

## **Magnetic and Structural Properties of Calcium doped BiFeO<sub>3</sub> Thin Films**

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### **ABSTRACT**

We here report synthesis and preparation of Bi<sub>1-x</sub>Ca<sub>x</sub>FeO<sub>3</sub> (where x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5) thin films using cost effect and low temperature sol-gel process. The films are characterized for their changes in structural, electrical, optical and magnetic properties. As Ca<sup>+2</sup> has a smaller ionic radius than Bi<sup>+3</sup> brings about the shrinkage of unit cell thus altering the Fe-O-Fe bond length and bond angle thus controlling the overlap of Fe3d and O2p orbital and in turn affect the electrical properties. The electronic structure is also affected by the charge compensation mechanism (oxygen vacancies) caused by replacement of trivalent ion with divalent anion. XRD results of doped BiFeO<sub>3</sub> show rhombohedrally distorted perovskite structure. Shift of peak positions with doping indicates that the unit cell parameters are affected by the presence of Ca<sup>+2</sup> ions. The addition of Ca<sup>+2</sup> form localized states within the forbidden band thus leading to decrease in band gap. The band gap varies from 2.7eV to 2.4eV with increasing calcium concentration. Improvement in magnetic properties is observed upon doping as a consequence of structural changes in the films that modify the magnetic exchange interactions among iron ions thus helping in achieving ferromagnetic behavior. Dielectric properties show dispersion at relatively low frequencies and are strongly affected by the structural changes in films with increasing concentration of calcium.

### **1. INTRODUCTION**

In recent years multiferroic materials have attracted wide attention due to its simultaneous ferroelectric and ferromagnetic properties. Among various multiferroic materials BiFeO<sub>3</sub> is the most widely studied material because of it shows ferroelectricity with high curie temperature (T<sub>c</sub>=1103K) and G-type antiferromagnetic order with relatively high Neel temperature (T<sub>N</sub>=643K) with long range cycloidal arrangement of 62nm (Kianinia 2011, Quan 2008, Gautam 2010, Ramachandran 2012). In BiFeO<sub>3</sub> 6s

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lone pair of electrons is responsible for ferroelectric properties while magnetic ordering is because of partially filled d orbitals of iron. When electric field or magnetic field is applied the coupling effect between electric and magnetic behavior arises due to the lattice distortion of BiFeO<sub>3</sub> (Gautam 2010). Saturation polarization of 60 μC/cm<sup>2</sup> can be reached in this material that is much smaller than the bulk values due to large leakage current (Ramachandran 2012).

On the other hand, there are still drawbacks associated with BiFeO<sub>3</sub> most important of which is obtaining pure BiFeO<sub>3</sub> phase. High volatility of Bi<sub>2</sub>O<sub>3</sub> leads to formation of bismuth deficient phase Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and small excess of Bi<sub>2</sub>O<sub>3</sub> can lead to the formation of Bi<sub>25</sub>FeO<sub>39</sub>. Moreover, pure BiFeO<sub>3</sub> phase has got certain drawbacks like high coercive field, large dielectric loss, in-homogenous spin structure, small remnant polarization (Quan 2008). One way to overcome these problems is to dope BiFeO<sub>3</sub> on A-site, B-site or A-B site using Ce (Quan 2008, Bhushan 2009), Mn, Nb (Jun et al. 2005), Pb (Mazumder and Sen 2009) etc.

