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Magnetic Investigation and optimization of microwave based sol gel synthesis of $BiFeO_3$ Thin Films

Waqar Azeem[1)], Saira Riaz[2)] and *Shahzad Naseem[2)]

[1), 2)] *Centre of Excellence in Solid State Physics, Punjab University, Lahore, Pakistan*
[*]waqar.azeem@lgu.edu.pk

ABSTRACT

$BiFeO_3$ is multi ferroic Bismuth iron oxide, the most promising multiferroic material for magneto-electronic industry which is drawing the attention of material scientists because of its dual ferroic nature having high ferroelectric Curie temperature T_C of above 1100 K as well as high antiferromagnetic Neel temperature near 650 K. Bismuth iron oxide exhibit antiferromagnetic nature in bulk form but to achieve ferromagnetic manifestation require the synthesis of pure phase $BiFeO_3$ thin films. Whereas synthesizing the single/pure phase $BiFeO_3$ thin films is strenuous because of volatile nature of $BiFeO_3$ due which impurity phases also get developed during synthesis. This difficulty is overcome by various research techniques, mostly by annealing of prepared thin films as reported in most of literature at high temperature of 400 ºC to 700 ºC. However, we achieved pure phases of BiFeO3 thin films at low temperatures using microwaves radiations. Strong ferromagnetic behavior by variation of bismuth and ferrous (Bi and Fe) ratio in the range 1.0-1.10 at relatively lower annealing temperature of 300 ºC using 72% of microwave intensity. In this paper, the results regarding the best optimization for strong ferromagnetic behavior of $BiFeO_3$ thin film for (Bismuth and Ferrous) Bi and Fe Ratio 1.10 at low annealing temperature is reported.

1. Introduction

Multiferroic nature of $BiFeO_3$ makes it versatile and suitable material for diverse applications in electronics and spintronic devices and sensors. $BiFeO_3$ is among the tens of reported multiferroics which have high Neel and Curie temperatures, receptively 643 K and 1103 K for $BiFeO_3$. The volatile character of Bi_2O_3 phase steer to the formation of bismuth rich and bismuth deficient phases which may be undesirable for electronic and magnetic applications (Wang et al. 2006; Chen et al. 2012; Prashanthi et al. 2013; Soram et al. 2012; Ahmed et al. 2012). The impurity phases cause the inhomogeneity in spin structure which adversely effects macroscopic magnetization. The impurity phases can be reduce by leaching in concentrated HNO_3 solution however this method has poor reproducibility (Tripathy et al. 2013).

To overcome the difficulties in achieving pure phase of $BiFeO_3$ thin films various methods are discussed in literature by variation in synthesis, deposition and annealing conditions. (Kuk et al. 2005) synthesized thin films of $BiFeO_3$ by sol gel technique by nitrates of the bismuth and iron. They obtained pure phase of BFO by leaching out minor phases of Bi_2O_3 in diluted nitric acid. (Xu et al. 2009) reported synthesis of BFO films at relatively low temperature of 450 ºC using sol-gel method. They prepared the controlled solution using ethylene

[1)] Graduate Student
[2)] Professor

alcohol. (Prashanthi et al. 2013) prepared pure phase BFO thin films using Pulsed Laser in controlled annealing environment. The phase purity can also be achieved by addition and variation of compatible dopants (Khomchenko et al. 2009; Xue et al. 2013). Zheng et al. (2018) achieved the phase purity at high calcination temperature of 700^{o}C to 800^{o}C at molar ratio of Bi/Fe 1/1. Zheng et al. (2018) later reported the phase purity of BFO at relatively lower temperature of 450^{o}C by using the microwave assisted synthesis. However in literature less consideration is focused on synthesis of BFO films by variation of Bi/Fe molar ratios. Ke et al. (2011) reported the phase pure preparation of BFO film by variation of Bi/Fe ratio of 1 to 3% at calcination temperature of 400^{o}C to 600^{o}C.

The synthesis of $BiFeO_3$ solution using route of sol-gel method for variation in the molar ratios of Bi/Fe 1.0, 1.05 and 1.10, with 72% intensity of microwaves, are reported. The copper substrates were used to deposit BFO thin films by using spin coating of sol. The thin film was prepared in an evacuated environment, annealed for 60 minutes at 300^{o}C temperature, in presence of magnetic field 500Oe. Phase purity was achieved and results showing the magnetic and structural properties were correlated with varying ratio of Bismuth and Iron (Bi/Fe).

