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Role of Microwave Power on Phase Purity and Magnetic Analysis of Bismuth Iron Oxide Thin Films

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ABSTRACT

Multiferroic materials of type ABO_3 that exhibit coupling of ferromagnetic and ferroelectric ordering at room temperature are of particular interest in next generation memory devices. In the midst of various multiferroic materials, bismuth iron oxide is the only known single phase material with room temperature coupling and high Neel and Curie temperature. However, for preparation of $BiFeO_3$ thin films use of conventional methods (both wet chemical methods and physical vapor deposition methods) requires high annealing/calcination temperatures. For overcoming this difficulty, we report an alternate method for preparation of bismuth iron oxide thin films where sol synthesis is carried out using microwaves. Power of microwaves (P) is varied as 36P, 45P, 63P and 81P. Films are annealed at 300˚C in vacuum under the application of 500Oe magnetic field. X-ray diffraction results indicate formation of phase pure bismuth iron oxide at 63P. Mix bismuth iron oxide phases are obtained at 36P, 45P and 81P. Ferromagnetic behavior of bismuth iron oxide thin films at microwave power of 63P with saturation magnetization of 0.001580emu arises due to suppression of spiral spin structure. Weak magnetic behavior was observed at microwave power of 36P, 45P and 81P.

1. INTRODUCTION

Both ferroelectric and ferromagnetic ordering at room temperature in multiferroic materials makes them multifaceted and felicitous choice of material for researchers. The properties of multiferroic materials can be manipulated by electric and magnetic fields, which is favorable for magentoeletric devices, sensors and especially for data storage memories (Eerenstein et al. 2006; Cheong et al. 2007). Among the most studies multiferroics, rhombohedrally distorted $BiFeO_3$ stands front runner because of its high Curie temperature (T_c=1103K) for ferroelectric transition, high Neel temperature (T_n= 643K) for antiferromagnetic transition and most importantly the cycloidal spin arrangement which plays functional role in ferromagnetism. But the undesirable phases during the synthesis process of $BiFeO_3$, needs to be optimized for making $BiFeO_3$ suitable for considerable and potential room temperature applications. The undesirable impurity phases leads to leakage current, low dielectric constant and remnant magnetic polarization due to reduced crystallinity of material structure (Fiebig 2005; Zhao et al. 2006; Kianinia et al. 2011).

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Enhanced ferroelectric and ferromagnetic and dielectric properties, crystallinity and phase purity in $BiFeO_3$ can be addressed by various processing conditions. Variations in synthesis/ annealing temperature, and/or in variation of doping conditions are the major attempts, which have been reported in literature for optimization of desired properties (Quan et al. 2008; Jun 2005; Mazumder and Sen 2009). Moreover there are many reported methods for synthesis of $BiFeO_3$ thin films in both chemical and physical categories. The most simple and cost effective method is sol-gel technique, which provides stoichiometric control over the synthesis (Kartopu et al. 2008; Wang et al. 2003; Kartavtseva et al. 2007).

Electromagnetic radiations of frequency 2.45GHz have been in use for decades in synthesis of organic compounds. In recent years this radiations is also gaining interest of researcher for synthesis of inorganic material structures as well, because it provides rapid volumetric heating which helps to achieve better crystallinity and phase purity at low cost procedure. These radiations target the polar molecules of solvent and cause them to vibrate, due to which molecular rearrangement occurs at elevated thermal nucleation (Lindtrom et al. 2001; Huang and Shannigrahi 2011). However, only few reports are found in literature which discuss the use of radiations for synthesis of $BiFeO_3$ thin films (Huang and Shannigrahi 2011; Singh et al. 2008).

Furthermore, the phase purity of $BiFeO_3$ thin films is mostly achieved at high annealing temperature of 500ºC to 700ºC (Zhao et al. 2013; Oliveira and Pirota 2013). Where as in the present study the use of electromagnetic radiations (microwaves) with varying power (P) as 18P, 45P, 72P and 81P, helped to achieve high phase purity, better crystallinity and enhanced magnetic properties at much low annealing temperature.

2. EXPERIMENTAL DETAILS

For synthesis of single phase $BiFeO_3$ thin films research grade bismuth nitrate and iron nitrate were arranged in 99.99% pure form to be utilized as precursor material having chemical formulas $Bi(NO_3)_3.5H_2O$ and $Fe(NO_3)_3.6H_2O$ respectively. In sol gel method precursors needs to be dissolved separately in some solvent, then to combined afterward. For present experiment ethylene glycol is chosen as solvent. For $BiFeO_3$ thin films, ethylene glycol has been reported best solvent to achieve better hydrolysis rate and pure phase synthesis. To prepare BFO solution, two separate solutions were first prepared. First Solution were prepared by dissolving $Bi(NO_3)_3.5H_2O$ in ethylene glycol and second was prepared by dissolving $Fe(NO_3)_3.6H_2O$ in ethylene glycol in a beaker with magnetic stirrer and stirring was done for 30 minutes. Then to achieve $BiFeO_3$ Solution, first and second solutions were mixed together in equal molar ratio.