Introducing A-site dopant atoms in BFO leads to homogenous canting of spin structure. Such spin canting arises from Dzyaloshinskii–Moriya interaction whose strength strongly depends on spin orbit coupling (Khomchenko et al. 2008). Ferromagnetic behavior instead of antiferromagnetism is highly desirable for low field applications. Doping elements causes a change in symmetry of BiFeO<sub>3</sub> thus enhancing the piezoelectric properties (Ahadi et al. 2012). Also with doping long range order of spin cycloid can be suppressed thus leading to increase in magnetic moment and thus more efficient magneto-electric effect (Ahadi et al. 2012). Doping experiments with Ca<sup>+2</sup> (replacing Bi<sup>+3</sup>) are of particular interest. Ca<sup>+2</sup> has a small ionic radii as compared to Bi<sup>+3</sup> that leads to contraction of the unit cell volume. Ahadi et. al reported a three order of rise in conductivity with incorporation of 15% calcium. However, conductivity decreases with further increasing the calcium content (Ahadi et al. 2012). The substitution of Bi<sup>+3</sup> cations with Ca<sup>+2</sup> cations also require charge unbalance in the host lattice and his charge unbalance is compensated by either the creation of oxygen vacancies that act as electron donor or by conversion of Fe<sup>+3</sup> cations to Fe<sup>+2</sup> cations and both of these reasons are responsible for decrease in conductivity. Moreover, it can also lead to existence of two different crystallographic phases (Yang et al. 2009). Rubi et al. (2012) suggested that addition of calcium to BiFeO<sub>3</sub> lattice created oxygen vacancies that weaken the spinel structure of BiFeO<sub>3</sub>. Ramachandran et al. (2012) obtained weak ferromagnetic behavior in upon Ca doping in BiFeO<sub>3</sub> due to lattice reduction.

However, these reports are limited over a very narrow dopant concentration range. Rubi et al. (2012) studied Bi<sub>0.9</sub>Ca<sub>0.1</sub>FeO<sub>2.95</sub>. Ahadi et al. (2013) covered the range of x=0, 0.15 and 0.3 for Bi<sub>1-x</sub>Ca<sub>x</sub>FeO<sub>3-δ</sub>. And variation in magnetic and structural properties is due to the change in deposition and synthesis conditions and the limited range studied for dopant. We here report the structural, optical and magnetic properties of Bi<sub>1-x</sub>Ca<sub>x</sub>FeO<sub>3</sub> thin films deposited using conventional sol-gel method.

## 2. Experimental Details

For undoped  $\text{BiFeO}_3$  thin films, two different solutions were prepared using  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in ethylene glycol. Ethylene glycol being a linearly structured molecule helps in compensating for the difference in hydrolysis rate of bismuth and iron. The two solutions were mixed. The solution was stirred at  $60^\circ\text{C}$  to obtain a stable sol. Calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) was added to ethylene glycol and then to the bismuth iron oxide sol for doping purpose. The details of sol-gel synthesis can be seen in Fig. 1. Calcium doped  $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_3$  doped films were prepared with varying ratio of calcium from  $x=0.0-0.5$ . The inset Fig. 1 show variation of color for Ca doped  $\text{BiFeO}_3$  thin films.

For deposition of thin films on copper substrate the substrate was first etched by diluted HCl and then placed in ultrasonic bath in acetone and IPA for 10 mins. Films were spin coated at 3000rpm for 30sec. Several coatings were done in order to obtain the required film thickness. During each successive coating the films were heated on a hot plate at  $150^\circ\text{C}$  for 10min in order to evaporate the solvent. The films were further annealed at  $300^\circ\text{C}$  for 60min in the presence of air. In order to study the effect of annealing in the presence of magnetic field the films deposited under same conditions were annealed in a magnetic field value of 500Oe at  $300^\circ\text{C}$  in vacuum.

The orientation and crystallinity of the thin films was studied using Bruker D8 Advance X-ray Diffractometer using copper target and nickel filter ( $\text{CuK}\alpha = 1.5405\text{\AA}$ ). Magnetic properties are studied using 7407 Vibrating Sample Magnetometer (VSM). 6500B impedance analyzer was used to study the dielectric properties of the films within the frequency range of 100Hz-1MHz. Optical properties are studied by M-2000 Spectroscopic Ellipsometry at an angle of incidence of  $70^\circ$ .

