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Magnetic and Structural Properties of La doped $BiFeO_3$ Thin Films

Aseya Akbar[1)], Saira Riaz[2)], Shahid Atiq[2)] and Shahzad Naseem[2)]

Centre of Excellence in Solid State Physics, University of the Punjab, Lahore, Pakistan
[*)] saira_cssp@yahoo.com

ABSTRACT

Multiferroic materials like Bismuth Iron Oxide ($BiFeO_3$), $YMnO_3$, $BiMnO_3$, $TbMnO_3$ has attracted worldwide attraction due its wide range of applications in data storage devices, spintronic devices, sensors and multiple stage memories. Among these materials $BiFeO_3$ is a promising candidate as it exhibit room temperature antiferromagnetic and ferroelectric properties. However, $BiFeO_3$ suffers from some drawbacks including large leakage current, inhomogeneity in spin structure and volatile nature of Bi_2O_3. 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, optical, magnetic and dielectric properties has been studied. Undoped $BiFeO_3$ thin films show the presence of impurity phase of $Bi_2Fe_4O_9$ however it is seen that La doping hinders the formation of secondary phases and gives pure rhombohedrally distorted perovskite structure. Moreover, with increasing La content transition from rhombohedral to orthorhombic symmetry is also observed. XRD peaks shift to low angles arises due to slight difference in ionic radii of La^{+3} (1.06Å) and Bi^{+3} (1.03Å). Band gap of undoped $BiFeO_3$ is low as compared to La doped for x=0.1 due to the presence of impurity phase and with increase in La content the band gap decreases from 2.7-2.6eV. La^{+3} doping also affect the dielectric properties as dielectric constant increases with x. Ferromagnetic behavior, as opposed to antiferromagnetic, in undoped and doped $BiFeO_3$ is due to suppression of spiral spin structure. An enhancement in magnetization is observed with increasing La content.

1. INTRODUCTION

Multiferroic materials like Bismuth Iron Oxide ($BiFeO_3$) (Lin 2013), $YMnO_3$ (Kumar 2013), $BiMnO_3$ (Prokhorov 2012), $TbMnO_3$ (Osuna 2012) has attracted worldwide attraction due its wide range of applications in data storage devices, spintronic devices, sensors and multiple stage memories. Among these materials $BiFeO_3$ is a promising candidate as it exhibit room temperature ferromagnetic and ferroelectric properties

[1)] Graduate Student
[2)] Professor

(Ahmed 2012). $BiFeO_3$ has a rhombohedrally distorted perovskite structure belonging to $R3_c$ space group. It exhibit high G-type antiferromagnetic Neel temperature (T_N=643K) and high ferroelectric Curie temperature (T_c=1043K) (Prashanthi 2013). The ferromagnetic nature of BFO is due to canted spin structure of Fe^{+2} cation that leads to residual magnetic moment. The ferroelectric properties are because of $6s^2$ lone pair of Bi^{+3} cation (Sen 2012, Chen 2012). When an external electric or magnetic field is applied coupling effect arises between electrical and magnetic behavior due to the lattice distortion of $BiFeO_3$ (Sen 2012).

However, there are some complexities associated to Bismuth Iron Oxide. (1) Bi_2O_3 has a low melting point and is highly volatile. So it becomes difficult to synthesize pure $BiFeO_3$ phase as both deficiency and excess of Bi_2O_3 leads to bismuth rich and deficient phases. (2) The kinetics of formation and thermal stability limits are still under consideration. A lot of contradictory reports are present in literature related to temperature and phase transitions in Bi_2O_3-Fe_2O_3. (3) Valence fluctuations in iron between Fe^{+2} and Fe^{+3} give a large leakage current (Sen 2012, Ishiwara 2012). Inhomogeneity in the spin structure of BFO cancels out the magnetization and magneto electric effect is not observed in case of pure $BiFeO_3$ phase (Kumar 2012). Low impurity levels of bismuth rich and bismuth deficient phases are known not to affect the magnetic and structural properties but even small impurity level has a tremendous effect of optical, electrical and dielectric properties (Ishiwara 2012, Casper 2013).

