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Structural and Dielectric Properties of $Bi_{1-x}La_xFeO_3$ Thin Films

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ABSTRACT

Multiferroic materials like Bismuth Iron Oxide ($BiFeO_3$), $YMnO_3$, $BiMnO_3$, $TbMnO_3$ has attracted worldwide attraction due their applications in data storage devices, spintronic devices, sensors and multiple stage memories. Among these materials $BiFeO_3$ is a promising candidate as it exhibits room temperature antiferromagnetic and ferroelectric properties. However, $BiFeO_3$ suffers from some drawbacks including weak magnetic behavior, inhomogeneity in spin structure and large leakage current. In order to overcome these problems we here report Lanthanum (La) doped $Bi_{1-x}La_xFeO_3$ (where, x=0.0-0.5) thin films prepared by sol-gel method. The effect of La substitution on structural and dielectric properties has been investigated. The films show pure phase rhombohedrally distorted perovskite structure of $BiFeO_3$. XRD peak shifts to high angles due to slight difference in ionic radii of La^{3+} (1.16Å) and Bi^{3+} (1.17Å). The dielectric constant and tangent loss decreases as frequency increases and becomes constant at high frequencies showing normal dispersion behavior for all concentrations (i.e. x=0.0-0.5). The dispersion in dielectric constant occurs due to the time required by the carriers to get align in the direction of field. At high frequencies the field reversal is so high that the carriers do not get enough time to get aligned in the direction of field thus resulting in low dielectric constant at high frequency. The dielectric constant is strongly affected by changes in grain size. Decrease in grain size leads to increase in number of grain boundaries hindering the hopping process between the different states and grains thus resulting in accumulation of cations at the grain boundaries thus affecting the dielectric constant.

1. INTRODUCTION

Multiferroic oxides are materials that combine the properties of both ferroelectric and ferromagnetic materials in single phase. This opens new applications of multiferroic materials in data storage devices, magnetic field sensors etc. (Wang 2013, Wei 2013)

Bismuth iron oxide ($BiFeO_3$), exhibiting room temperature multiferroic properties, has drawn considerable research attention owing to its potential applications in spintronic devices. In $BiFeO_3$ both electric and magnetic orders exists simultaneously with ordering temperature of 643K and 1103K respectively. The coupling between

magnetic and electrical properties allows synchronized control of magnetism and electric polarization (Yan 2013, Liu 2014). Bismuth iron oxide crystallizes in rhombohedrally distorted perovskite structure. It exhibits G-type antiferromagnetic behavior. The spin periodicity of $BiFeO_3$ between two successive planes is reported to be 620Å. Ferromagnetic interaction is cancelled out in $BiFeO_3$ due to the spiral spin structure. As a result of which, reduction in magnetoelectric coupling arises (Suresh 2013). According to Bi_2O_3-Fe_2O_3 phase diagram, bismuth iron oxide ($BiFeO_3$) is a linear compound (Lahmar 2011). Deviation from stoichiometry leads to formation of bismuth rich and/or bismuth deficient phases. The presence of secondary phases results in high leakage current and low magnetic moment. High leakage current and low magnetic behavior is the two main limiting factors for extensive use of $BiFeO_3$ (Dhir 2014, Jian 2013)

In order to overcome these difficulties, various dopants have been reported in literature including Ca, Mn, Ni, Zr etc. Rare earth dopants are substituted for Bi site. This type of substitution leads to decrease in oxygen vacancies and thus reduce the leakage current. Doping of rare earth elements also leads to enhanced ferroelectric properties. This effect is achieved by presence of strain caused by dopant atom. On the other hand, transition metal atoms are substituted for Fe site. This suppresses the valence fluctuation in of iron atom (3+ and 2+) and reduces leakage current. Among the various dopants lanthanum substitution is the most important as its ionic radius matches well with bismuth (Arora 2014, Dhir 2014).

We here report the preparation, structural and dielectric properties of lanthanum doped bismuth iron oxide thin films using sol-gel method. The changes in dielectric and structural properties are correlated with variation in dopant concentration.

