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# Structural Properties of $\text{BiFeO}_3$ and $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$ Powders Synthesized by Sol-Gel Process

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**Abstract.** The present work aims to design and study novel functional materials with multiferroic properties required in electric applications, such as magnetic and magnetoresistive sensors, actuators, microwave electronic devices, phase shifters, mechanical actuators etc. Complex oxides  $\text{BiFeO}_3$  and  $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$  for analysis of its structural properties were synthesized as powders by sol-gel method. The size, shape, and degree of crystallinity of the formed nanoparticles can be changed by varying the temperature and the concentrations of the initial reactants and the stabilizer. This work is devoted to interrelation between composition of sol-gel  $\text{BiFeO}_3$  and  $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$  nanopowders and their nanostructural properties.

**Keywords:** Sol-gel · Powder · Bismuth ferrite · Ferromagnets

## 1 Introduction

Need of efficient materials having outstanding functional properties with controllable characteristics and those which meet demanding ecological restrictions motives researchers to look at complex transition metal oxides with perovskite-like structure. It is well known that ferrites possess several unique properties such as magnetization/magnetotransport and magnetoelectric coupling being enhanced near the structural phase boundaries [1].

Multiferroics have been known as materials with ferromagnetic and ferroelectric properties at the same time, which have exhibited interesting physical properties as well as a possibility of practical applications. Multiferroic materials, owing to the coexistence of ferroelectricity, ferromagnetism, and even ferroelasticity in the same phase, have shown promising applications in nonvolatile information storages, spintronic devices, and magnetoelectric sensors. Among the multiferroic materials studied so far,  $\text{BiFeO}_3$  (BFO) is known to have a rhombohedrally distorted perovskite structure described by space group  $R3c$ . At present, the ceramics of BFO have been extensively investigated [2, 3]. Although rhombohedral  $\text{BiFeO}_3$  (BFO R-phase) has been studied since first discovery in 1960s, electrical properties of the pure BFO R-phase have been

rarely reported due to its high conductivity, which may originate from uncertain oxygen stoichiometry, high defect density and poor sample quality [3–5]. It is known [6, 7] that the introduction of small impurity (up to 10%) of rare-earth ion into sol composition facilitates the formation of the perovskite phase and consequently leads to an increase in the antiferromagnetic properties of  $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$  nanopowders in comparison with  $\text{BiFeO}_3$ .

Wet chemical methods are promising routes to prepare fine and homogeneous oxide powders [8, 9]. Various wet chemical methods such as hydrothermal, co-precipitation, combustion synthesis, molten-salt method, thermal decomposition, and sol-gel process have been developed and designed to prepare  $\text{BiFeO}_3$  and  $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$  nanopowders. However, many of these routes do not lead to obtain a pure phase. Controllability of the functional parameters can be achieved particularly using sol-gel synthesis method favoring the superior properties via modification of chemical bond character, variation of the structural parameters, and controlling the defectiveness/stoichiometry of the compounds [10]. However many parameters of the sol-gel  $\text{BiFeO}_3$  and  $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$  nanopowders are not studied. This work is devoted to interrelation between composition of sol-gel  $\text{BiFeO}_3$  and  $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$  nanopowders and their nanostructural properties.

## 2 Experimental

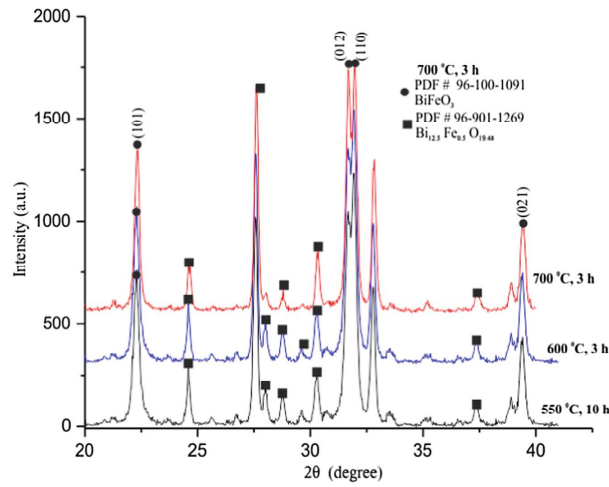
Synthesis of  $\text{BiFeO}_3$  powder used nitrate salts of Fe and Bi,  $\text{HNO}_3$ , and citric acid. The compounds were dissolved in distilled water, which was then evaporated on a hot plate at 80–90 °C to form a gel (about 4–5 h). The resulting gel was then heated in an oven at a temperature of 180 °C for 2 h. The aim is to remove water molecules. The annealing temperature for powders was 550 °C (during 3 or 10 h), 600 °C (during 3 h), 700 °C (during 3 h), 800 °C (during 3 h) (see Fig. 1). The  $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$  (BLFO) powder were synthesized using the same procedure.  $\text{La}(\text{NO}_3)_3$  was used as lanthanum source.

X-ray diffraction was carried out on diffractometer PANalytical X'Pert MPD Pro in the reflection mode (geometry Bragg - Brentano) using  $\text{Cu-K}\alpha$  radiation. The identification of the diffraction peaks was performed using the data bank JCPDS affordable software company Search-Match. Processing of the diffraction patterns was made in the JANA2006 program.

The resulting powder (previously introduced into ethyl alcohol) was applied to the substrate by centrifugation. Single-crystal silicon wafer was used as a substrate. Heat treatment at a temperature of 100 °C for 10 min. Surface scanning was measured by atomic force microscopy (AFM) on 47 SOLVER-PRO and was analyzed using the program Gwyddion.