Doping of La in BFO is known to reduce oxygen vacancy thus leading to enhanced insulating and ferroelectric properties (Simoes 2012, Kumar 2010). Moreover studies have shown inhomogeneity in spin structure of $BiFeO_3$ is suppressed by La doping thus leading to better magnetic properties as compared to undoped BFO films (Lee 2005, Simoes 2007, Lazenka 2012). Moreover, Lanthanum being non-volatile helps in controlling the volatile nature of bismuth and in turn suppresses the formation of oxygen vacancies that arises due to charge compensation. Further, due to electronegativity difference of Bi^{+3} (2.02) and La^{+3} (1.1), the ionic bond strength of Bi-O is less than that of Bi-O. Therefore, enthalpy of formation of La- doped BFO is less than that of un-doped BFO (Kumar 2010).

2. Experimental Details

The Research grade iron nitrate ($Fe(NO_3)_3.6H_2O$), bismuth nitrate ($Bi(NO_3)_,$.5H2O) and lanthanum nitrate ($La(NO_3)_3.6H_2O$) were used as precursors without further purification. The precursor solutions of bismuth and iron were prepared by separately dissolving $FeCl_3.6H_2O$, $La(NO_3)_3.6H_2O$ and 10%wt excess of $Bi(NO_3)_3.5H_2O$ separately in ethylene glycol. Bismuth and nitrate have different electronegativities that lead to different hydrolysis rate. Ethylene glycol is a linearly structured molecule with two hydroxyl groups which helps to compensate for the difference in hydrolysis rate thus leading to the synthesis of a stable sol. the solutions were then mixed in appropriate proportions and heated for several hours to get $Bi_{1-x}La_xFeO_3$ stable sol where x varies from 0-0.5. Excess 10% wt bismuth was added to compensate for the loss of bismuth upon annealing. As bismuth is volatile so it would not have been possible to obtain pure $BiFeO_3$ phase without excess of bismuth. The BFO and BLFO were spin coated on copper substrate using Delta 6RC spin coater at 3000rpm for 30sec. Before spin coating copper substrates were first etched by diluted HCl followed by ultrasonication in acetone and IPA for 10mins. Several coatings were done before the required film thickness was obtained. During successive coatings the films were kept on hot plate at 150˚C for 10min in order to remove the residual solvent. The films were then annealed in closed atmosphere at 300˚C. To study the effect of magnetic annealing on magnetic properties of thin films the films deposited under same conditions were annealed in vacuum in the presence of 500Oe magnetic field at 300˚C.

BFO and BLFO thin films were characterized structurally using Bruker D8 Advance X-ray Diffractometer using CuKα (λ=1.5405Å) with nickel filter. The copper target is operated at voltage of 30kV and current value of 22.5mA. For studying the microstructure of thin films S-3400N Scanning Electron Microscope was used operated at an acceleration voltage of 30kV and working distance of 7mm. Surface roughness was measured using Atomic Force Microscope (Veeco CP-II Scanning Probe Microscope). Magnetic properties were studied using Lakeshore's 7407 Vibrating Sample Magnetometer. The dielectric constant was measured using 6500-B Impedance Analyzer within the frequency range of 100Hz-1MHz.

2. Results and Discussion

Fig. 1 show X-ray diffraction pattern for undoped $BiFeO_3$ thin films under as deposited conditions. Substrate peaks are eliminated. Peaks belonging to BFO are indexed according to JCPD card no. 20-169. No peaks of secondary BFO i.e. $Bi_2Fe_4O_9$ and $Bi_{46}Fe_2O_7$ were detected indicating the formation of pure phase polycrystalline $BiFeO_3$ distorted rhombohedral perovskite structure. Non-perovskite phases are suppressed by using equimolar ratio of Bi and Fe content that leads to excess bismuth thus compensating for the volatility of bismuth ions. Two prominent shoulder peaks in inset of Fig. 1 is because of two closely mis-oriented planes (320) and (321). Moreover, splitting of planes (110) and (110) is observed in case of film b. These results indicate that copper can act as a suitable substrate for deposition and stability of $BiFeO_3$ thin films.

