

Multifunctional characteristics of Barium doped BiFeO₃

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Abstract:

Pure and Ba (x=0.3,0.4,0.5) doped BiFeO₃ samples were synthesized by auto combustion method. X-ray diffraction result showed distorted rhombohedral structure. The lattice parameters were found to increase with increasing concentration of Barium. Magnetic measurements showed antiferromagnetic behavior for pure BiFeO₃ while ferromagnetic behavior was observed for doped samples. The existence of magnetoelectric coupling was indicated by the observation of the dielectric anomaly in the dielectric constant and dielectric loss near antiferromagnetic neel temperature in all samples. Ferroelectric polarization is found to improve with Ba substitution.

Keywords: Powder diffraction, Crystal structure, Dielectric properties, Magnetic properties

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INTRODUCTION:

Multiferroic material manifest simultaneously two or more ferroic order parameters namely ferromagnetism, ferroelectricity and ferroelasticity in a single phase [1]. Work in the field of multiferroics gained momentum in recent years due to its promising applications on the magnetic control of ferroelectric polarization for novel devices [2-4]. An ideal multiferroic would be a ferroelectric-ferromagnetic that would exhibit coupling between these order parameters at room temperature. Bismuth ferrite is found to be one such material which demonstrate a coupling between magnetic and ferroelectric order, having curie temperature $T_c \approx 1100^0\text{K}$ and G

type antiferromagnetic temperature $T_N \approx 640^0\text{K}$ [5,6]. However BiFeO_3 suffers from several major issues like high leakage current, spiral spin structure, large difference in transition temperature (T_c and T_N). A lot of efforts have been made to overcome these issues like doping transition metals [7] and rare-earth metals [8] into BiFeO_3 , also modifying material by including solid solution of BiFeO_3 with BaTiO_3 etc [9,10].

In this paper we focus on the effect of Barium doping on BiFeO_3 in order to overcome the problems associated with it. As Barium is found to induce multiferroic properties in BaFeO_3 [11] hopefully this diamagnetic ion could also hold good for BiFeO_3 .

MATERIALS AND METHODS:

The BiFeO_3 and $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x=0.2,0.3,0.4$) ceramics were prepared by auto-combustion synthesis. The chemical $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Urea used were analytical reagent grade and used without further purification. Stoichiometric amount of metal nitrate (Oxidizer) and fuel when ignited undergo self propagating, gas producing combustion reaction to yield voluminous metal oxide in less than 5 min. The as synthesized samples were crushed and grinded in an agate mortar [12]. The oxidizer/fuel ratio was figured on the basis of oxidizing valencies of the metal nitrates and reducing valency of the fuel.

The samples were then characterized by using various techniques. X-ray powder diffraction data was collected using an XPERT-PRO diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15456\text{nm}$) at step of 0.02 in the range $2\theta=20^0$ to 80^0 . The magnetic properties were measured by a vibrating sample magnetometer (Lakeshore VSM 7410) at room temperature. Dielectric measurements were performed on an impedance analyzer (Weynn Kerr 6500 B) for which the sintered samples were mechanically pressed in hydraulic press and an Ag paste was applied to both sides of the polished pellets. Ferroelectric hysteresis loops were studied by a P-E loop tracer.

RESULT AND DISCUSSION:

Structural Analysis

Room temperature powder x-ray diffraction was carried out on $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x=0,0.2,0.3,0.4$). All the peaks could be indexed in the rhombohedral distorted perovskite structure with space group- $R3c$. In order to confirm the crystal structure, the diffraction pattern were Rietveld refined using FULLPROF 2000 program. The profile fits for the Rietveld refinement of $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x=0,0.2,0.3,0.4$ samples are shown in fig [1-4] respectively. The simulated XRD pattern of all the three samples coincide well with measured XRD pattern. Doubly split peaks observed in pure BiFeO_3 are found to merge gradually as the Barium concentration increases. This merger of splitted peaks into single peak is a signature of structural phase transition from distorted rhombohedral to pseudo cubic symmetry. The ionic radii of Ba atoms is larger than that of the Bismuth atoms as a consequence of which the lattice parameter is found to increase. This could be also observed from the peaks where the increase in concentration causes the peaks to shift towards lower angle.

