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Preparation of BiFeO₃ Films by Sol-Gel Technique and Their Characterization

The present paper describes a simple low-temperature synthesis method of preparing bismuth ferrite thin films by sol-gel route, using bismuth nitrates and iron chloride, acetic acid and ethylene glycol. The films were layer by layer deposited on substrate (copper) using the spin-coating technique. The thickness of the layers was controlled by viscosity of the solutions and withdrawing speed parameters. After specific annealing, in air, the samples were characterized by x-ray diffractometer (XRD), scanning electron microscopy (SEM) and electrical properties measurements. A more thoroughly control of the processing parameters seems to be essential in obtaining BiFeO₃ thin films. Solution chemistry variations (differences in precursor type) can have a significant impact on the film properties. Conditions for synthesizing single BiFeO₃ phase are critical since the temperature stability range of the phase is very narrow. Moreover, it is also difficult to control oxygen stoichiometry in the sample.

Keywords: BiFeO₃; Sol-gel; Low-temperature synthesis; Thin films

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1. Introduction

The next-but-one generation of microelectronic devices (45 nm base length) will have to experience three-dimensional (3D) packaging to a large extent. The heat release of the central processing units in computers will become a serious challenge [1], in particular after the introduction of novel 3D storage devices with current controlled read-write protocols like magnetic random access memories, MRAM [2]. The need of purely electric field-controlled devices with a minimum amount of Joule heating becomes of paramount interest [1]. In this situation the revived interest in magnetoelectric (ME) materials [3] finds its utmost pertinence. ME response signifies magnetic control via electric fields and vice versa [4]. It promises to maximize in multiferroic materials close to their ordering temperatures [5]. That is why ME multiferroics, *i.e.* materials undergoing phase transitions into long range magnetic and electric order close or above room temperature are declared the ‘holy grail’ in materials science [6], which is still far from being reached.

In recent years, there has been a revival of interest in developing multiferroic materials possessing ferroelectric polarization and magnetic ordering in the same phase [7]. Coupling between the corresponding order parameters gives rise to a magnetoelectric effect, which might be used in technological applications [8]. However, single phase magnetic ferroelectrics with a large polarization and magnetization coexisted near room temperature have hitherto not been identified. The scarcity of the materials results from the contradiction between the conventional mechanism for cation off-centering in ferroelectrics and the formation of magnetic order (so called “ d^0 vs. d^n problem”) [7]. Accordingly, to combine

ferroelectricity and magnetism in a single phase, the atoms that move off centre to form an electric dipole moment should be different from those that carry a magnetic moment. This approach is realized in case of the multiferroic perovskite BiFeO₃ [8], which is known as a unique material possessing spontaneous polarization and magnetic ordering at room temperature. In BiFeO₃, the stereochemical activity of $6s^2$ lone pair of Bi³⁺ gives rise to ferroelectricity ($T_C \sim 1100$ K), while the superexchange interaction between Fe³⁺ ions causes G-type antiferromagnetism ($T_N \sim 640$ K). Though crystal symmetry of BiFeO₃ (the compound has $R3c$ structure at ambient conditions [9]) permits the existence of a weak ferromagnetic moment [10], a spiral spin modulation, superimposed to the G-type antiferromagnetic spin ordering [11], prevents the observation of any net magnetization and of the linear magnetoelectric effect [12]. Taking into account that the crystal structure of bismuth ferrite cannot accommodate any other transition metal ions in an amount sufficient to compete with the dominant antiferromagnetic superexchange interactions Fe³⁺-O-Fe³⁺, Bi substitution by magnetically-active rare-earth ions (which suppress the spiral spin modulation to give rise to weak ferromagnetism and whose magnetic moments contribute to the resulting magnetization through $f-d$ exchange coupling) has been considered as an effective way to improve multiferroic properties of the parent compound [13,14].