The most important thing is the polycrystalline nature of $BiFeO_3$ observed in our films without any heat treatment. To the best of our knowledge there is no report on polycrystalline nature of $BiFeO_3$ thin films using chemical methods without heat treatment. Huang (2011) reported pure $BiFeO_3$ films on $Pt/Ti/Si/SiO_2$ substrate in the temperature range of 400-500°C using chemical solution deposition method. Sharma (2011) prepared nanostructured $BiFeO_3$ thin films on glass substrate via sol-gel and obtained crystalline $BiFeO_3$ phase upon annealing at 450°C. Das (2010) used wet chemical route and obtained the required phase after annealing the films at 400°C and 500°C. Zhang (2010) obtained polycrystalline $BiFeO_3$ thin films, prepared via chemical solution deposition method, upon annealing at 500°C. This literature overview and our XRD results indicate that there is so far no report on polycrystalline pure $BiFeO_3$ films at room temperature, and that copper can act as a suitable substrate for obtaining single phase BFO thin films which is being observed in our case for the first time.

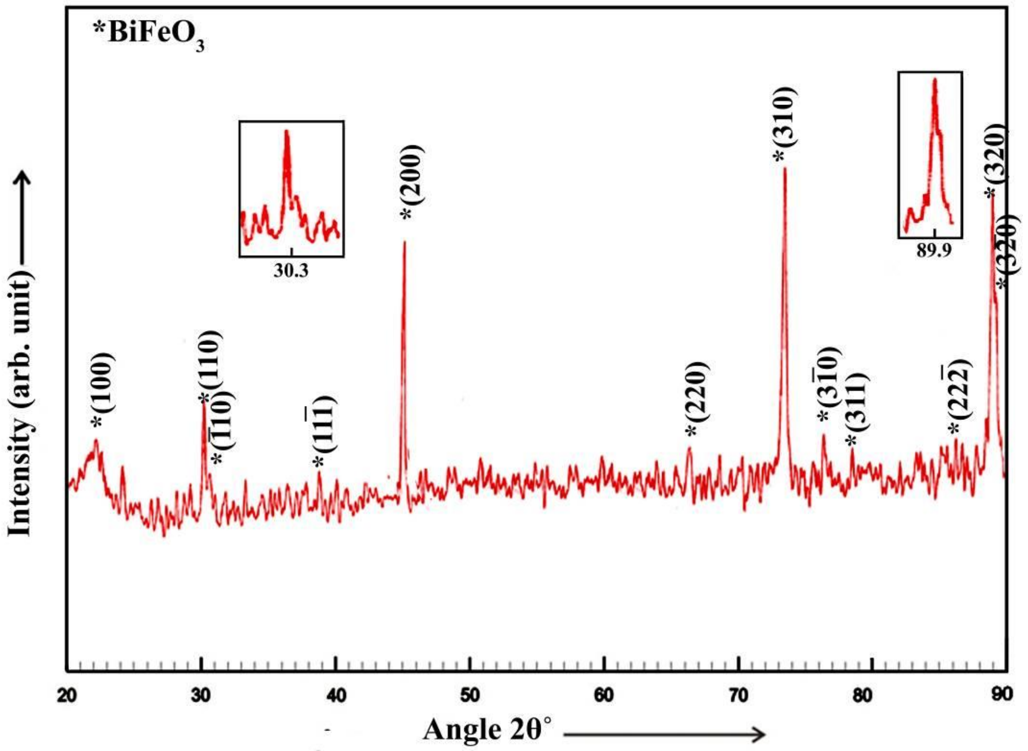

Fig. 1 XRD pattern of BFO thin films for x=0.0.