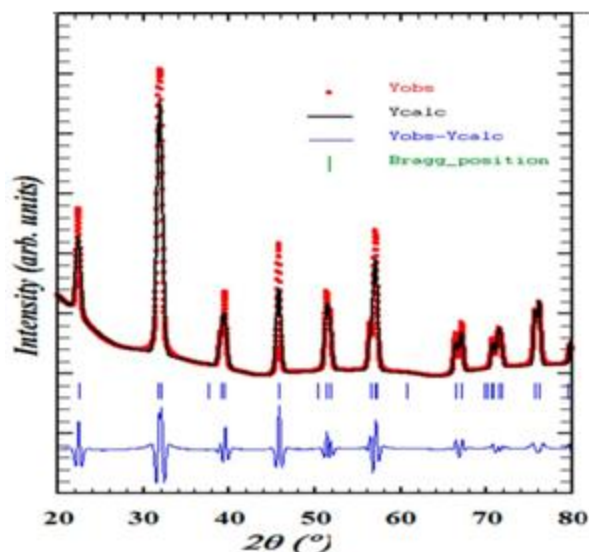


Fig [1] The XRD pattern of pure BiFeO_3 .

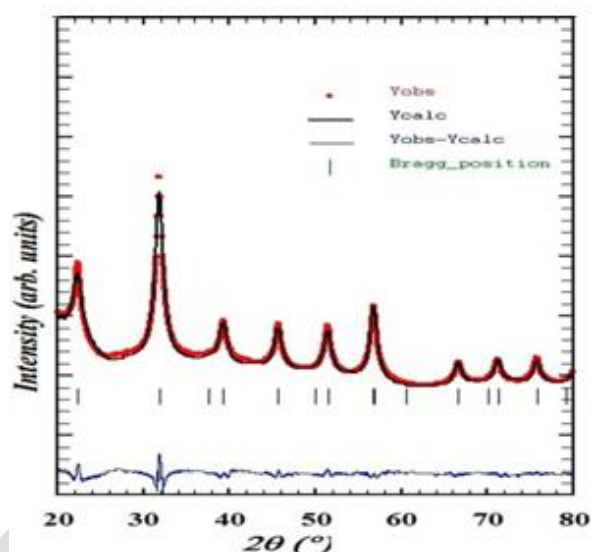


Fig [2] The XRD pattern of $\text{Bi}_{0.8}\text{Ba}_{0.2}\text{FeO}_3$.

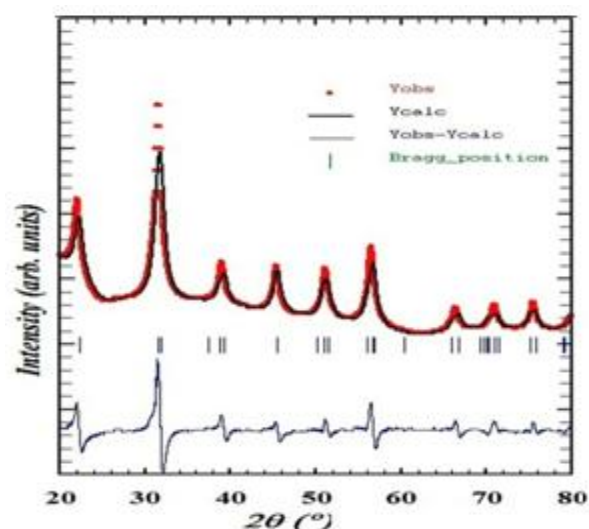


Fig [3] The XRD pattern of $\text{Bi}_{0.7}\text{Ba}_{0.3}\text{FeO}_3$.

