Synthesis of $BiFeO_3$-Powders 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 $BiFeO_3$ for analysis of its magnetic properties were synthesized by sol-gel method as powders. The size, shape and degree of crystallinity of the nanoparticles formed by sol-gel method can be controlled by varying the temperature and the ratio of the concentrations of the initial reactants and the stabilizer. To stop the growth of particles in all cases, it is usually enough to cool quickly the reaction mixture. To isolate the nanoparticles, the precipitating solvent is added, which mixes with the reaction system, but poorly dissolves the "protective shells" of the nanoparticles and, therefore, destabilizes the suspension. As a result, the nanoparticles precipitate as powder, which can be separated by centrifugation. The sol-gel method makes it possible to obtain practically monodisperse nanoparticles of various metals oxides.

Keywords: sol-gel, film, powder, ferromagnets

Introduction

Multiferroics have been known as materials exhibiting ferromagnetic and ferroelectric properties at the same time, which have exhibited interesting physical properties as well as a possibility of practical applications. The rhombohedrally distorted simple perovskite structure of $BiFeO_3$ is one of the representative multiferroic materials and has been much interested due to the antiferromagnetic behavior with a relatively high Neel temperature and the ferroelectric behavior with a high Curie temperature. 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, $BiFeO_3$ (BFO) is known to have a rhombohedrally distorted perovskite structure described by space group R3c. It has two order parameters at room temperature: a ferroelectric ordering with high Curie temperature T_C of 1103 K, and long range antiferromagnetic ordering of the G-type with a magnetic transition temperature T_N of 643 K. As the only one single phase multiferroic material which simultaneously possesses ferroelectric and magnetic properties at room temperature, BFO has been one of the most interesting materials studied. At present, the ceramics of BFO have been extensively investigated. Although rhombohedral $BiFeO_3$ (BFO R-phase) has been studied extensively since first discovery in 1960s, electrical properties of the pure BFO R-phase have been rarely reported due to its high conductivity, which may originated from uncertain oxygen stoichiometry, high defect density and poor sample quality [1]. In order to understand the properties of multiferroic BFO, it is very important that the fabrication of pure BFO phase should be established. If temperature and oxygen partial pressure were not controlled accurately during crystallization of the BFO R-phases, the kinetics of phase formation always lead to other impurity phases in Bi-Fe-O system such as $Bi_2Fe_4O_9$, Bi_2O_{3-d} and $Bi_{46}Fe_2O_{72}$.

Experimental

Wet chemical methods are promising routes to prepare fine and homogeneous powder. 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 pure $BiFeO_3$ nanopowder. Recently, acid-assisted gel strategy has been proved to be an effective way to synthesize metastable $BiFeO_3$ nanopowder. Pure $BiFeO_3$ phase could be obtained by leaching out the minor Bi_2O_3 phase using diluted nitric acid. Pure $BiFeO_3$ powder can be directly synthesized through the acetic acid-assisted or the tartaric acid-assisted sol-gel method. However, $BiFeO_3$ powder synthesized by the organic acid-assisted sol-gel method might have relatively low phase purity resulting from easy formation of bismuth-rich phase during calcining. Therefore, mineral acid should be considered as an adjuvant to prepare $BiFeO_3$ nanopowder.

Two versions of the sol-gel method [2, 3] were used to synthesize the $BiFeO_3$ powders.

1. $Fe_xBi_yO_z$-citrate-based powder was synthesized using citric acid, ethylenediamine and nitric acid salts of Fe and Bi. Ethylene glycol was used as a solvent. In the beginning, the nitric acid salts of Fe and Bi were dissolved in ethylene glycol without addition of water. Then, citric acid was added to form Fe and Bi citrate. After that, the pH of the solution was adjusted to a value of 7-8 by neutralizing excess citric acid with ethylenediamine. The last neutralization step should be carried out with constant stirring, dropwise adding ethylenediamine and waiting for a constant pH to be established before the next drop is added. After homogenization of the resulting solution, ethylene glycol was added thereto. The solution was stirred for 30 minutes and then dried at 100 °C until the gel formed and condensed, and then at a temperature of 250 °C until a powder was formed.

2. Synthesis of $BiFeO_3$ powder used nitrate salts of Fe and Bi, water, HNO_3, and citric acid as a solvent. The basic compounds were dissolved in HNO_3 acid, which

was then heated on a hot plate at 80-90 °C to form a gel (about 4-5 hours). The resulting gel was then heated in an oven at a temperature of 180 °C for 2 hours. The aim is to evaporate the water.

