PREPARATION OF $BIFEO_3$ FILMS BY SOL-GEL TECHNIQUE AND THEIR CHARACTERIZATION

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ABSTRACT: 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 $BiFeO_3$ thin films. Solution chemistry variations (differences in precursor type) can have a significant impact on the film properties. Conditions for synthesizing single $BiFeO_3$ 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.

Key Words: $BiFeO_3$, Sol-gel, low temperature synthesis, x-ray diffraction, scanning electron microscopy, electrical properties.

1. INTRODUCTION

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 ~643 K) and ferroelectric with high Curie temperature (T_c ~1103 K) [1]. These compounds present opportunities for potential applications in information storage, the emerging field of spintronics, and sensors [2]. 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 $BiFeO_3$, $Bi_2Fe_4O_9$, $Bi_3Fe_5O_{12}$, $Bi_4Fe_2O_9$ and $Bi_{46}Fe_2O_{72}$. 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 $Bi_2Fe_4O_9$, $Bi_{46}Fe_2O_{72}$ 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 BiFeO3 thin films have been prepared almost by physical methods [1, 3, 4, 5]. 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 Figure 1.

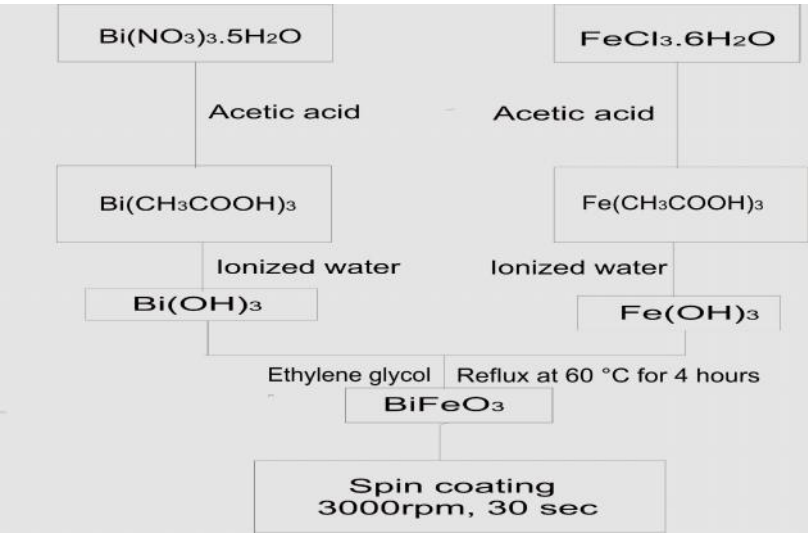


Figure 1: Scheme for the preparation of $BiFeO_3$ thin film by using iron chloride, bismuth nitrate and acetic acid.\

Different schemes were adopted by researchers to synthesize BFO solution [6,7,8,9]. 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 hrs. 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.

X-ray diffraction (XRD) studies

Figure 2 presents the XRD patterns of BFO thin films deposited on copper substrate. It shows the formation of $BiFeO_3$ and $Bi_2Fe_4O_9$ phases. 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 [10] have tried to prepare pure phase $BiFeO_3$ in the bulk form but indeed reached up with final compound with small traces of $Bi_{46}Fe_2O_{72}$.