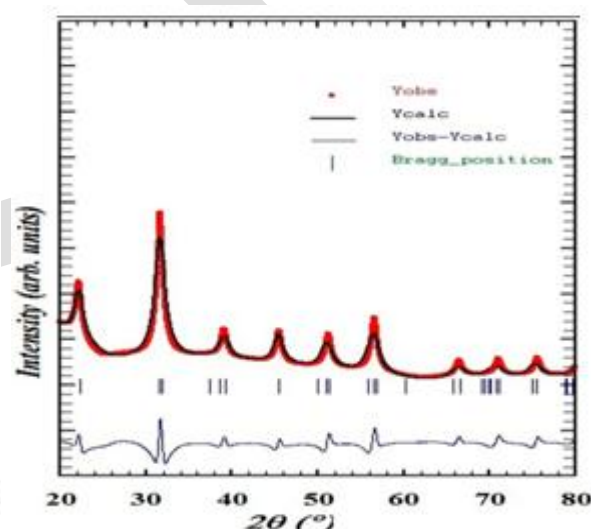


Fig [4] The XRD pattern of $\text{Bi}_{0.6}\text{Ba}_{0.4}\text{FeO}_3$.

Magnetic properties :

The room temperature magnetic hysteresis loops are shown in figure [5]. In case of pure BiFeO_3 , the magnetization varies nearly linearly with the applied magnetic field confirming that sample is antiferromagnetic having a G-type magnetic structure [13]. However, the sample has a residual magnetic moment due to canted spin structure (weak ferromagnetic). The values of saturation magnetization for $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x=0.2, 0.3, 0.4$) samples are $M_s=2.819\text{emu/g}$, 3.08emu/g , 4.21emu/g respectively. These values are much larger than that of BiFeO_3 prepared under similar conditions $M_s=0.004\text{emu/g}$. The Ba doping into BiFeO_3 is found to increase the net magnetization. This increase in the magnetization may be attributed to the structural distortion caused on increasing the Barium concentration, which suppresses the spiral spin structure by destroying spin cycloid completely. Divalent substitution at Bi-site requires charge compensation, which leads to formation of Fe^{4+} or oxygen vacancies. This presence of Fe^{3+} and

Fe^{4+} ions in the octahedral may lead to a net magnetization. The oxygen vacancies lead to an increase in the Fe-O-Fe bond angle due to which more spins are canted. This canting of spins subsequently enhances the magnetization.

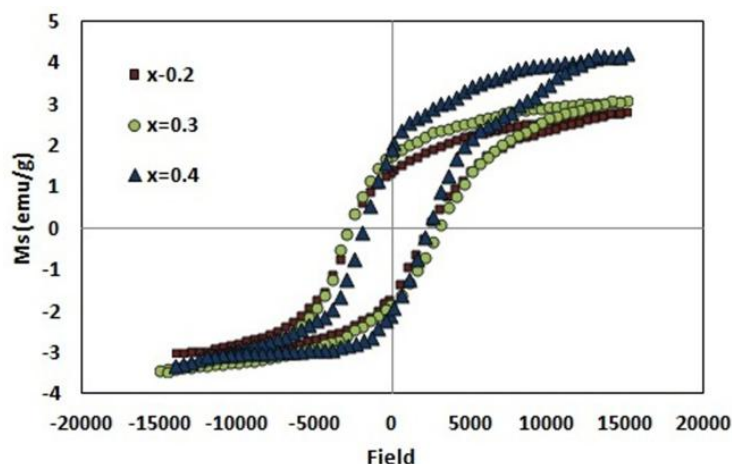


Fig [5] The M-H plot of $\text{BiFe}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0, 0.2, 0.3, 0.4$) at 300K.

Dielectric Properties:

Fig.[6&7] show temperature dependence of dielectric constant and $\tan\delta$ at 100Hz. Dielectric constant and $\tan\delta$ both show anomaly peak near antiferromagnetic Neel temperature. This phenomenon is a signature of magnetoelectric coupling. The Landau-Devonshire theory of phase transitions predicted this type of dielectric anomaly in magnetoelectrically ordered systems as an effect of diminishing magnetic order on the electric order [3]. The dielectric anomaly is found to shift towards the lower temperature with increasing Barium concentration. The shift in the anomaly may be considered as an effect of structural distortion caused by Barium substitution.