2. EXPERIMENTAL DETAILS

Lanthanum doped bismuth iron oxide thin films were prepared using sol-gel method. $Bi(NO_3)_3.5H_2O$ and $Fe(NO_3)_3.9H_2O$ were used as precursor. $Bi(NO_3)_3.5H_2O$ and $Fe(NO_3)_3.9H_2O$ were dissolved in ethylene glycol and stirred at room temperature for 60mins. The two solutions were mixed together and heated on hot plate at 60˚C to obtain bismuth iron oxide sol. The details of sol-gel synthesis are reported earlier (Shah 2014(a), Shah 2014(b)). For doping purpose, $La(NO_3)_3.6H_2O$ was dissolved in ethylene glycol and added to $BiFeO_3$ sol to obtain $Bi_{1-x}La_xFeO_3$. The dopant concentration was varied as x=0.0-0.5. The sols were spin coated on copper substrate and annealed at 300˚C for 60mins. Prior to spin coating, copper substrates were etched using diluted HCl and the rinsed repeatedly using DI water. The substrates were placed in ultrasonic bath in acetone and isopropyl alcohol for 10mins and 15mins respectively (Asghar 2006(a), (b)).

The films were characterized structurally using Bruker D8 Advance X-ray diffractometer (XRD) with λ=1.5406Å. Dielectric properties were carried out using 6500B Precision Impedance Analyzer.

3. RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns for $Bi_{1-x}La_xFeO_3$ (x=0.1, 0.3, 0.5) thin films prepared using sol-gel method and annealed at 300˚C. The presence of diffraction peaks

corresponding to planes (024), (122) and (128) indicate the formation of phase pure bismuth iron oxide. No peaks corresponding to bismuth rich and/or bismuth deficient phase was observed. In addition, no diffraction peaks corresponding to lanthanum and/or lanthanum oxide were present. The peak positions corresponding to (024) and (122) planes slightly shift to high diffraction angles.

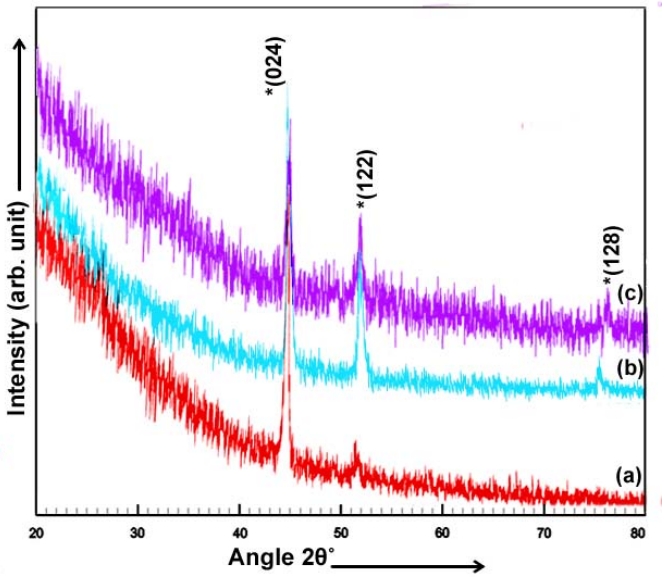

Fig. 1 XRD patterns for La doped $BiFeO_3$ thin films for x= (a) 0.1, (b) x=0.3, (c) x=0.5