2. Experimental Details

In order to prepare the Sol-gel of $BiFeO_3$, two precursors Bismuth Nitrate and Iron Nitrate having chemical formula of $Bi((NO_3))_3$ and $Fe(NO_3)_3.9H_2O$ respectively were utilized. $BiFeO_3$ sol prepared by sol-gel route is simple and cost effective in chemical synthesis. To prepare BFO sol $(Bi(NO_3)_3$ and $Fe(NO_3)_3.9H_2O$ were dissolved in $C_2H_6O_2$ ethylene glycol solvent. Then two solutions were separately prepared. As reported by (Ke et al. 2011; Moniz et al. 2013), the ethylene glycol $C_2H_6O_2$ is the optimized solvent for obtaining strong ferromagnetic properties. Both the solutions were then mixed together in such a way to keep the Bismuth and Iron molar-ratio as 1.0, 1.05 and 1.10.

Mixed solution was heat treated with microwaves at selected microwave intensity of 72% and aged for 24 hours at room temperature. To deposit BFO thin films, the sols were then spin coated onto the clean copper substrates for 30 s at rpm of 500. Copper substrates were cleaned before deposition, by ultrasonication in acetone C_3H_6O and isopropyl alcohol C_3H_8O. After deposition, the thin-films were annealed for 60 minutes at 500Oe was applied magnetic field in a vacuum environment. In order to analyze and investigate, the structural and elemental properties characterization of thin film samples, Advance (XRD) the Bruker X-ray diffractometer D8 was used for magnetic properties of BFO films Lakeshore's 7407 vibrating sample magnetometer was employed shown in figure 1.

Lakeshore's 7407 Vibrating Sample Magnetometer

Bruker D8 Advance X-ray Diffractometer

Fig. 1 Characterization equipment.

3. Results and Discussion

The XRD patterns (Fig. 2) show the variation in the crystallinity and phase purity of BFO which are matched with JCPDS card no 86- 1518. The sample of molar ratio 1.0 indicated impurity phases of bismuth rich i.e. $Bi_2Fe_4O_9$ phase (Fig. 2(a)). During the investigation, the samples regarding molar ratio of Bismuth and Iron as 1.0 and 1.05 (Fig. 2(a,b)) peaks of rich Bismuth and deficient were evident to reduce the increasing crystallinity of BFO films. No impurity phases of Bismuth rich or deficient were seen at molar ratio of 1.10 (Fig. 2(c)).

Chen et al. (2012) synthesized pure phase BFO film over Si substrate at temperature 500°C. According to Ahmed et al. (2012), $BiFeO_3$ phase pure films were prepared at the temperature of 400-700 °C. Zheng et al. (2012) describes the synthesis of pure phase of BFO using molten salt at higher temperature of 750°C, whereas in the present work, the achievement was the phase purity of BFO films prepared at much lower temperature of 300°C.

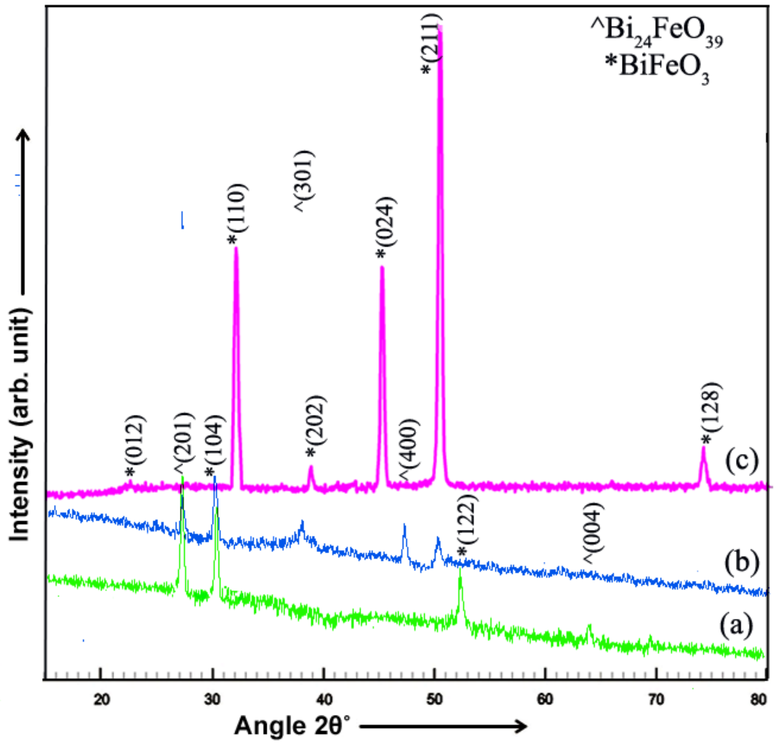


Fig. 2 XRD patterns for bismuth iron oxide thin films with Bi/Fe ratio (a) 1.0 (b) 1.05 (c) 1.10

Crystallinity of thin films depends on crystallite size and dislocation densities in crystal structure. XRD patterns confirm the pure phase BFO films which crystallize in rhombohedral perovskite structure. Crystallite was calculated by Scherer formula in Equation 1:

$$T = \frac{k\lambda}{B\cos\theta} \tag{1}$$

In this formula k is the shaping factor; the value of k is generally taken 0.9. B is width, λ represents wavelength and θ is angle of diffraction. At Bi/Fe ratio below 1.1 we observed impurity phases and so the increased dislocation densities which reduces the crystallinity and thereby will exhibit poor ferromagnetic properties.

