_2\text{Fe}_4\text{O}_9 + \text{Bi}_{25}\text{FeO}_{39}$ . To prevent during synthesis of  $\text{BiFeO}_3$  from oxides the formation of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  phase, solid phase reactions are carried out with a large excess of  $\text{Bi}_2\text{O}_3$  [9]. However, in this case the impurities  $\text{Bi}_2\text{Fe}_4\text{O}_9$  and  $\text{Bi}_{25}\text{FeO}_{39}$ , are present which do not disappear even after additional heat treatment or bismuth ferrite leaching in dilute nitric acid [9].

The authors propose the solid-phase method of synthesis of multiferroic  $\text{BiFeO}_3$  from  $\text{Bi}_{25}\text{FeO}_{39}$  precursor and  $\text{Fe}_2\text{O}_3$  oxide and optimal conditions for obtaining the final product are selected.

**Main part.** To accomplish this goal it was necessary to perform the following tasks:

- to synthesize  $\text{Bi}_{25}\text{FeO}_{39}$  precursor from  $\text{Bi}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  oxides by the solid phase method;
- to get by the solid phase method a sample of bismuth ferrite  $\text{BiFeO}_3$  of previously prepared  $\text{Bi}_{25}\text{FeO}_{39}$  precursor and  $\text{Fe}_2\text{O}_3$  oxide;
- to examine the impact of different modes of heat treatment on the crystal structure of  $\text{BiFeO}_3$  and the presence of impurity phases.

X-ray diffractograms were obtained on a D8 ADVANCE diffractometer using  $\text{CuK}_\alpha$ -radiation. The parameters of the crystal structure were determined by X-ray spreadsheet RTP and filing data of International Centre for Diffraction Data (ICDD JCPDS).

Preliminary  $\text{Bi}_{25}\text{FeO}_{39}$  precursor from  $\text{Bi}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  oxides has been synthesized by solid phase reactions method. Powders of the starting materials, taken in a predetermined molar ratio, were mixed and milled for 30 minutes in a planetary mill with the addition of ethanol. The resulting charge was compressed with the addition of ethanol at a pressure of 50–75 MPa into tablets with a diameter of 25 mm and a height of 5–7 mm, which were then calcined at  $750^\circ\text{C}$  in air for 4 hours.

There was carried out X-ray phase analysis of the obtained  $\text{Bi}_{25}\text{FeO}_{39}$  sample, the results of which are shown in Fig. 1.

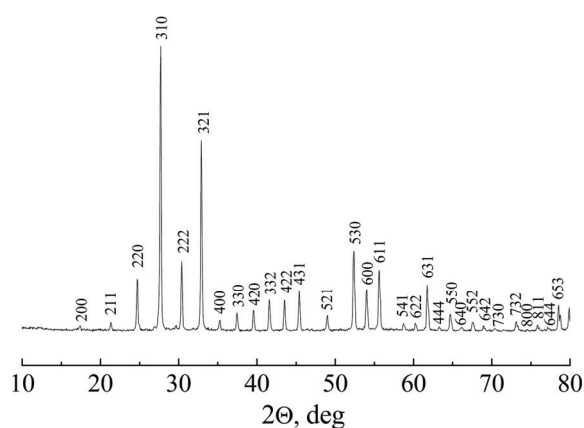
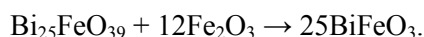


Fig. 1. X-ray diffractogram of  $\text{Bi}_{25}\text{FeO}_{39}$  ferrite, prepared from a mixture of  $\text{Bi}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  oxides

It is found that the resulting sample of  $\text{Bi}_{25}\text{FeO}_{39}$  was a single phase one and had a cubic crystal sillenite structure (sp. gr. *I23*) with lattice parameters решетки  $a = 10,1911(3) \text{ \AA}$ ,  $V = 1058,430(105) \text{ \AA}^3$ , which are in good agreement with the literature data ( $a = 10,18120 \text{ \AA}$ ,  $V = 1055,350 \text{ \AA}^3$ ) [10].