In order to study the optical properties of undoped $BiFeO_3$ thin films and effect of lanthanum doping Variable Angle Spectroscopic Ellipsometry (VASE) was carried out at an angle of incidence of 70˚ near the Brewster angle. Detailed optical properties are to be reported elsewhere. However in order to get an overview of the optical parameters the band gaps of the films are shown in Fig 2. It can be seen that the band gap of the films decreases as the concentration of lanthanum increases. This is due to the fact that incorporation of impurity in the host lattice induces localized states near the conduction band or valence band edge. This effect leads to decrease of the band gap.

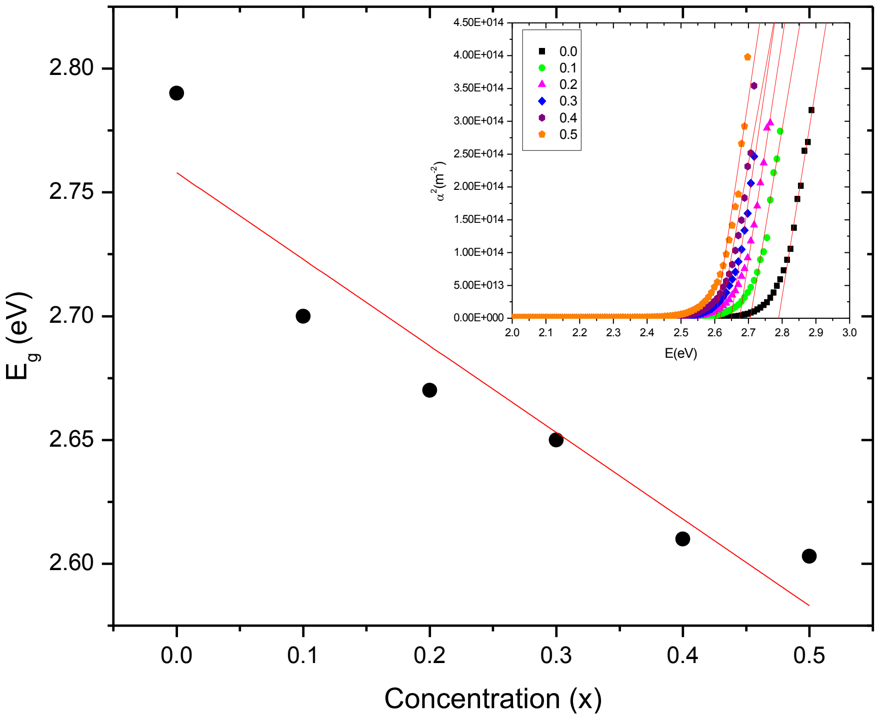

Fig. 2 Band gap of $Bi_{1-x}La_xFeO_3$ films as a function of lanthanum concentration

Fig. 3 show magnetic hysteresis curve at 300K for undoped $BiFeO_3$ and La doped $BiFeO_3$ thin films. All the films show ferromagnetic behavior. Even the presence of small open hysteresis at low field strength in undoped $BiFeO_3$ films indicates the presence of ferromagnetic domains as opposed to antiferromagnetic nature of bulk $BiFeO_3$. It can be seen that lanthanum addition strongly affects the magnetic properties of $BiFeO_3$ films. Ahmed (2013) obtained antiferromagnetic behavior of undoped bismuth iron oxide films and observed enhancement of magnetization with increase in lanthanum content to 0.3. Jangid (2012) observed antiferromagnetic behavior in undoped $BiFeO_3$ specimen and observed ferromagnetic hysteresis at dopant concentration of 50%. Antiferromagnetic behavior in undoped bismuth iron oxide is reported also by Chaudhuri (2012).