$BiFeO_3$ solution was then separately subjected under the different powers of microwave radiations 36P, 45P, 63P and 81P, respectively to form $BiFeO_3$ sol. After $BiFeO_3$ sol preparation, Copper substrates were cleaned by ultrasonic process in acetone for 10 minutes and afterwards in isopropyl alcohol for another 10 minutes. Thin film samples were prepared by using spin coating on cleaned copper substrates. After sample preparation all the samples were annealed at moderately low temperature of 300 ºC.

X-Ray diffraction of samples were performed by Bruker D8 diffractometer machine to analyze the structural properties and Vibrating Sample Magnetometery were performed by Lakeshore's VSM 7407 to investigate magnetic properties of $BiFeO_3$ thin film samples.

3. RESULTS AND DISCUSSION

X-Ray diffraction patterns of thin film samples given in Fig. 1 show the successful deposition of bismuth iron oxide. The indexing XRD peak corresponding to bismuth iron oxide are in agreement with JCPDS card 86-1518. However, it can be observed from the results that not all the sample shows crystalline behavior. The bismuth rich phase ($Bi_{25}FeO_{40}$) and $BiFeO_3$ both were observed in samples prepared at 36P and 45P due to insufficient thermal nucleation provided to by electromagnetic radiations for molecular rearrangements to develop phase purity. At 63P pure phase deposition of $BiFeO_3$ were observed because 63P provided sufficient volumetric heating in the solution which was favorable for crystalline rearrangement and phase purity. Moreover, at 63P the solubility of $Fe(OH)_3$ and $Bi(OH)_3$ is considered to be enhanced which leads to the formation of pure phase synthesis of $BiFeO_3$ thin film. Further at 81P increased volatility of bismuth oxide (Bi_6O_6) takes place which leads to the formation of bismuth deficient phases ($Bi_2Fe_4O_9$) along with $BiFeO_3$ thereby, reducing the crystallinity due to destruction of crystalline structure.

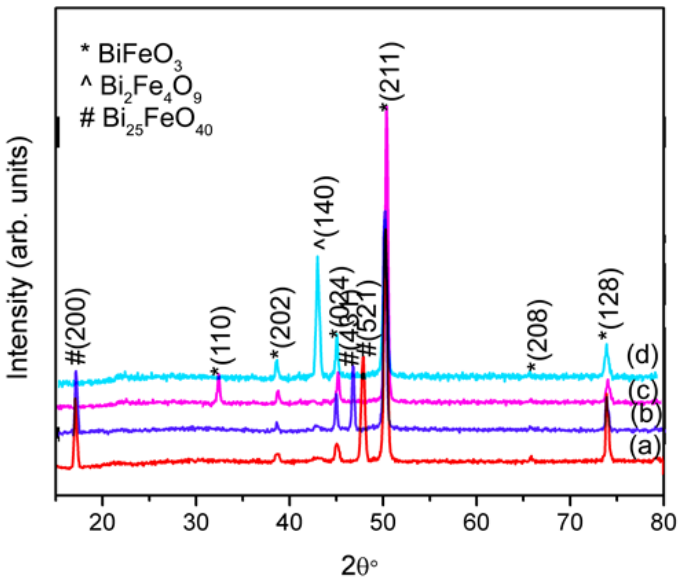

Fig. 2 XRD results of $BiFeO_3$ thin films (a) 36 P (b) 45P (c) 63P (d) 81P

In material synthesis lattice parameters of prepared structure are greatly responsible of exhibiting basic properties. The variation in lattice parameters changes the dimensionalities of crystal structure to exhibit divergent characteristics. The $BiFeO_3$ crystallizes in R3c rhombohedral structure and its lattice parameters can be calculated by equation 1 :

$$sin\theta = \frac{\lambda^2}{3a^2}(h^2 + k^2 + hk) + \frac{\lambda^2 l^2}{4\,c^2} \quad (1)$$

Figure 2 shows the variation of lattice parameters *a* and *c* in $BiFeO_3$ thin film. It can be observed that initially for samples 36P and 45P lattice parameters slightly decreases due to the incorporation of Fe^{3+} having smaller atomic radii 1.26Å than Bi^{3+} having atomic radii 1.56Å. This effect also arise due to mixed phases (Fig. 1(a,b)). Then 63P shows significant elevation in lattice parameters due to the pure phase synthesis of $BiFeO_3$. At 81P the lattice parameters considerably decreases to their minimum values due increased solubility of $Fe(OH)_3$ in $BiFeO_3$ solution which caused the formation of bismuth deficient phases, an effect also observed in XRD patterns in Fig. 1(d).