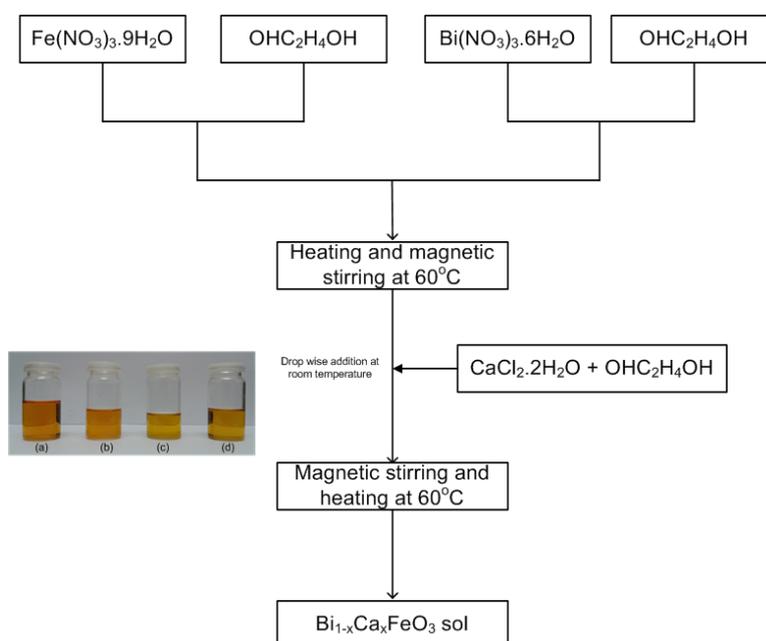


Fig. 1 Flow chart for the synthesis of  $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_3$  sol; (a)  $x=0.0$  (b)  $x=0.1$  (c)  $x=0.3$  (d)  $x=0.5$

## 2. Results and Discussion

Fig. 1 show XRD pattern for undoped BiFeO<sub>3</sub> thin film under as-deposited conditions. All the peaks are indexed according to BiFeO<sub>3</sub> (JCPDS card no. 85-1518). Presence of (100) and (110) planes show that films have polycrystalline rhombohedrally distorted perovskite BiFeO<sub>3</sub> structure. No impurity phase corresponding to bismuth rich or bismuth deficient phase is obtained. This is because of the reason that the sol synthesis was carried out using equimolar ratios of bismuth and iron thus balancing the volatile nature of bismuth ions during high temperature treatment.