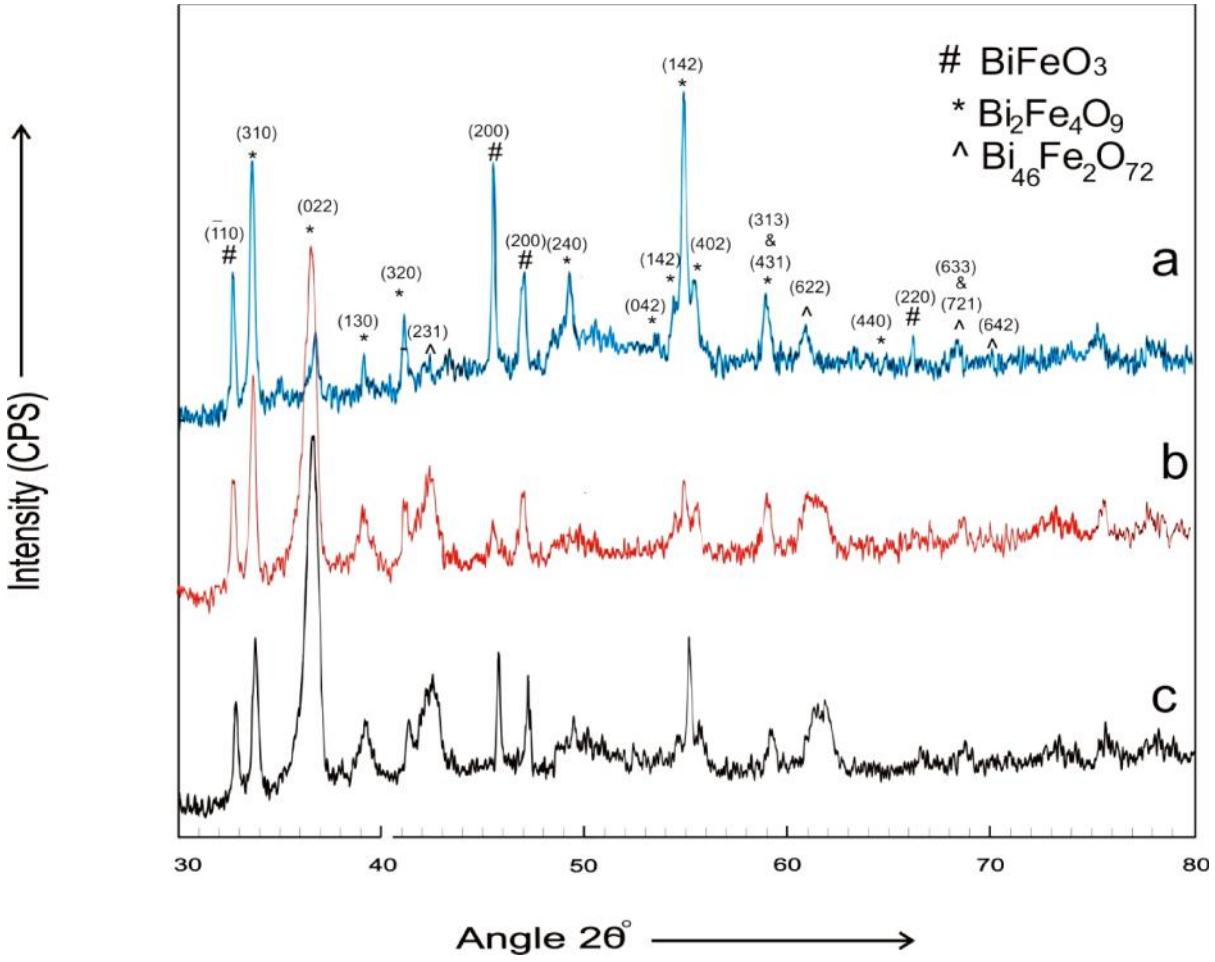
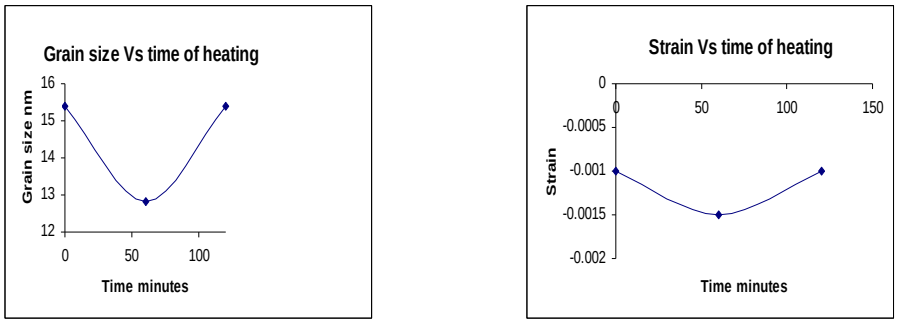
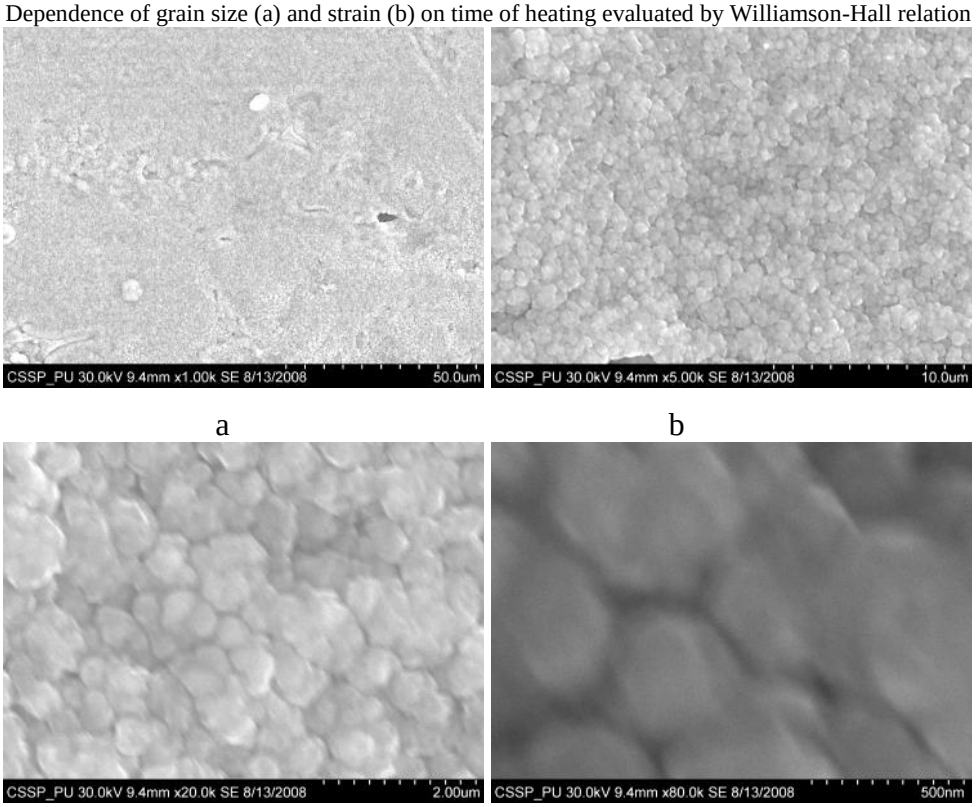


