$BiFeO_3$ syntheses on the basis of fuel precursors on the solar furnace

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Synthesis and properties of bismuth ferrite BiFeO3 are investigated quite widely [1-17]. However, obtaining a single-phase sample of BiFeO3 still presents a serious problem. For example, a material synthesized from a mixture of Bi2O3 + Fe2O3 always contains Bi25FeO39 and Bi2Fe4O9 impurities, not depending on the synthesis method [5-8]. The use of a mixture with a large excess of Bi2O3 also did not lead to a single-phase BiFeO3 ferrite [9]. The complexity of preparation of single-phase BiFeO3 is noted in [10], which is associated with the features of the Bi2O3-Fe2O3 system state diagram (the presence of three compounds), the Bi2O3 volatility above its melting point [11] and the thermodynamic instability of BiFeO3 in air in the absence of an equilibrium solution of Bi2O3-Fe2O3 melt [12]. An analysis of the literature data shows the impossibility of obtaining a single-phase compound BiFeO3 by solid-phase synthesis [13-17].

Thus, the existing thermal (solid-phase reactions at high temperatures (Tsin <Tpl) and chemical (reactions in solutions) methods do not allow obtaining single-phase bismuth ferrite.In this aspect, the scientific interest is the use of solar technologies, ie synthesis from the melt obtained influence on the substance of concentrated high-density light radiation, at which compounds are formed during reactions in melts, and then this state is fixed by quenching.

At the first stage of the experiments, the oxides of bismuth (Bi2O3) and iron (Fe2O3) were melted on the focal plane of the solar furnace under the action of a concentrated light flux of 450 W / cm2 density and held in the melting state for 15 minutes. The melts are quenched in water (104 deg / s). Molten melts in a ball mill by a wet method (material: water: grinding media = 1: 1: 1) for 10 hours. Sifted through a sieve of 0.05. Based on the fused oxides, a mixture of Bi2O3 + Fe2O3 was produced in the stoichiometric ratio. Imagery-tablets are pressed by pressing at an effort of 1 ton on a C-100 press. The firing was carried out in an electric resistance furnace with silicate heaters at various temperatures. The samples were designated A-type.

In the second stage, bismuth ferrite was synthesized from a mixture of oxides without melting on a solar furnace (B-type samples) were used as control.

The thermogravimetric analysis of the Bi2O3 + Fe2O3 mixture was carried out in the temperature range 100-10000C on a Q-1500 D derivatograph at a heating rate of 15 oC / min.

The X-ray diffraction patterns were taken on powders using a DRON-3M diffractometer with an anode of copper. The determination of the apparent density of the samples, ρ, was carried out by the hydrostatic weighing method in octane, the calculation of the X-ray density, the ρent, was carried out according to the formula: ρrent = 1.66 × M / V (M weight of the formula unit in grams, V-volume of the perovskite cell in Å3) , ρotn - on the formula (ρkazh / ρrent) × 100%. The structural looseness was determined by the formula: ω = M / (nρ); where M is the molecular weight equal to the sum of the atomic weights of the elements of the

compound, n is the number of structural units (atoms, ions, complexes or radicals) in the formula unit of the compound, ρ is its density.

Figure 1 shows the differential-thermal analysis curve for the Bi2O3 + Fe2O3 mixture in the temperature range 100-1000C.

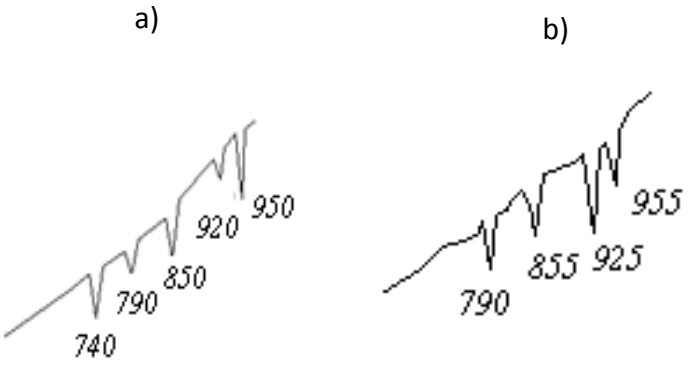

Fig.1. The thermogravimetric analysis of the Bi2O3 + Fe2O3 mixture in the temperature range 100-10000C: a) with components not melted in the solar furnace and b) with components melted in the solar furnace.

From Fig. 1 a) that the curve of thermogravimetric analysis of the mixture Bi2O3 + Fe2O3 in the temperature range 100-10000C shows 5 endothermic effects. It is clear that at 7400C there is a polymorphous Bi2O3 transformation, the peak at 7900C is due to the melting of the eutectic in the Bi2O3-Fe2O3 system at which the synthesis of BiFeO3 begins. As the analysis of the DTA curve shows, BiFeO3 begins to decompose at 9200C and 9500C. Analysis shows that the DTA curve for a mixture of oxides melted on a solar furnace, there is no peak at 7400C (Fig. 1b). This indicates that the preliminary melting of the Bi2O3 and Fe2O3 components on a solar furnace leads to an increase in the chemical activity of the oxides. In addition, the endothermic peaks are shifted toward high temperatures by 50 ° C.