Crystallite size (*t*), strain and dislocation density (*δ*) (Cullity 1956) of lanthanum doped bismuth iron oxide thin films is calculated using Eq. (1)-(3)

$$t = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

$$Strain = \frac{\Delta d}{d} \quad (2)$$

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

Where, *λ* is the wavelength (1.5406Å), *B* is the Full Width at Half Maximum (FWHM), *Δd* is the change in d-spacing (*d*) with respect to standard data. The crystallite size, dislocation density and strain are plotted as a function of dopant concentration in Fig. 2. Crystallite size dislocation density and strain are plotted as a function of dopant concentration in Fig. 2. Crystallite size increases from 29 nm to 42 nm as the dopant concentration is increased from 0.1 to 0.3. Further increasing the dopant concentration to 0.5 resulted in decrease in crystallite size to 30nm. Crystallite size depends on 1) accumulated strain energy. With increase in crystallite size to 42 nm reduction in strain was observed as can be seen in Fig. 2(b). Increase in crystallite size to 42nm also resulted in decrease in dislocation density to 5.69×10^{14} lines/m^2 due to reduced number of grain boundaries. 2) Neighboring grains due to curvature of energetic grain boundaries (Riaz 2007).

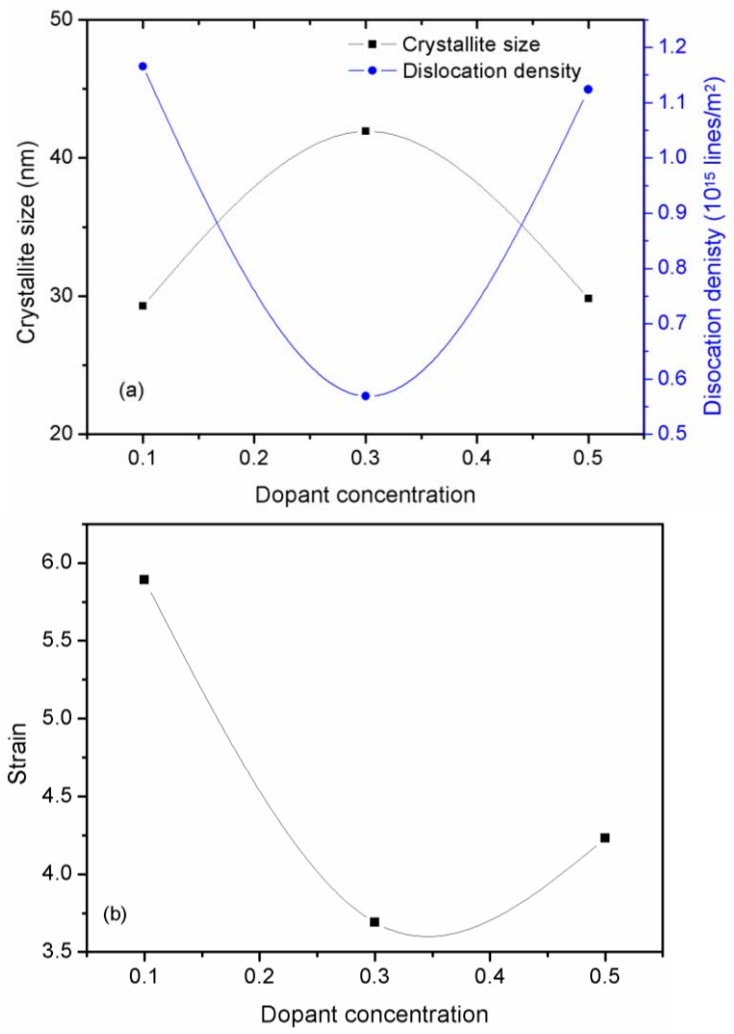

Fig. 2 (a) Crystallite size and dislocation density (b) strain as a function of dopant concentration

For studying the dielectric properties of $BiFeO_3$ thin films impedance analyzer was used in parallel plate configuration. The parallel capacitance and parallel resistance were measured and then using Eq. 4 and Eq. 5 the dielectric constant ε and dielectric loss (tangent loss tan δ) were calculated.

$$\varepsilon = \frac{C \times d}{\varepsilon_O \times A} \tag{4}$$

$$\tan\delta = \frac{1}{2\pi\varepsilon\varepsilon_O\rho} \tag{5}$$

Where, *C* is the capacitance, *d* is the thickness of the specimen, *A* the area of the device, ε_o is permittivity of free space and ρ is the resistivity of the thin films. Dielectric constant and tangent loss decreases as the frequency of externally applied field increases. At low frequencies, the space charge carriers follow the orientation of

applied field. As frequency of the field increases, space charge carriers do not get enough time to get aligned in the direction of externally applied field thus make no contribution to polarization. As the result of which, dielectric constant becomes steady at high fields.