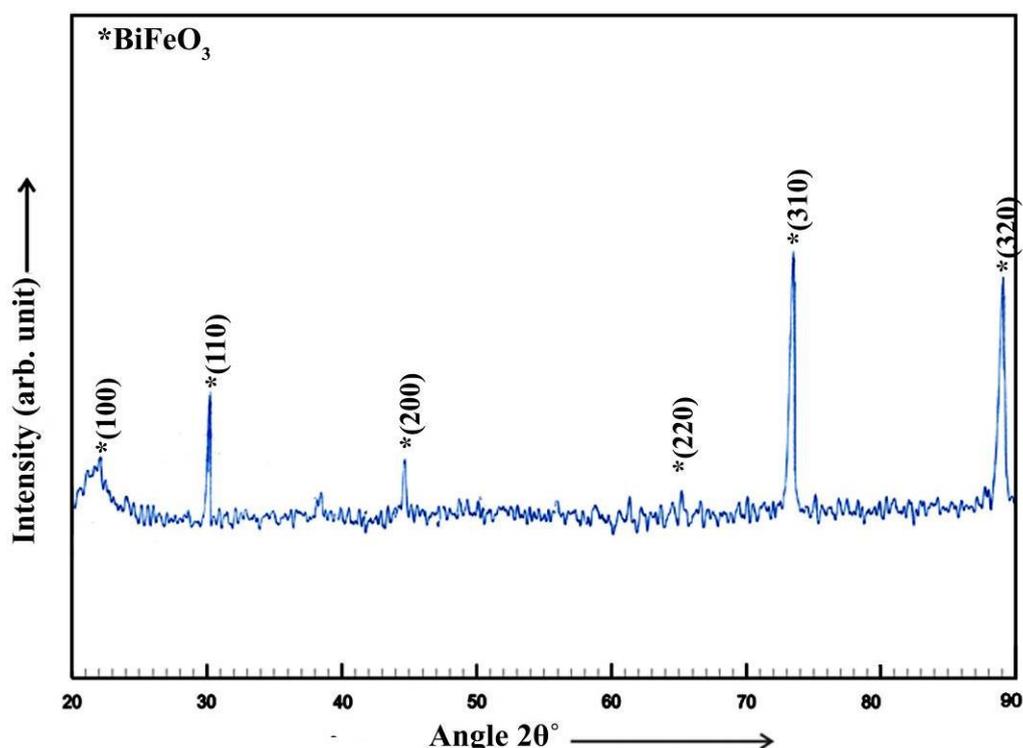


Fig. 1 XRD pattern for BiFeO<sub>3</sub> undoped thin film

In order to study the optical properties of bismuth iron oxide thin films Variable Angle Spectroscopic Ellipsometer (VASE) was used operated near the pseudo Brewster angle of 70° for BiFeO<sub>3</sub>. Details of the optical properties are to be reported elsewhere however the refractive index vs. wavelength curve is shown in Fig. 2. High refractive index of the films indicates high density and compact structure of the films. The refractive index decreases as the wavelength increases. It can be seen in Fig. 2 that as the dopant concentration increases the refractive index of the films increases.

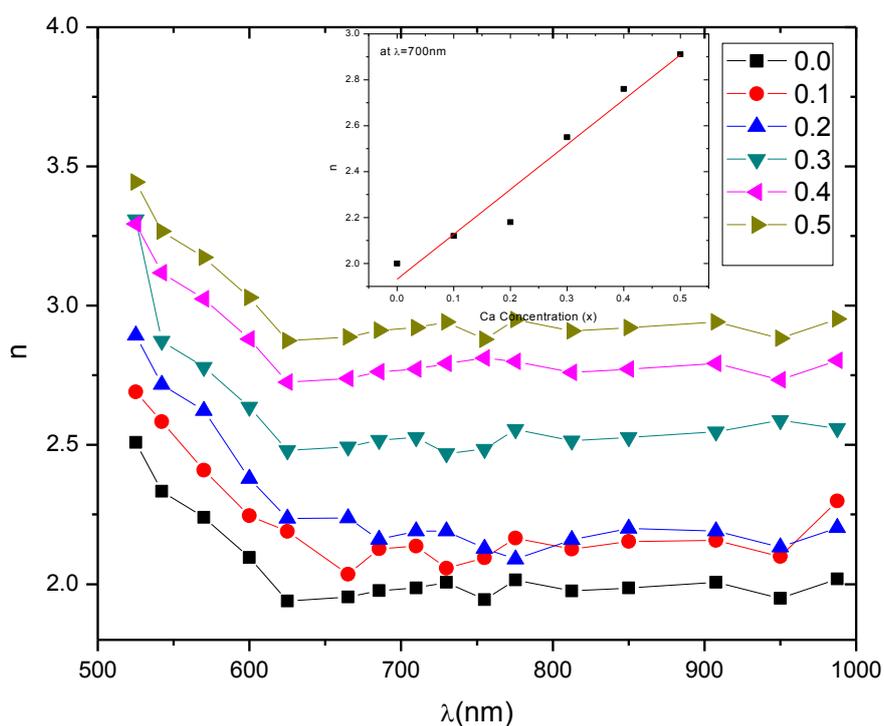


Fig. 2 Refractive index as a function of wavelength; inset show refractive index as a function of dopant concentration

Fig. 3 show magnetic properties of undoped and Ca-doped BiFeO<sub>3</sub> thin films. The most important thing is the ferromagnetic nature of undoped BiFeO<sub>3</sub> films. Bismuth iron oxide is antiferromagnetic in nature in which the spins in the same plane are ferromagnetically coupled and spins in the adjacent planes are antiferromagnetically coupled. This arrangement of spins leads to canting of spiral spin structure thus giving rise to antiferromagnetic behavior instead of ferromagnetic behavior. However in our case the ferromagnetic behavior indicate the suppression of spiral spin structure. Another reason for the ferromagnetic behavior instead of antiferromagnetic can be the conversion of Fe<sup>+3</sup> cations to Fe<sup>+2</sup> cations and the presence oxygen impurities.