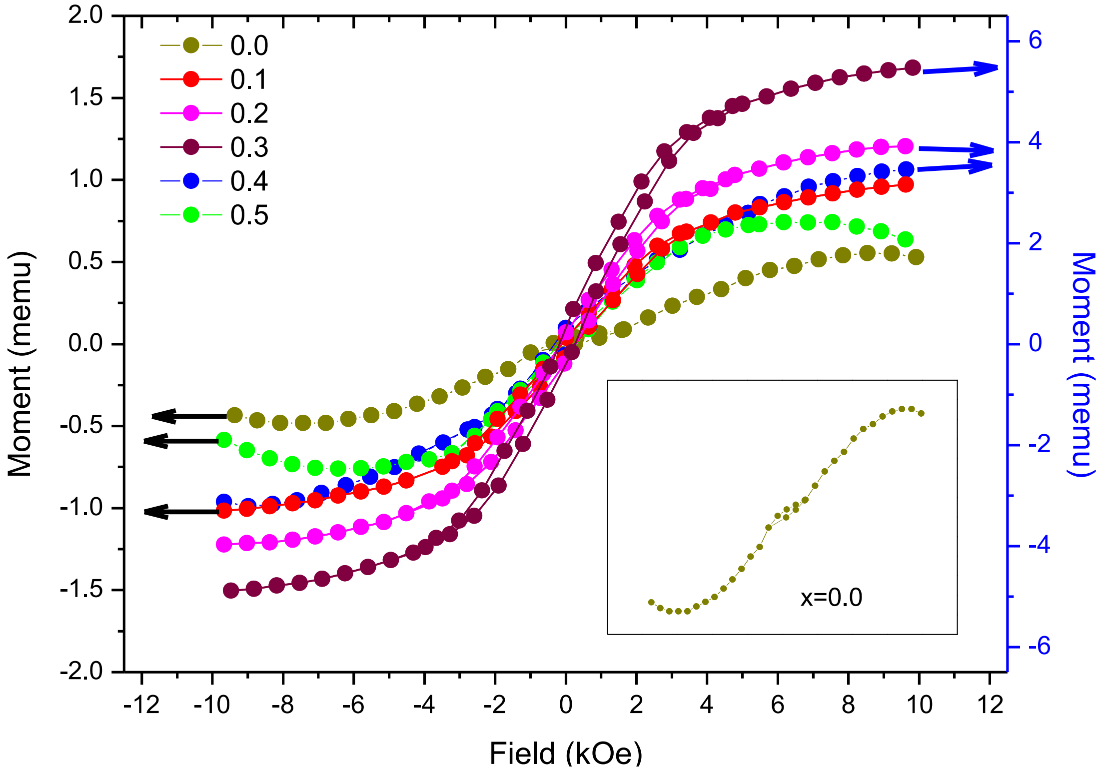

Fig. 3 M-H curves for undoped and doped $BiFeO_3$

For a given specimen, the modifications that take place in the magnetic properties occur through the creation of energy barrier. The physical phenomenons that are accountable for the formation of energy barrier have some related length scale (Ahmed 2013). These length scales include "*crystalline anisotropy*", "*applied field*" and "*magnetostatic*" length scale. This length determines the minimum distance over which the direction of magnetic moment can diverge substantially. This can also be a representative of domain wall width of the specimen. So if the crystallite sizes turn out to be smaller than this length scale the magnetization of specimen will not follow the random orientation of the easy axis of magnetic moment. For pure $BiFeO_3$ this length scale is reported to be 62nm (620Å) (Thakuria 2012. Moreover it has been reported earlier that BiFeO3 show G-type antiferromagnetism where the spins in the adjacent planes are antiferromagnetically coupled and spins in the same plane are ferromagnetically coupled. This causes canting of spin structure due to Dzyaloshinskii-Moriya interaction. And when this canting of spiral spin structure is suppressed ferromagnetic behavior is induced in other wise antiferromagnetic. Another reason of the ferromagnetic behavior of undoped $BiFeO_3$ can be the presence of oxygen vacancies and/or conversion of Fe^{+3} cations to Fe^{+2}.