### 3 Results and Discussion

As can be seen from the XRD data (Fig. 1), the BFO reaction product was not monophasic (rhombohedral phase). The determining factor is associated with the peculiarities of the sol-gel synthesis technique. The increasing of the synthesis temperature leads to the decrease in the content of the perovskite phase due to the weak bond of bismuth ions in the crystalline cell which causes the removal of bismuth from the crystal lattice. Further annealing of the formed material at higher temperatures does not lead to an increase in the content of the required phase (Table 1).



**Fig. 1.** XRD of BiFeO<sub>3</sub> powder after heat treatment at 550 °C during 10 h and after 600 °C and 700 °C during 3 h.

**Table 1.** Rhombohedra phase content of BiFeO<sub>3</sub> powder.

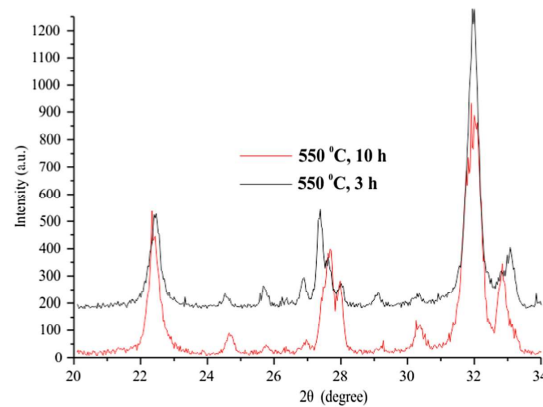
Powder	Temperature and processing time, °C	Phase content BiFeO <sub>3</sub> , %
BFO	550-10 h	74
	700-3 h	64
	800-3 h	63

**Table 2.** Rhombohedral phase content of Bi<sub>0.9</sub>La<sub>0.1</sub>FeO<sub>3</sub> powder.

Powder	Temperature and heat treatment time, °C	Perovskite phase content, (%)
BLFO1	180-2 h	—
BLFO2	550-10 h	80.5
BLFO4	700-3 h	59.8
BLFO5	800-3 h	65.5

The heat treatment conditions of BLFO nanopowders and results of XRD analysis are presented in Table 2.

After synthesis at 180 °C, the sample does not have any crystalline structure. As can be seen from the XRD data (Fig. 1 and Table 2), the BFLO reaction product was not monophasic. The increasing of the synthesis temperature firstly leads to the decrease of the content of the required phase due to the weak bond of bismuth ions in the crystalline cell. But the total content of the required phase in doped nanopowders is higher than in powders without the addition of lanthanum annealed at similar temperatures. This is explained by the expansion of the region of the concentrations of the initial metals necessary to form the required phase by increasing the number of components. The increasing of the content of the required phase from 60% to 65% with the increasing of heat temperature from 700 °C up to 800 °C is bound with the restructuring of the crystal structure of the nanomaterial. However, the limiting phase content at high heat treatment temperatures is lower than at heat treatment of 550 °C. The low annealing temperature should be compensated by the long annealing time (see Fig. 2).



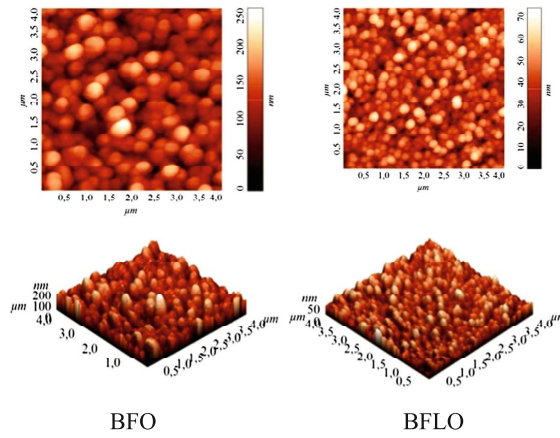
**Fig. 2.** XRD of  $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$  powder after heat treatment at 550 °C during 3 h and during 10 h.

**Table 3.** Domains sizes in BFO and BFLO nanopowders heat treated in different conditions.

Sample	Annealing temperature, °C, Annealing time, hour	Domain size, nm
BFLO	550, 3 h	25
	600, 3 h	19
	700, 3 h	18
	800, 3 h	16
BFO	550, 10 h	15
	600, 3 h	15
	700, 3 h	15

The sizes of domains are also determined (see Table 3).

The results of the investigation of the surface of the synthesized powder after heat treatment at 550 °C during hours are shown in Fig. 4 (AFM image) and Table 4. It has been established that the doping by lanthanum in BFO leads to the significant (about 1.5 times) reduction of the average grain size and decrease (about 3.5 times) in the surface roughness. From the point of view of potential using in nanoelectronics, these facts increase the applicability of the material.



**Fig. 4.** AFM image of BiFeO<sub>3</sub> (left) and Bi<sub>0,9</sub>La<sub>0,1</sub>FeO<sub>3</sub> (right) powders.

**Table 4.** Surface parameters of BiFeO<sub>3</sub> and Bi<sub>0,9</sub>La<sub>0,1</sub>FeO<sub>3</sub> powders

Sample	Ra, nm	Average grain size, nm	Number of grains
BFO	28	127	380
BFLO	8	90	705

## 4 Conclusion

In conclusion, the mixture of different phases BFO with the perovskite phase content about 70% and BLFO with the perovskite phase content about 80% were synthesized using sol-gel method. The highest content of the required rhombohedral phase is observed for Bi<sub>0,9</sub>La<sub>0,1</sub>FeO<sub>3</sub> powder annealed for 10 h at the temperature of 550 °C.

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