Figure 2 shows the X-ray diffraction patterns of calcined samples at a temperature of 885° C.

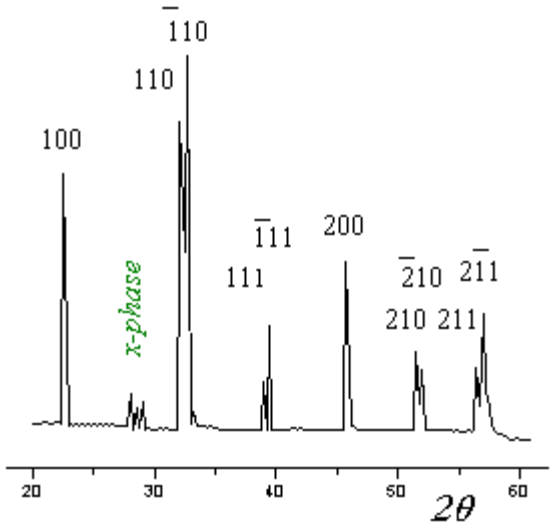

Fig.2. The x-ray diffraction pattern of bismuth ferrite BiFeO3 synthesized at a temperature of 8850 ° C. X-phase corresponds to a solid solution of Bi2Fe4O9 = [Fe2O3 2BiFeO3]

As is known, bismuth ferrite is characterized by a rhombic distortion of the perovskite cell [18] and temperature-dependent non-stoichiometry [19,20], which complicate the synthesis of single-phase bismuth ferrite, as well as compounds containing BiFe03.

The x-ray density of bismuth ferrite was ρ = 8.39 g / cm^3.

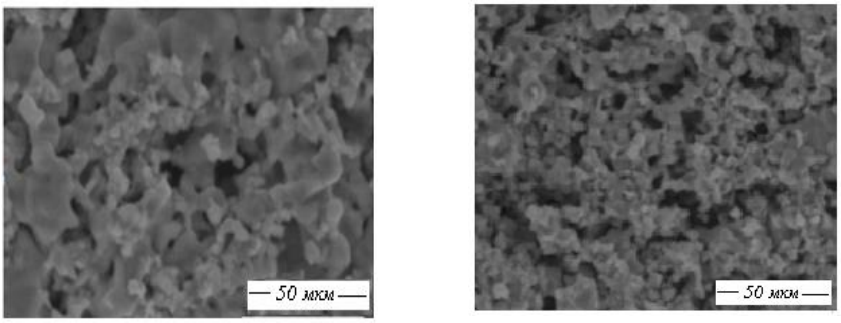

Fig.3. Microstructure of bismuth ferrite a) A- and b) B-types.

Figure 3 shows that, depending on the type of samples, the size and shape of the grains of ferrite of bismuth ceramics change. Thus, in the case of A-type samples, the grain size varies between 5-20 μm and 10-30 μm for B-type.

Table 1 shows the values of porosity, apparent density and coefficient of linear thermal expansion of the samples, depending on the synthesis method. It can be noted that the sinterability of bismuth ferrite is somewhat improved when it is synthesized from fused oxides.

Table 1. The values of apparent density (ρ_{app}), porosity (P), relative density (ρ_{rel}), structural looseness (ω) and coefficient of linear thermal expansion (α) of ceramic bismuth ferrite samples, depending on the history of the components.

Samles	P_{app}, г/см^3	P, %	P_{rel}, %	ω	$\alpha.10^6$, К$^{-1}$
A-type	5.40	36	64,36	7,36	13.4
B-type	4.87	42	58,04	11,44	11.9

The coefficient of linear thermal expansion was 13x10-6K-1 for A-type samples with a predominance of the rhombic phase and 11x10-6K-1 for B-type samples in which the orthorhombic phase predominated. The difference between the structural looseness of materials is due to the fact that preliminary melting of oxides on a solar furnace promotes the synthesis of bismuth ferrite with a denser structure.

Table 2 presents the results of the synthesis of bismuth ferrite as a function of the prehistory of the Fe2O3 and Bi2O3 components. It can be seen that ferrite of bismuth, obtained from fused oxides, is characterized by a small content of impurity phases. It can be assumed that the fused oxides are a more active form of the reagent, as a result of which the formation of impure Bi2Fe4O9 begins at a lower temperature than the formation of bismuth ferrite.

Table 2. Results of synthesis of bismuth ferrite as a function of the prehistory of Fe2O3 and Bi2O3 components.

prehistory Fe_2O_3 and Bi_2O_3.	Technology mode	Phase composition , %	
		$BiFeO_3$	$Bi_2Fe_4O_9$
Not melted on solar furnace	885^0C, 5 ч	88	12
melted on solar furnace		97	3

Thus, bismuth ferrite synthesized on the basis of precursors - iron and bismuth oxides melted on a solar furnace has a denser structure, a low coefficient of thermal expansion, in comparison with the traditionally synthesized bismuth ferrite. The technology of creating ceramic materials based on bismuth ferrite requires careful regulation of the physico-chemical state of the starting materials.

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