From the literature it is known that at  $790^\circ\text{C}$  the melting of eutectic occurs in the  $\text{Bi}_2\text{O}_3 - \text{Fe}_2\text{O}_3$  system, at  $850^\circ\text{C}$  – structural phase transition of  $\text{BiFeO}_3$ , at  $950^\circ\text{C}$  – incongruent melting of  $\text{BiFeO}_3$ , which indirectly indicates that the formation of the compound  $\text{BiFeO}_3$  under the heating of a mixture of  $\text{Bi}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  powders occurs at temperatures below  $850^\circ\text{C}$  [11]. These differential thermal analysis data [11] and kinetic studies [5] show that the reaction in equimolar mixture of  $\text{Bi}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  is complex. Below  $675^\circ\text{C}$  the reaction does not go to the end, at temperatures above  $675^\circ\text{C}$   $\text{BiFeO}_3$  decomposes slowly, and at temperatures above  $830^\circ\text{C}$  decomposes quickly to release  $\text{Bi}_2\text{Fe}_4\text{O}_9$  [5, 7].

That is why the solid phase synthesis of  $\text{BiFeO}_3$  was carried out at a temperature  $750^\circ\text{C}$  for 4 hours according to the reaction:



After pre-firing the tablets of  $\text{Bi}_{25}\text{FeO}_{39}$  ferrite were crushed in an agate mortar and milled in a planetary mill for 30 min with addition of ethanol and mixed in predetermined proportions with ferric oxide  $\text{Fe}_2\text{O}_3$ . The resulting charge was compressed with the addition of ethanol at a pressure of 50–75 MPa into tablets with a diameter of 25 mm and a height of 5–7 mm, which were then calcined at  $750^\circ\text{C}$  in air for 4 hours. Fig. 2 shows the X-ray diffractogram of the obtained  $\text{BiFeO}_3$  sample.

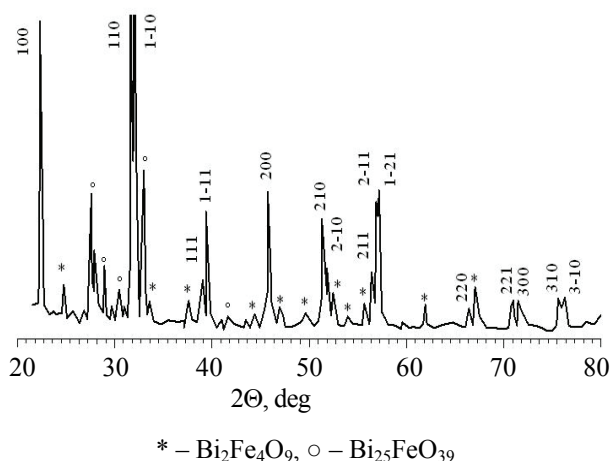


Fig. 2. X-ray diffractogram of bismuth ferrite  $\text{BiFeO}_3$ , prepared from a powder mixture of  $\text{Bi}_{25}\text{FeO}_{39}$  precursor and  $\text{Fe}_2\text{O}_3$  oxide

Analysis of the diffractogram (Fig. 2) showed that the sample of ferrite had a crystal structure of a rhombohedral perovskite. At the same time on

the X-ray diagram small reflexes of impurity phases were present, in particular, traces of the antiferromagnetic phase of  $\text{Bi}_2\text{Fe}_4\text{O}_9$ , mullite and of the paramagnetic phase of  $\text{Bi}_{25}\text{FeO}_{39}$ , sillenite. This indicates that these conditions of the synthesis did not allow to avoid the presence of impurity phases.

Therefore a synthesized  $\text{BiFeO}_3$  sample was further calcined under the following conditions: I –  $750^\circ\text{C}$ , 2 h; II –  $800^\circ\text{C}$ , 2 h; III –  $750^\circ\text{C}$  4 hours. The diffractograms of the obtained samples are shown in Fig. 3. For the comparison of the data obtained the same figure also shows the diffractogram of the sample of bismuth ferrite synthesized by solid phase method from the corresponding oxides [12].