Bismuth ferric oxide (BFO) is one of the new classes of materials known as magneto-electric materials, which exhibit co-existence of interrelated electric and magnetic dipole structures within a certain range of temperatures. It is antiferromagnetic with a relatively high Neel temperature ($T_N \sim 643$ K)

and ferroelectric with high Curie temperature ($T_c \sim 1103$ K) [15]. These compounds present opportunities for potential applications in information storage, the emerging field of spintronics, and sensors [16]. Furthermore, BFO has some unusual electric, thermal, optical and solid-state properties that have not yet been fully investigated. It is well known that the BFO has main five crystallite phases, denoted by BiFeO_3 , $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_3\text{Fe}_5\text{O}_{12}$, $\text{Bi}_4\text{Fe}_2\text{O}_9$ and $\text{Bi}_{46}\text{Fe}_2\text{O}_{72}$. Many techniques have been utilized to obtain the single-phase BiFeO_3 material. However, preparation of single-phase BiFeO_3 is a critical task other thermodynamically more stable phases such as $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{46}\text{Fe}_2\text{O}_{72}$ are formed because the temperature stability range is very narrow for BiFeO_3 . Moreover, bismuth and iron show the affinity of oxygen and to form multiphase materials. The literature survey showed that the BiFeO_3 thin films have been prepared almost by physical methods [15,17-19]. However chemical methods are relatively cheaper as compared to physical methods.

2. Experimental Procedure

In the present work, bismuth nitrate and ferric chloride were used as the starting materials for the precursor of BFO. The mole ratio of bismuth nitrate and ferric chloride was Bi:Fe 2:1, excess bismuth was used to compensate the evaporation of bismuth during high temperature annealing. The starting materials were dissolved in acetic acid. Ethylene glycol was added to the solution as a drying control chemical agent, in order to restrict the cracking of thin films before spin coating. The solution was refluxed for 5 hrs. Synthesis route of BiFeO_3 is given in Fig. (1).

Different schemes were adopted by researchers to synthesize BFO solution [20-23]. Solution chemistry variations (differences in precursor type) can change the film properties.

After cooling down to room temperature, the precursor was spin-coated on copper substrate at 3000 rpm for 30 s. To prepare thicker film, the spin coating process was repeated. After spin coating the substrate, the film was kept in ambient air for 1 h to form gel films by hydrolysis and polymerization. Heat treatment of dried film was carried out at a temperature of 300 °C for 2 hours. The Crystallization, densification and microstructure of the films were examined.

3. Results and Discussion

The ferroelectric thin films prepared by sol-gel onto copper substrates were examined for their structural, electrical and surface properties using the techniques discussed in the preceding sections. The results obtained are presented in accordance with the technique used.

Figure (2) presents the x-ray diffraction (XRD) patterns of BFO thin films deposited on copper

substrates in this work. It shows the formation of two phases of bismuth ferrite; BiFeO_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$. Preparation of single-phase BiFeO_3 is a critical task because the temperature stability range is very narrow. Moreover, bismuth and iron show the affinity of oxygen and to form multiphase materials. Tabares-Munoz [24] have tried to prepare pure phase BiFeO_3 in the bulk form but indeed reached up with final compound with small traces of $\text{Bi}_{46}\text{Fe}_2\text{O}_{72}$.

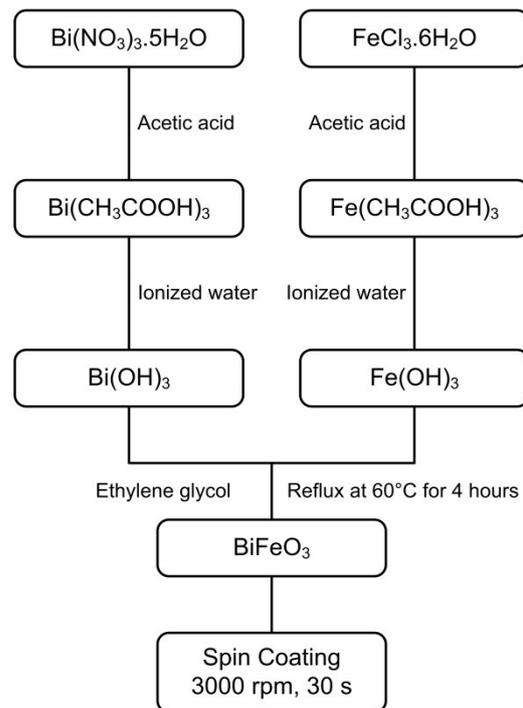


Fig. (1) Schematic diagram for the preparation of BiFeO_3 thin film by using iron chloride, bismuth nitrate and acetic acid