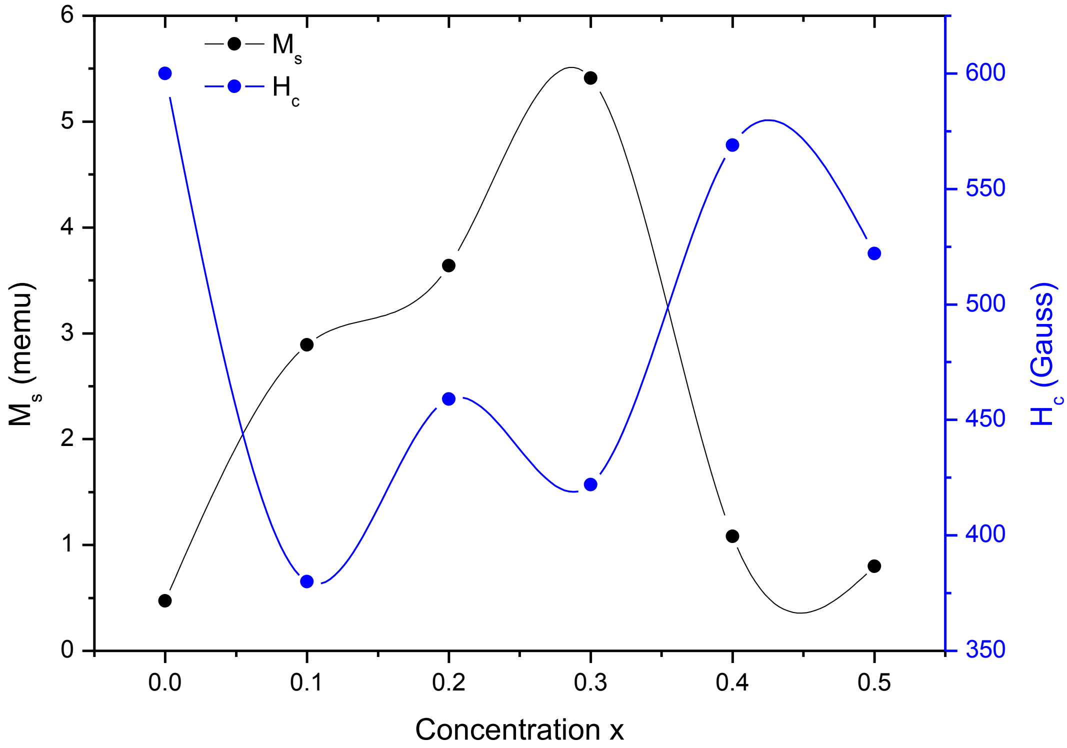

Fig. 4 Saturation magnetization and coercivity as a function of dopant concentration

The ferromagnetic nature of pure $BiFeO_3$ films increases as lanthanum was incorporated into the host lattice. With increase in lanthanum concentration to x=0.3, the saturation magnetization increases where as further increase in La content decreases the magnetic moments (Fig. 4). This indicates that substitution of Bi^{+3} ions with La^{+3} ions suppress the spiral arrangement of spins so that magnetic moment increases. Another likely reason for the enhanced magnetic moment is due to increase of Fe^{+2} cations and oxygen vacancies.

3. CONCLUSIONS

Undoped and lanthanum doped $BiFeO_3$ thin films are prepared using cost effective and application oriented sol-gel method. The films are then annealed at 300˚C in vacuum in the presence of magnetic field. The undoped films show rhombohedrally distorted perovskite pure $BiFeO_3$ phase without any trace of impurity phase. The optical band gaps show a decrease with the increase in lanthanum concentration due to formation of localized states within the forbidden band. Undoped films ferromagnetic behavior due to suppression of cycloidal spin structure and the ferromagnetic behavior increases with the increase in dopant concentration till x=0.3. Further increase in lanthanum concentration causes decrease in magnetic moment.

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