The annealing temperature for both powders was 550 °C (during 10 hours), 600 °C (during 3 hours), 700 °C (during 3 hours), 800 °C (during 3 hours (see Fig. 1).

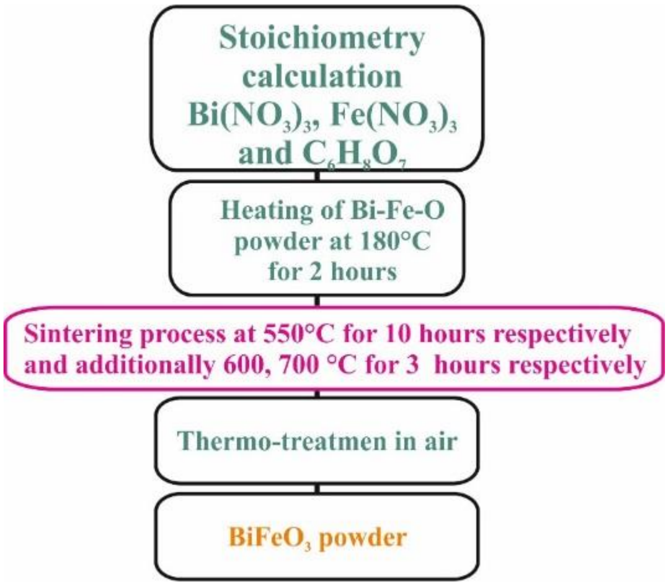


Fig. 1. The main stages of sol-gel synthesis of $BiFeO_3$ powders.

To study the particle size distribution the suspension based on $BiFeO_3$ powder was prepared. Isopropanol was used as the solvent. The resulting suspension was applied to the surface of single-crystal silicon for carrying out AFM investigation.

Results and discussion

The results of the investigation of the surface of the synthesized powder are shown in Fig. 2 (AFM image) and XRD in Fig. 3. The highest content of the required rhombohedral phase is observed for powder obtained by the first synthesis route annealed for 10 hours at a temperature of 550 °C.

The resulting phase is stable. Annealing at the higher temperatures leads to 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.

As can be seen from the XRD data, 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.

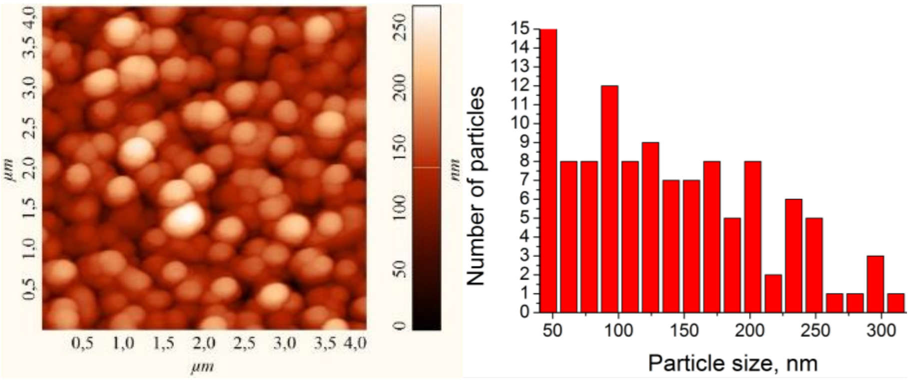
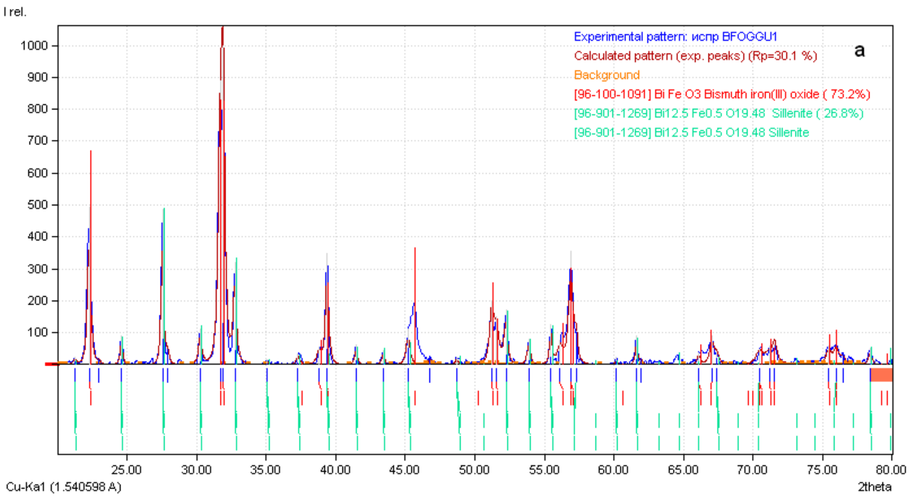