It is shown in Figure 3a that Bi/Fe ratio 1.10 size of crystallite increases. Due to increase in crystallite size the packing of crystal becomes denser because of increase of lattice parameter thereby exponentially decreasing the dislocation of densities. The decrease in dislocation densities leads to the more crystalline formation of structure which exhibits strong ferromagnetic properties.

Lattice parameters of rhombohedral unit cell is calculated by using equation (2) the X-ray density of unit cell having volume of V = 0.866 a^2c was calculated using (3). Larger value of lattice parameter at Bi/Fe molar ratio 1.10 arises due to phase purity as was observed in Fig. 2(c).

$$\sin^2\theta = \frac{\lambda^2}{3a^2}\left(h^2 + k^2 + hk\right) + \frac{\lambda^2 l^2}{4c^2} \tag{2}$$

$$\rho = \frac{1.66042\,\Sigma A}{V} \tag{3}$$

The lattice parameters a and c represent lattice of unit cell, whereas h, k and l are the miller indices. The summation Sigma A (∑A) is total atomic weight related to unit cell and the unit cell volume V is measured in Angstroms.

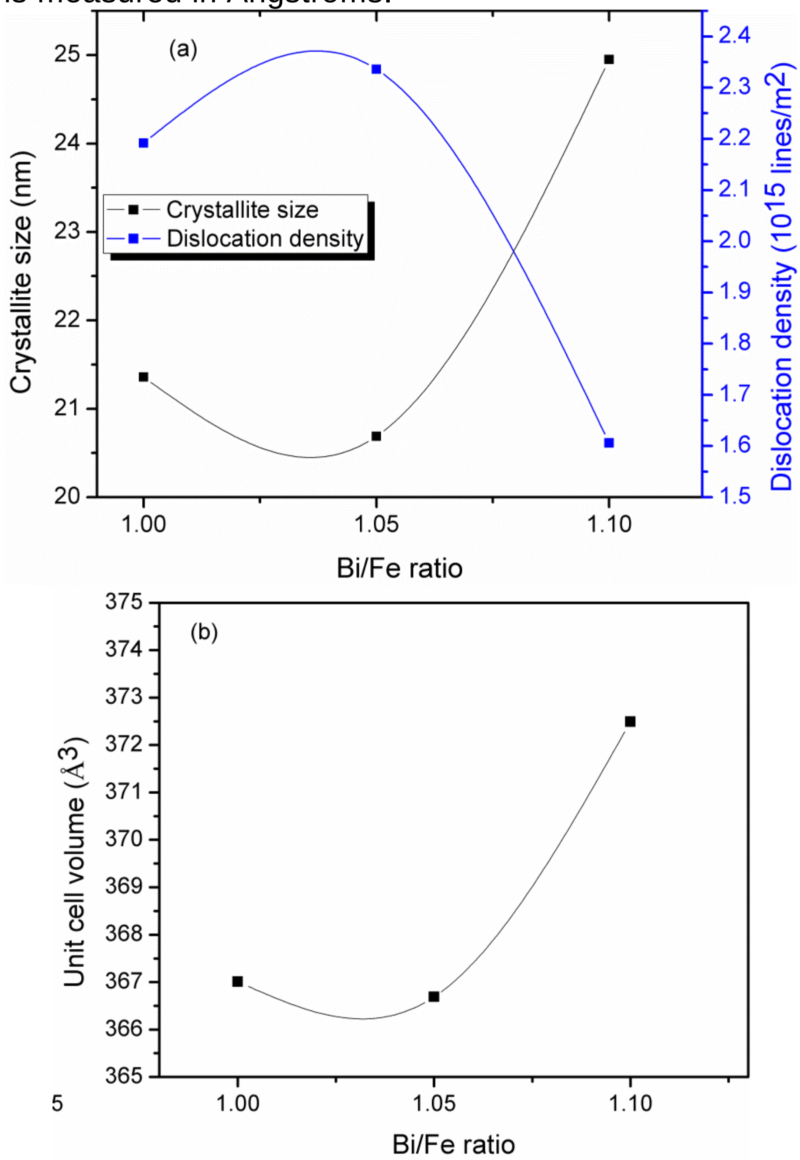
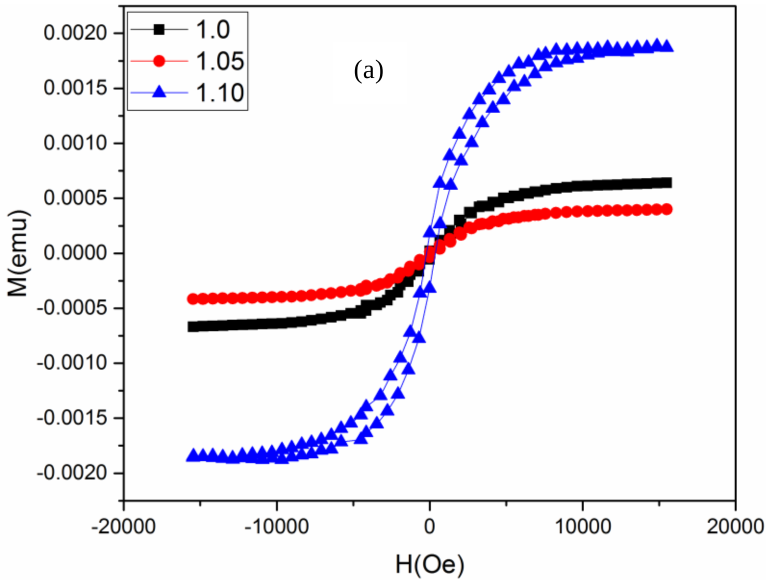