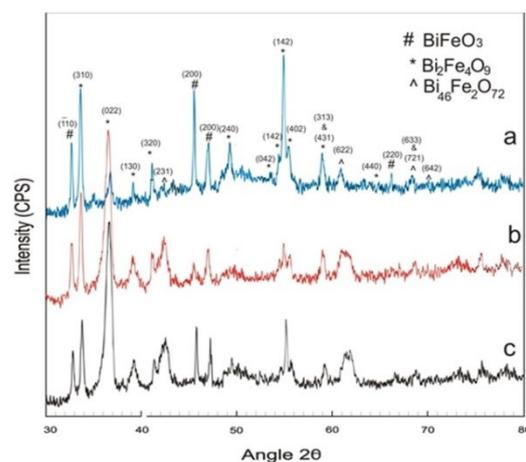


Fig. (2) The XRD patterns of the BiFeO_3 thin film (a) as-deposited, (b) heated for one hour at 300 °C, and (c) heated for two hours at 300 °C

Reasonable suppression is observed in the intensities of peaks belonging to the three bismuth

ferrite compounds due to heat treatment. However, all peaks appeared in the final product.

Prolonged heating at the same temperature has little effect on peaks of $\text{Bi}_{46}\text{Fe}_2\text{O}_{72}$ phase. Intensity of peaks of BiFeO_3 phase is decreased with increase of temperature which shows instability of this phase at high temperature. Multiphase BFO thin films are reported by other researchers [18,22]. The grain size for the prepared BFO thin films are in the range of 12.84-15.40 nm as shown in Fig. (3).

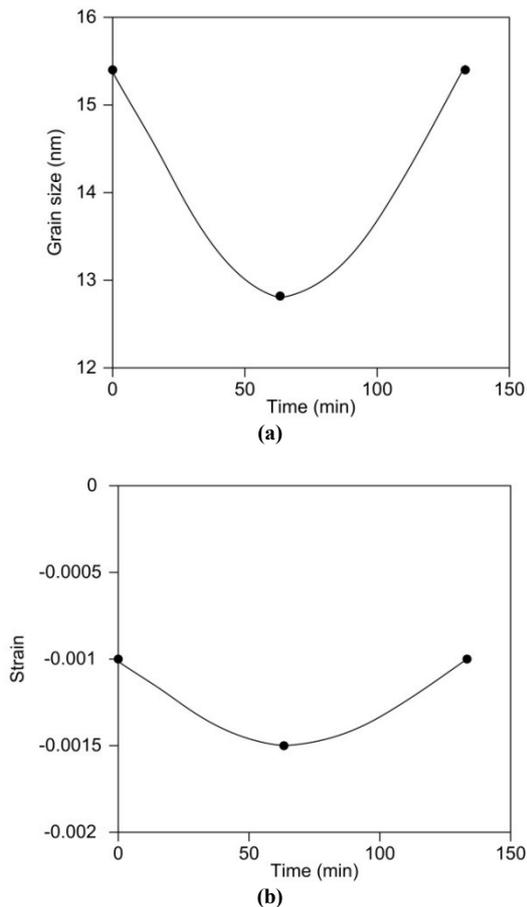


Fig. (3) Dependence of grain size (a) and strain (b) on time of heating evaluated by Williamson-Hall relation [25]

These figures show a minimum value in both cases for a heating time of 60 minutes. The plot of grain size indicates a re-structuring of the grains with heating since the grain size reduces upon first heating when compared with the as-deposited film's grain size. The grain size eventually rises upon heating indicating a particular structure formation and smoothing. This fact is supported by the surface micrographs shown in the next section.

Scanning electron micrographs of BFO thin film are shown in Fig. (4). These images were taken for the thin film sample after final heating as discussed in the preceding sections. SEM image shown in Fig. (4a) reveals a dense microstructure with a uniform surface when viewed at low magnification. High magnification micrographs, Figure (4) shows the presence of regular shaped particles with an average

particle size of 350 nm. It should be clarified here that when grain size is mentioned in the x-ray diffractograms the values are far too less as compared with the electron micrographs due to the reason that we might be looking at a cluster of grains in the electron micrographs.