Figure 2: XRD patterns of the $BiFeO_3$ thin film (a) as deposited, (b) heated for one hour at 300 °C, (c) heated for two hours at 300 °C;



a b

Figure 3: Dependence of grain size (a) and strain (b) on time of heating evaluated by Williamson-Hall relation [11]



a b

c d

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

increase of temperature. Prolonged heating at the same temperature has little effect on peaks of $Bi_{46}Fe_2O_{72}$ 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 [4, 8]

The grain size for the BFO thin films are in the range of 12.84–15.40 nm as shown in Figure 3.

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 1st 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 microscopy (SEM) studies

Scanning electron micrographs of BFO thin film are shown in Figure 4. These images were taken for the thin film sample after final heating as discussed in the preceding sections. SEM image of Figure 4a reveals a dense microstructure with a uniform surface when viewed at low magnification. High magnification micrographs, Figure 4 b-d show the presence of regular shaped particles with an average particle size of 350nm. 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.

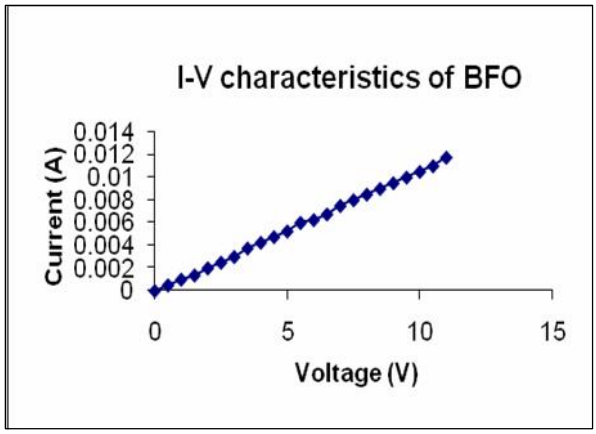


Figure 5: I-V characteristics of BFO thin film.

Electrical Properties

Figure 5 shows I-V characteristics of BFO thin film. I-V measurements of BFO thin film heated for two hours at 300 °C showed ohmic behaviour in milii-Ampere range. Maximum current was 14 mA and minimum current was 20 mA.

4. CONCLUSIONS

In conclusion, BFO thin film was prepared at room temperature using sol-gel technology. The XRD study revealed the formation of $Bi_2Fe_4O_9$, $BiFeO_3$ and $Bi_{46}Fe_2O_{72}$ 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 $Bi_2Fe_4O_9$, $Bi_{46}Fe_2O_{72}$ 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 diffract grams 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 Ω-cm. This low resistivity is unexpected from oxides however since the BFO films prepared in this study had mixed phases (as shown in the XRD section) it is not too unexpected to see low resistivity.

5. REFERENCES

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