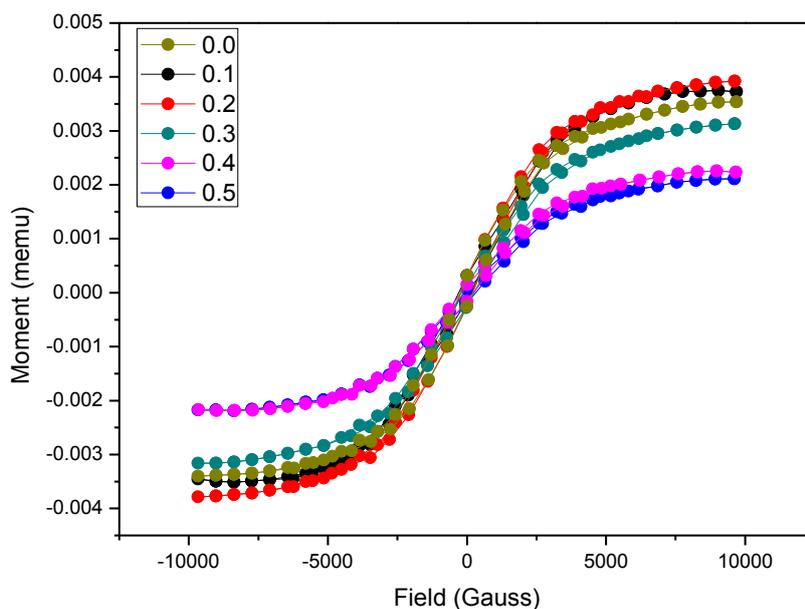


Fig. 3 M-H curve for Bi<sub>1-x</sub>Ca<sub>x</sub>FeO<sub>3</sub> films

Fig. 4 show saturation magnetization ( $M_s$ ) and coercivity ( $H_c$ ) plotted as a function of dopant concentration and it can be seen that with increase in dopant concentration from  $x=0.0$  to  $x=0.2$  the saturation magnetization increases indicating enhanced magnetic properties as compared to undoped BiFeO<sub>3</sub>. Whereas, further increase in dopant concentration decreases the saturation magnetization. The coercivity value also increases as the concentration is increased to  $x=0.2$  where as further increasing the concentration decreases the saturation magnetization.

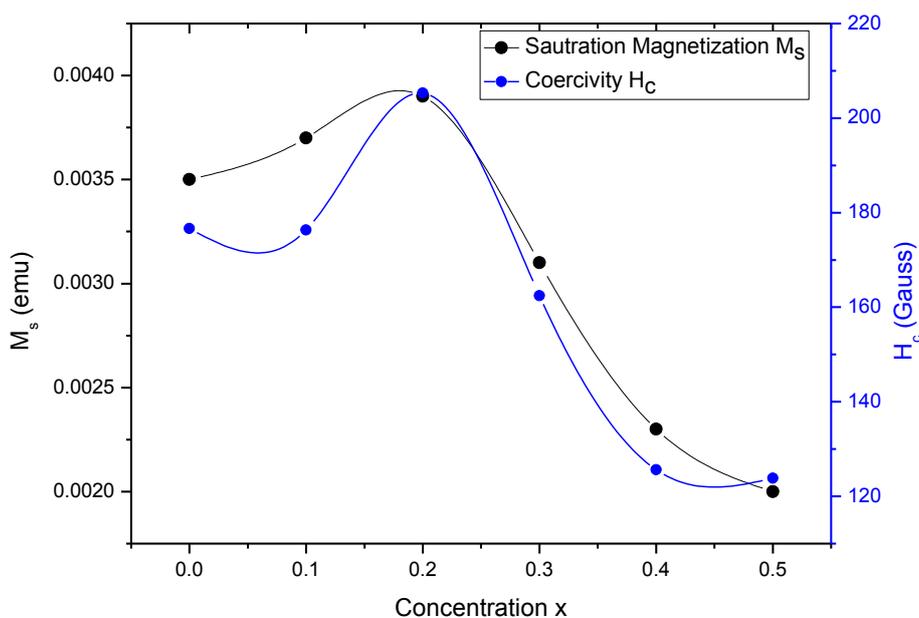


Fig. 4 Saturation magnetization and Coercivity as a function of Ca concentration

### 3. CONCLUSIONS

Pure polycrystalline BiFeO<sub>3</sub> are prepared using sol-gel method. XRD results show the pure BiFeO<sub>3</sub> phase with no traces of impurity. Optical analysis of films shows that refractive index of the films increases as calcium is incorporated into the host lattice. Undoped and calcium doped BiFeO<sub>3</sub> films show ferromagnetic behavior and enhancement in magnetic properties is observed with increase in dopant concentration.

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