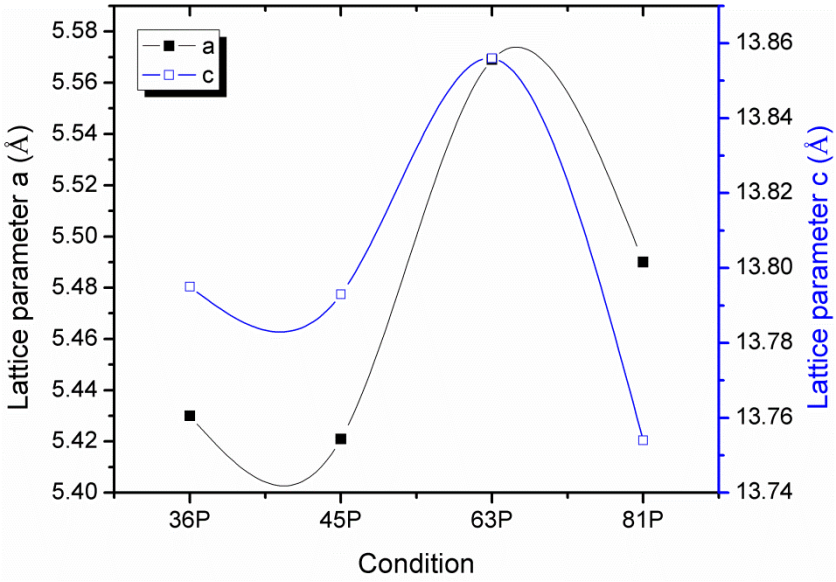

Fig.2 Variation of lattice parameters for bismuth iron oxide thin films

The crystallite size of material structure directly varies with lattice parameters. Crystallite size of thin films has defining role in ordering of spin structure material for magnetic properties. Crystallite size for thin films can be calculated using Scherer's formula given in equation 2:

$$D = \frac{0.9\,\lambda}{B\,cos\theta} \quad (2)$$

Where λ=1.5406 Å, is wavelength of X-Ray radiations emitting from CuKa source in XRD analysis. The value 0.9 belongs to constant of shaping factor k and B refers to maximum breadth of highest at θ angle of diffraction.

Figure 3 and 4 shows the variation in crystallite and unit cell volume for bismuth iron oxide thin films. At 36P and 45P, crystallite size and unit cell volume decreased due to reduced lattice parameters. At 63P solubility of $Fe(OH)_3$ and volatility of Bi_6O_6 were adjusted as to give rise to pure phase synthesis of $BiFeO_3$, which leads to increase in crystallite size and unit cell volume. Whereas, at 81P iron rich phases leads to decrease in crystallite size and unit cell volume. Figure 3 also shows the variation of

dislocation densities. The dislocation density δ inversely depends on crystallite size and it can be given by

$$\delta = \frac{1}{D^2} \quad (3)$$

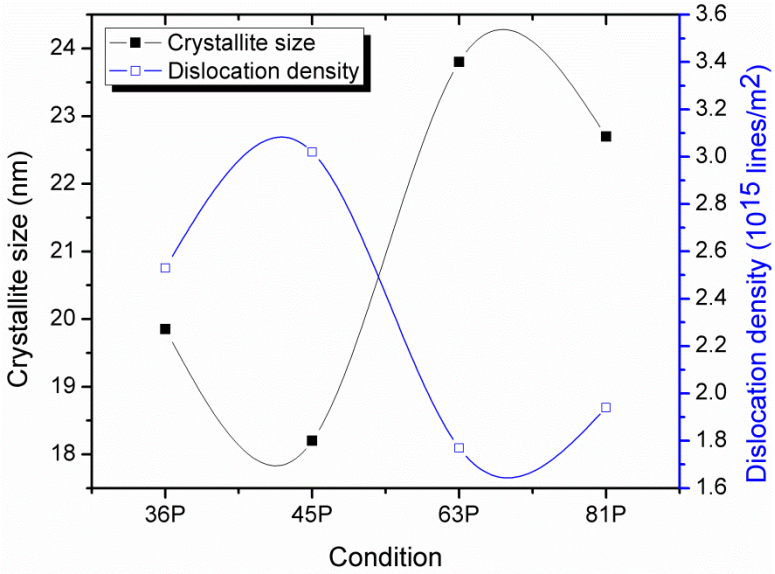

Fig. 3 Variation of crystallite size and dislocation densities for bismuth iron oxide thin films