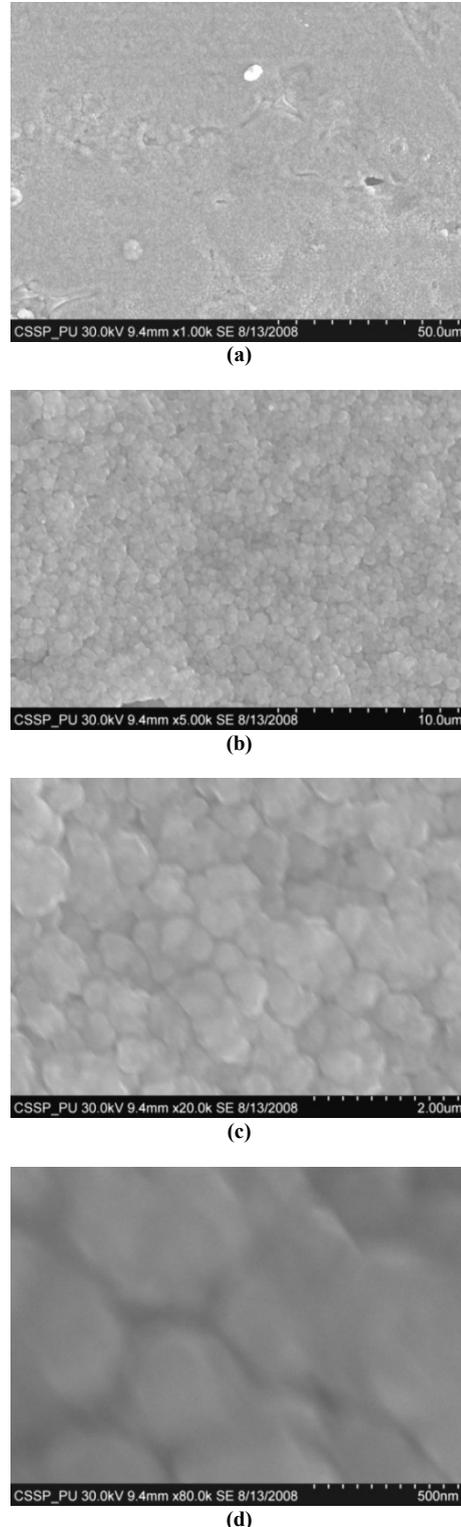


Fig. (4) Scanning electron micrographs (SEM) of thin film of BiFeO_3 with (a) magnification of 1000x, (b) magnification of 5000x, (c) magnification of 20000x and (d) magnification of 80000x

Figure (5) shows the voltage-current (I-V) characteristics of BFO thin films prepared in this work. The I-V measurements of BFO thin film heated for two hours at 300 °C showed Ohmic behaviour in milliampere range. Maximum current was 14 mA and minimum current was 20 mA.

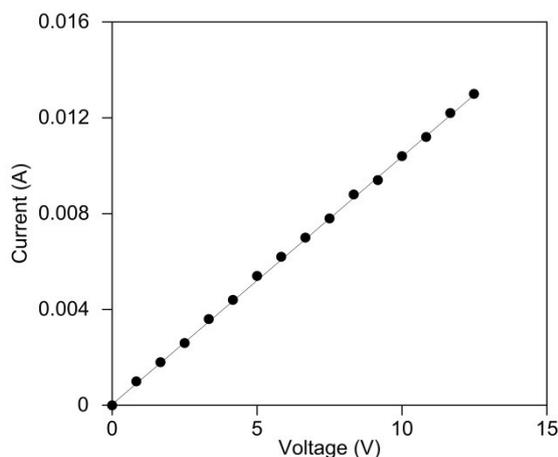


Fig. (5) The voltage-current (I-V) characteristics of BFO thin films prepared in this work

4. Conclusions

In conclusion, BFO thin film was prepared at room temperature using sol-gel technology. The XRD study revealed the formation of $\text{Bi}_2\text{Fe}_4\text{O}_9$, BiFeO_3 and $\text{Bi}_{46}\text{Fe}_2\text{O}_{72}$ phases. It is difficult to get the pure phase thin film of BiFeO_3 , since while forming BiFeO_3 , other thermodynamically more stable phases such as $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{46}\text{Fe}_2\text{O}_{72}$ are formed. The SEM studies showed a total coverage of substrate surface with smooth surface morphology.

Dense microstructure with a uniform surface was viewed at low magnification. High magnification micrographs showed the presence of regular shaped particles with an average particle size of 350 nm. It should be clarified here that when grain size is mentioned in the x-ray diffractograms the values are far too less as compared with the electron micrographs due to the reason that we might be looking at a cluster of grains in the electron micrographs. The I-V plot shows linear behaviour with a calculated resistivity of the order of 0.1 $\Omega\cdot\text{cm}$. This low resistivity is unexpected from oxides, however, since the BFO films prepared in this study had mixed phases, it is not too unexpected to see low resistivity.

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