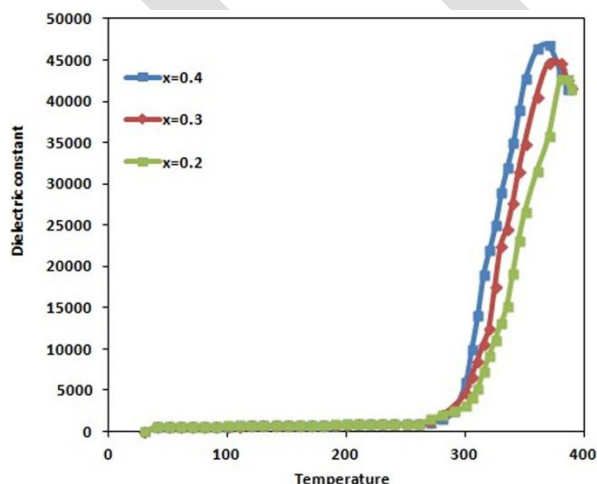


Fig [6] Temperature dependent dielectric constant Of $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x=0.2, 0.3, 0.4$) at 300K.

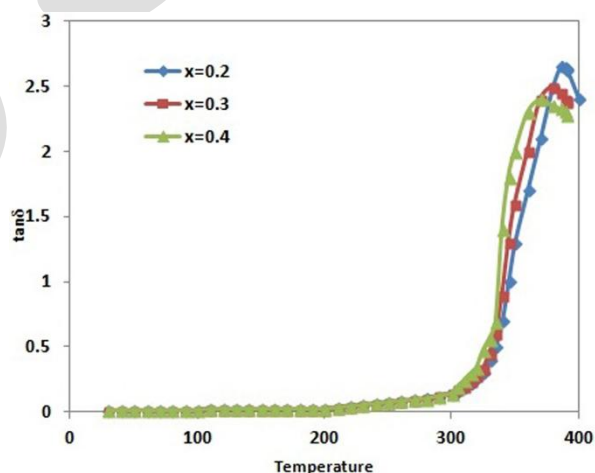
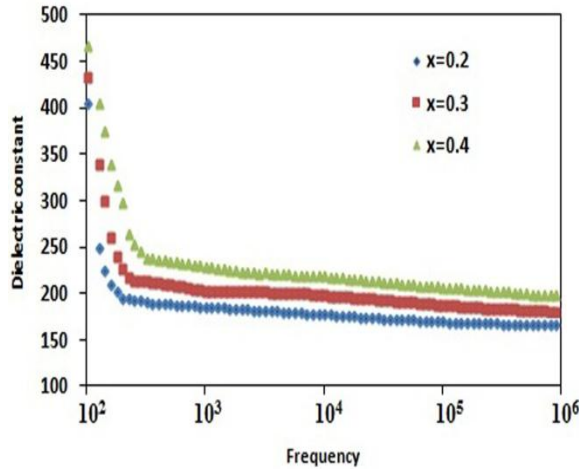


Fig [7] Temperature dependent $\tan\delta$ of $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x=0.2, 0.3, 0.4$) at 300K.

Fig[8&9] show frequency dependent dielectric constant and $\tan\delta$ for $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x=0.2, 0.3, 0.4$) respectively. The dielectric constant is found to be strongly frequency dependent.

The dielectric constant has maximum value at the lower frequency which decreases sharply with increasing frequency and then attains saturation. These values show a large dispersion due to Maxwell-Wegner type of interfacial polarization, which is in agreement with Koop's phenomenological theory [14,15].