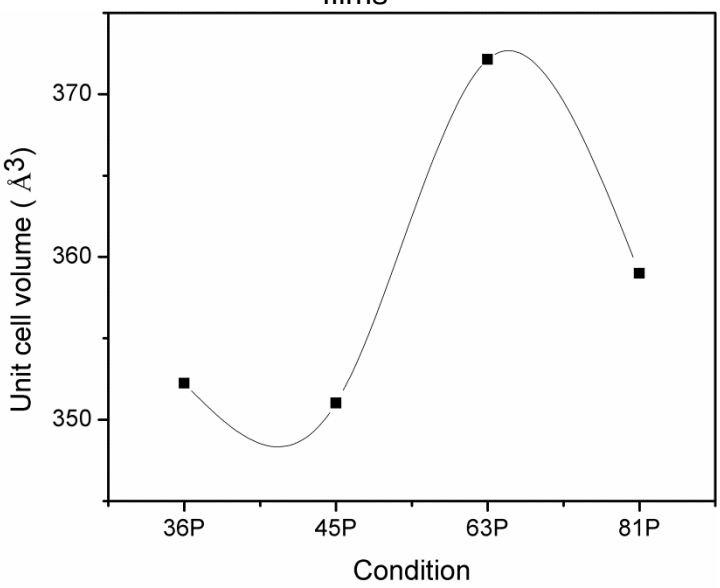

Fig. 4 Variation of unit cell volume for bismuth iron oxide thin films

The formation of crystal lattice induces some strain energy inside the molecules of material due to stress on crystal structure. When the molecules of materials having different atomic radii combines to form a compound structure the resulting lattice becomes under strain. The strain in lattice directly varies with dislocation densities because at higher dislocation density the stress will be higher which will also increase

the strain energy inside the structure and vice versa. Figure 5 shows the variation of strain energy with increasing microwave power. The increase in strain was observed for 36P, 45P and 81P due to appearance of $Bi_{25}FeO_{40}$ and Bi_2Fe4O_9 phases. Whereas, pure phase synthesis in 63P is the reason for reduced strain.

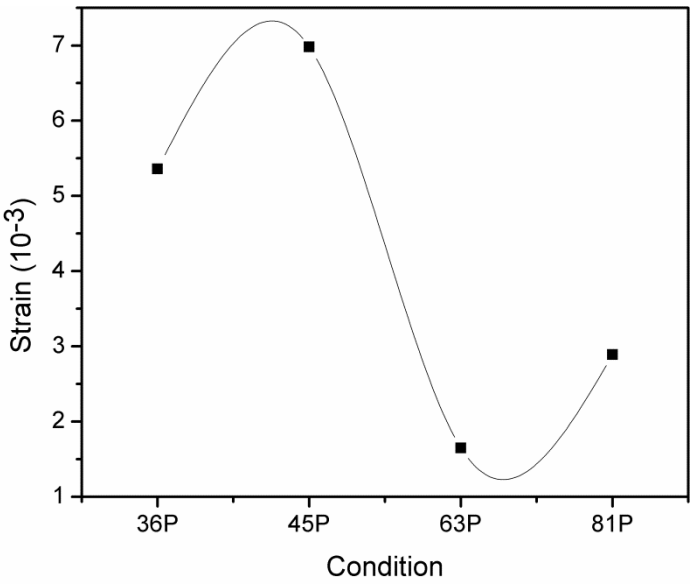

Fig. 5 Variation of strain energy for bismuth iron oxide thin films.

Magnetic behavior in thin films principally depend on the structure of magnetic domains. Figure 6 shows M-H curve for bismuth iron oxide thin films. It can be observed that 36P, 45P and 81P show weak magnetic behavior in comparison to that observed at 63P. At 36P and 45P this is associated with undeveloped ferromagnetic domain in $BiFeO_3$ solution due to insufficient thermal energy provided by electromagnetic radiations. Secondly bismuth rich phases in structure caused the deficiency of Fe^{3+} cations which could have been responsible for reduced magnetic behavior at 36P and 45P. At 63P pure phase synthesis of $BiFeO_3$ thin films leads to properly developed ferromagnetic domains in the structure, due which strong ferromagnetic behavior was observed. Moreover in $BiFeO_3$ structures the ferromagnetic behavior is also associated with the spiral spin arrangement having reported length ~ 62nm. Suppression of canting spin arrangement occurs below this reported length, giving rise to spontaneous ferromagnetism.