It is found that the diffractograms of the samples obtained by modes I and III, differ a little, but the increase in time of further heat treatment at a temperature  $750^\circ\text{C}$  leads to a slight increase in the content of impurities. This is probably due to the decomposition of bismuth ferrite  $\text{BiFeO}_3$  on  $\text{Bi}_2\text{Fe}_4\text{O}_9$  and  $\text{Bi}_{25}\text{FeO}_{39}$  by the reaction:

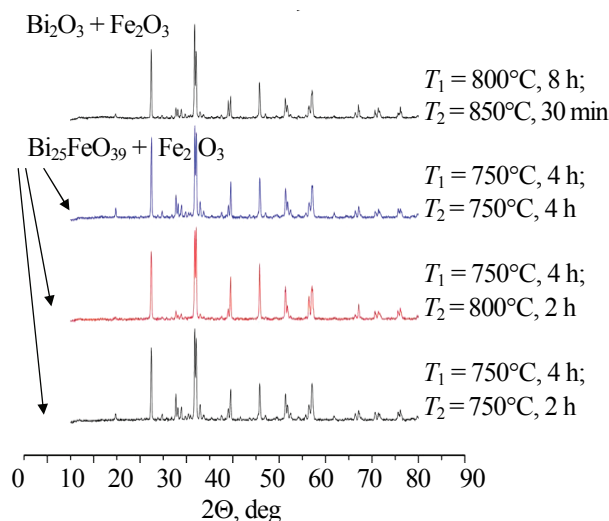
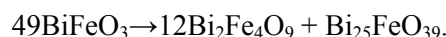


Fig. 3. X-ray diffractograms of samples of bismuth ferrite  $\text{BiFeO}_3$ , after an additional heat treatment at various modes

The comparison of the diffractograms of the samples obtained by modes I and II, in turn, allowed to establish that an increase in the firing temperature from  $750$  to  $800^\circ\text{C}$  (at the same time of heat treatment) results in a significant reduction in the amount of impurities. Thus, mode II is the most optimum of the three modes of heat treatment ( $T = 800^\circ\text{C}$  and the time 2 hours).

It should be noted that the proposed method of obtaining  $\text{BiFeO}_3$  from  $\text{Bi}_{25}\text{FeO}_{39}$  precursor and  $\text{Fe}_2\text{O}_3$  oxide also allowed to reduce the time and the temperature of the synthesis compared with the solid phase method of synthesis from correspond-

ing  $\text{Bi}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  oxides (for which  $T_1 = 800^\circ\text{C}$ , 8 h and  $T_2 = 850^\circ\text{C}$ , 30 min) and at the same time to reduce the content of impurity phases of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  and  $\text{Bi}_{25}\text{FeO}_{39}$  from ~5 to ~3%.

**Conclusion.** A solid phase method of synthesis of multiferroic  $\text{BiFeO}_3$  from  $\text{Bi}_{25}\text{FeO}_{39}$  precursor and  $\text{Fe}_2\text{O}_3$  oxide was proposed and developed. The study of the influence of different modes of heat treatment on the crystal structure of  $\text{BiFeO}_3$  was carried out. As a result of this work the optimal conditions for the synthesis of the sample of  $\text{BiFeO}_3$ , containing trace amounts of impurity compounds  $\text{Bi}_2\text{Fe}_4\text{O}_9$  and  $\text{Bi}_{25}\text{FeO}_{39}$  were chosen. Thus, it is concluded that obtaining of single phase samples of  $\text{BiFeO}_3$  requires a careful selection of the synthesis conditions, i. e. the optimum mode of heat treatment (temperature and time of firing), which would take into account both the thermodynamic characteristics and kinetic regularities of the occurring reactions.

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