Fig[8] Frequency dependent dielectric constant of $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x=0.2, 0.3, 0.4$) at 300K

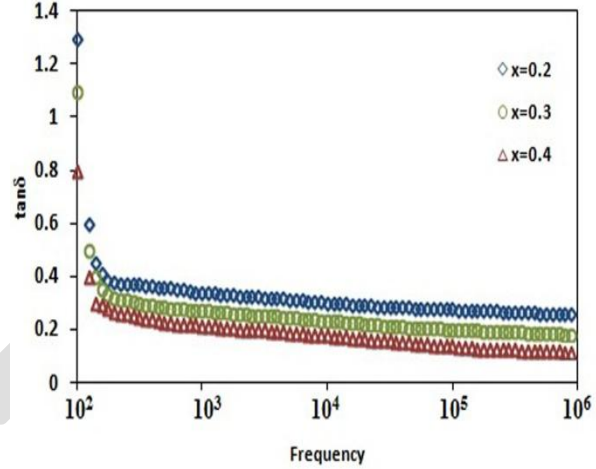
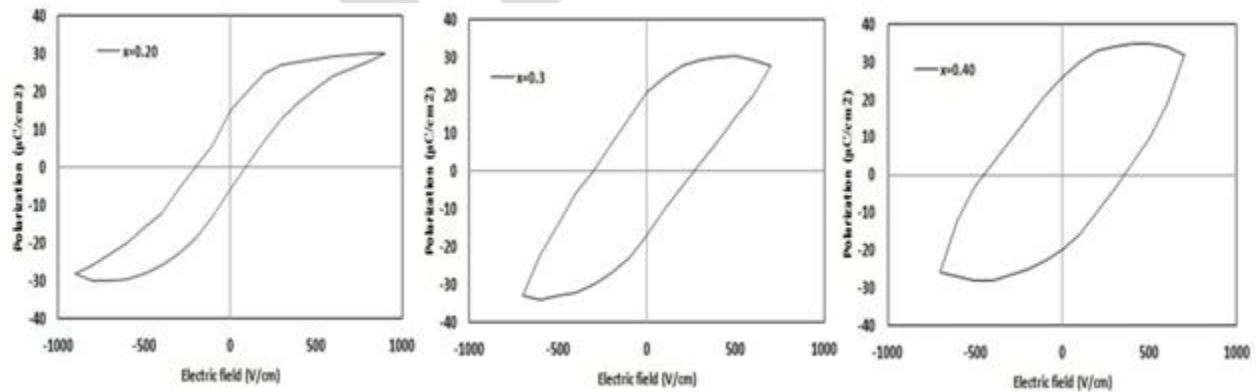


Fig [9] Frequency dependent dielectric loss of $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x=0.2, 0.3, 0.4$) at 300K.

The cause of this kind of behavior is that the large size and mass of dipoles can respond to only low frequencies but at high frequencies they are unable to respond and relax down [16]. The dielectric loss also shows a frequency dependence which has a high value in the low frequency region and goes on decreasing as the frequency increases. This type of phenomenon indicates a Debye like relaxation which can be attributed to the relaxation of charge carriers [17]. The material also exhibit small value of dielectric loss at higher frequencies as the field cannot induce the dipole moment.

Ferroelectric Properties:

The Polarization versus electric field (P-E) hysteresis loop of the $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x=0.2, 0.3, 0.4$) samples at room temperature with different applied field as shown in fig [10] at frequency of 50 Hz.



Fig[10] Ferroelectric hysteresis loop of $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x=0.2, 0.3, 0.4$) at 50Hz.

All the samples represent distinct ferroelectric behavior. The loop for $\text{Bi}_{0.8}\text{Ba}_{0.2}\text{FeO}_3$ is found to be saturated while those for $x=0.3$ & 0.4 are unsaturated hysteresis loops. Barium substitution is found to improve the ferroelectric properties of BiFeO_3 samples due to the distortion of oxygen octahedral by displacement of oxygen atom. Similar kind of behaviour was observed in A-site ion substituted $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [18].

CONCLUSION:

BiFeO_3 and $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ ($x=0.2, 0.3, 0.4$) materials were synthesized by auto-combustion method. The XRD pattern showed rhombohedrally distorted perovskite structure. Magnetization is found to increase considerably in doped samples than in pure BiFeO_3 due to canting of spins. Temperature dependent dielectric constant shows magnetic phase transition near Neel temperature. Dielectric constant also shows strong frequency dependence. Ferroelectric behavior is improved by the Barium substitution which may be attributed to the lattice distortion. Hence, small value of dielectric loss, enhanced magnetization and improved polarization make Barium doped BiFeO_3 a potential multiferroic material.

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