Fig. 3 a) Crystallite Size with variation of Bi/Fe ratio b) Unit cell volume with variation of Bi/Fe ratio

The multiferroics crystallite size strongly affects the magnetic properties of the material. If the size of crystallite is less then magnetic moments, divergence length of randomly oriented magnetic moments is suppressed thereby material exhibits strong ferromagnetic properties. For BFO the reported divergence length of magnetic moments is about 62 nm at which the canting of helical spin structure is suppressed and random orientation of magnetic moments decreases, due to which strong ferromagnetic behavior is induced in BFO having anti-ferromagnetic nature in bulk.
Relatively strong ferromagnetic behavior with saturation magnetization of ~28.5emu/cm^3 (Fig. 4) was observed at Bi/Fe ratio 1.10.



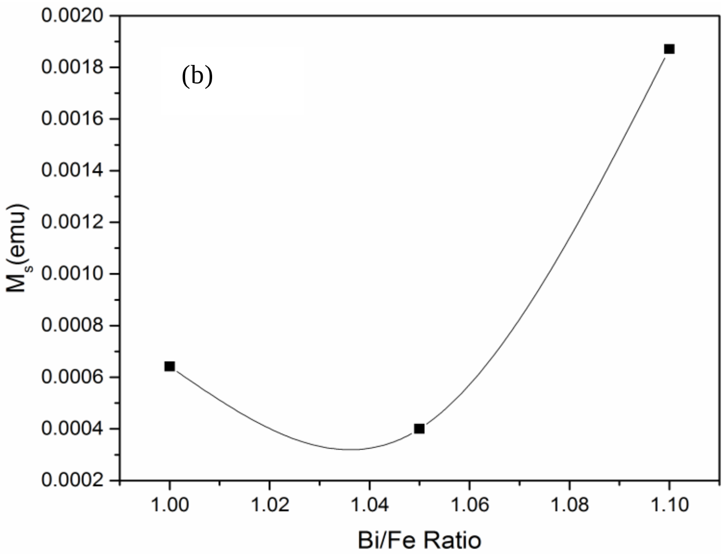


Fig. 4(a) MH curves (b) Variation of saturation magnetization for $BiFeO_3$ thin films

This type of strong ferromagnetic behavior of antiferro nature BFO has not been reported very much in literature. We reported strong ferromagnetism in BFO films prepared at much lower temperature as reported in literature in Table 1.

Table 1.Comparison of present Research work with literature

Bi/Fe	Our Work	Reported in Literature	
1.0	Annealing temp=300°C and M_s =0.0006	Annealing temp=700°C and Ms=0.00062	Moniz et al.2013
1.05	Annealing temp=300°C and M_s =0.0004		
1.10	Annealing temp=300°C and M_s =0.0016		

4. Conclusions

$BiFeO_3$ thin films were synthesized using microwave based sol gel technique. Thin films were deposited by spin coating over the copper substrate. Variation in Bi/Fe ratio results in strong ferromagnetic behavior of $BiFeO_3$ Thin Films. Pure phase of BFO films were achieved for the ratio of Bismuth/Iron at 1.10. The Ferromagnetism strongly depends on crystallite size and crystallinity of grown films. During the experimentation there is possible suppression of spiral-spin-structure. Therefore, for the Bismuth-Iron ratio at 1.1, strong ferromagnetic behavior is achieved in BFO thin films instead of antiferromagnetic behavior.

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