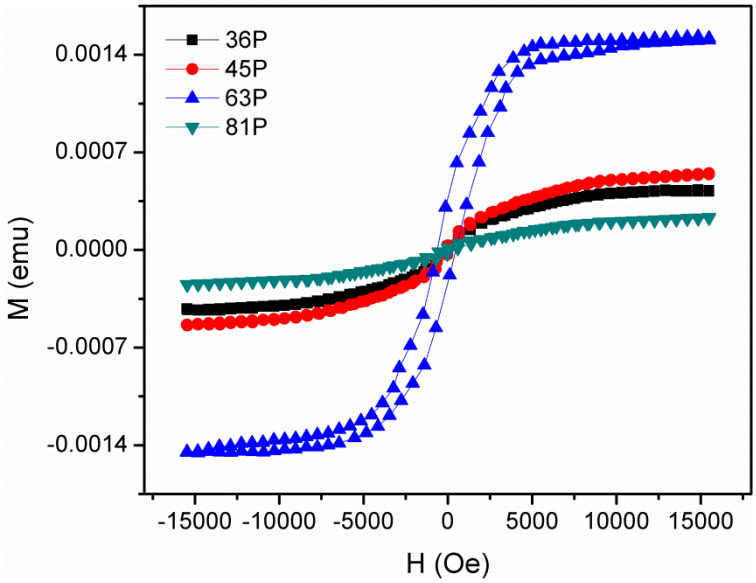

Fig. 6 M-H curves of $BiFeO_3$ thin films

Figure 7 shows the variation of saturation magnetization and coercivity of thin films. Saturation magnetization increases for 36P and 45P achieving maximum at 63P. Then with 81P saturation magnetization greatly drops to its minimum value. The coercivity of ferromagnetic material is strength of material against demagnetization force. Treatment of electromagnetic radiations caused the microstructural changes in crystal structure. Nucleation energy directly affects the grains and grain boundaries due to which ferromagnetic domains become isolated. For 63P isolation of magnetic domains increases, this results in decoupling of magnetic exchange interaction thus affecting coercivity. In magnetic materials ferromagnetism originates from small subdivided regions known as magnetic domains, whereas each domain individually responds to magnetization and contributes to spontaneous/ saturation magnetization.

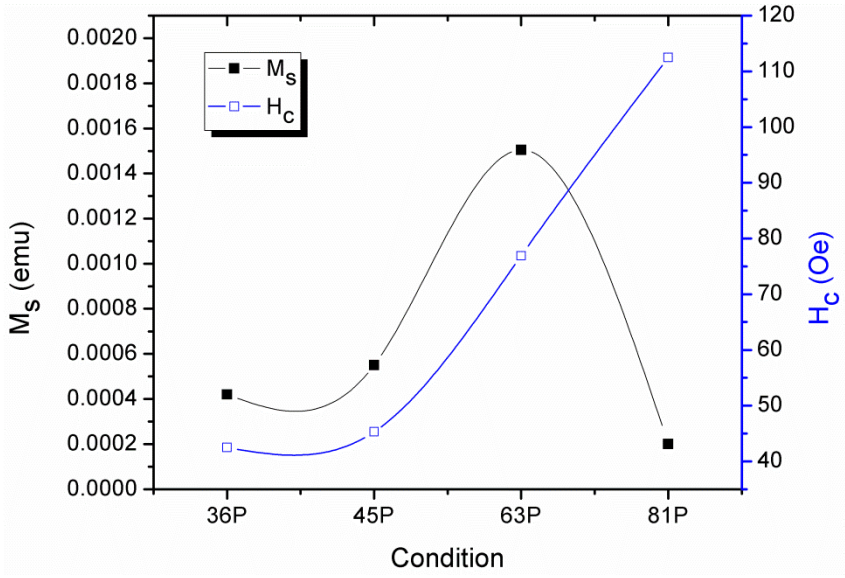

Fig. 7 Variation of saturation magnetization and Coercivity for bismuth iron oxide thin films

4. CONCLUSIONS

To study and enhance magnetic properties of $BiFeO_3$ thin films, electromagnetic radiations (frequency 2.45GHz) were used to prepare $BiFeO_3$ thin films designated as 36P, 45P, 63P and 81P. Annealing of thin films were done at low temperature of value 300^oC. Thin films of $BiFeO_3$ were characterized to observe magnetic properties. Thin films 36P, 45P and 81P showed mix phases and weak ferromagnetic behavior. Thin films 63P showed the strong ferromagnetic behavior due to pure phase synthesis.

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