Fig. 2. AFM-image of $BiFeO_3$ powder obtained by sol-gel method (annealing temperature 550 °C) – left image. Particle distribution graph is denoted on the right image.



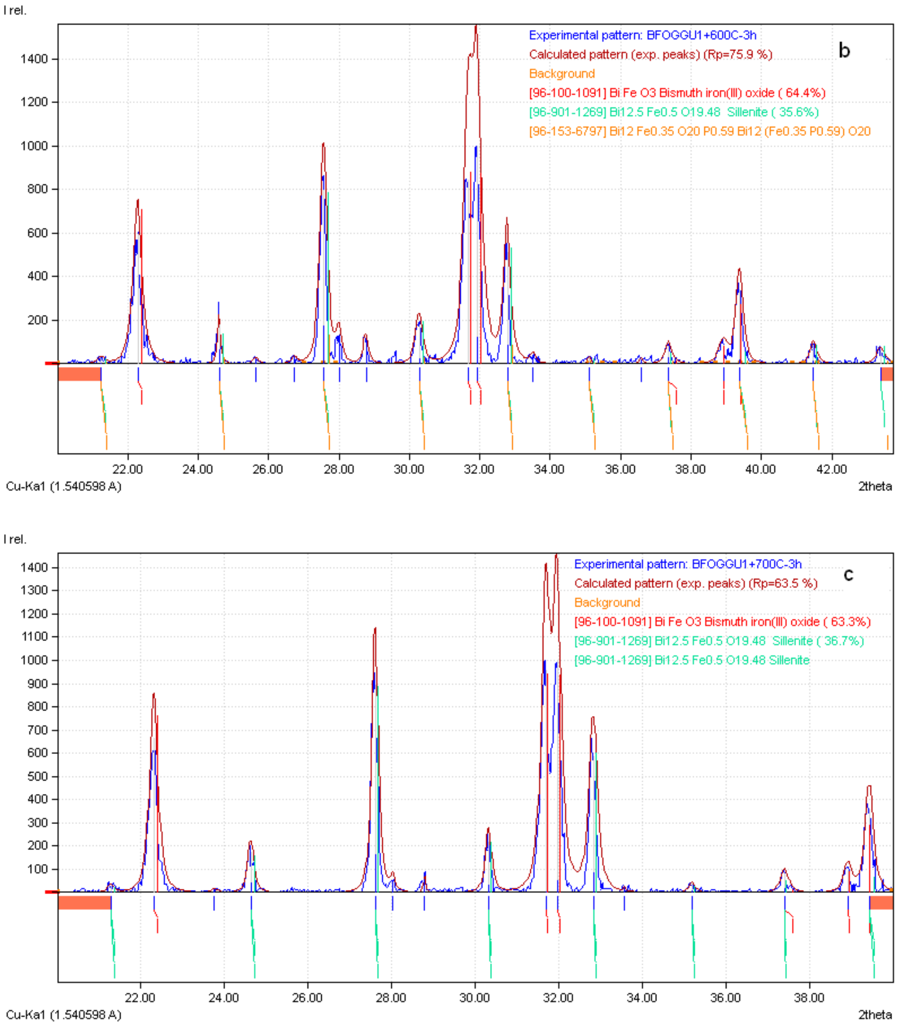


Fig. 3. XRD of $BiFeO_3$ powder obtained by sol-gel method.

Table 1. Phase content of $BiFeO_3$ powder obtained by sol-gel method.

Powder	Temperature and processing time, °C	Phase content $BiFeO_3$, %
BFO	*550-10h*	74
	700-3h	64
	800-3h	63

In conclusion, the mixtures of different BFO-related phases with the perovskite phase with a content R-phase up to about 75 % were synthesized using sol-gel method.

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