Dielectric constant increases from 26 to 44 (at f=500kHz) with increase in dopant concentration from 0.1 to 0.3. Further increase in dopant concentration to 0.5 resulted in decrease in dielectric constant to 34. The increase in dielectric constant till dopant concentration of 0.3 is due to reduced defects in thin films as was observed in Fig. 2.

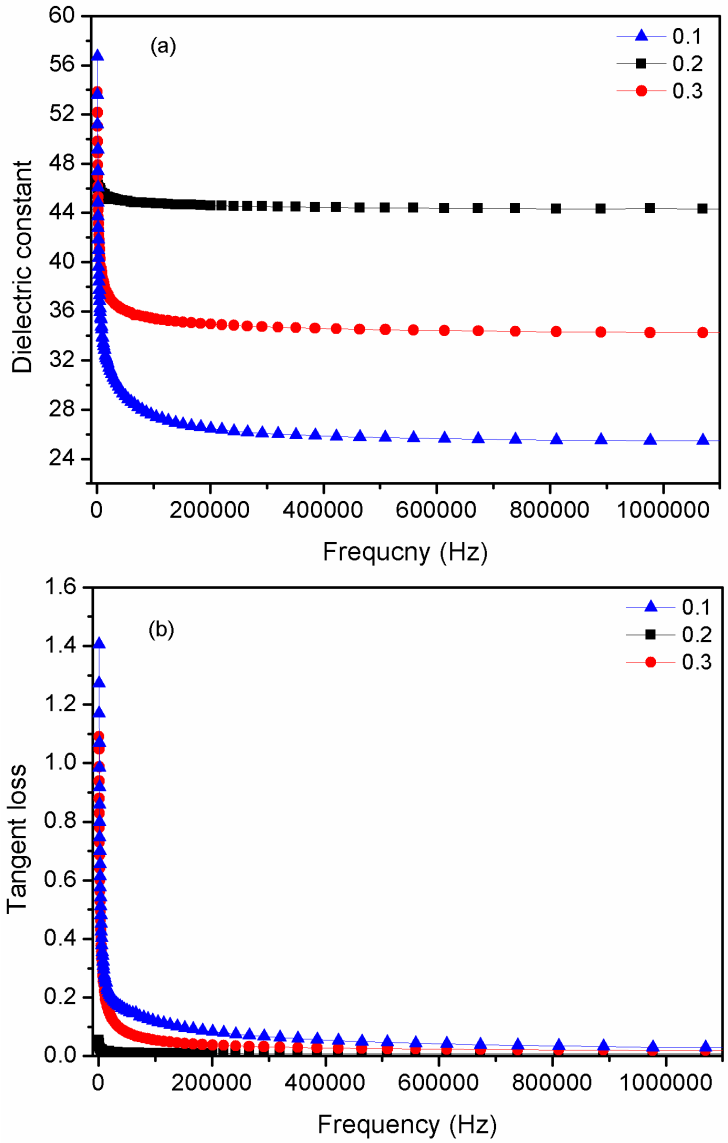

Fig. 3 (a) Dielectric constant (b) tangent loss for lanthanum doped bismuth iron oxide thin films

4. CONCLUSIONS

Lanthanum doped bismuth iron oxide thin films were prepared using sol-gel method. Dopant concentration is varied as 0.1, 0.3 and 0.5. XRD results indicate successful

incorporation of dopant in the host lattice. Crystallite size increases from 29 nm to 42 nm as dopant concentration was increased to x=0.3 and then decreases with further increase in dopant concentration. Dielectric constant and tangent loss show normal dispersion behavior. Dielectric constant increases as the dopant concentration was increased to x=0.3 due to reduction in crystal defects.

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