

Interesting properties of nano multiferroic $\text{BiCo}_x\text{Fe}_{1-x}\text{O}_3$ ceramic

Sen K.*, Singh K., Gautam A. and Singh M.

*Department of Physics Himachal Pradesh University, Shimla-5, sen.728@gmail.com

Abstract- Multiferroic have been known as materials exhibiting both ferroelectric and ferromagnetic properties in same phase, they have interesting physical properties as well as possibility of practical application in some new memories, spintronics and sensor devices. One of the interesting multiferroic material is BiFeO_3 which is the only known material exhibiting good ferroelectromagnetism and room temperature, because it has a high Curie temperature ($T_C \sim 830^\circ\text{C}$) and a high Neel temperature ($T_N \sim 370^\circ\text{C}$). BiFeO_3 ceramic have a rhombohedrally distorted perovskites like structure corresponding to space group $R3c$. Structural, dielectric, ferroelectric and ferromagnetic properties of multiferroic $\text{BiCo}_x\text{Fe}_{1-x}\text{O}_3$ ($x=0.0, 0.05, 0.10, 0.15, 0.20, 0.25$) ceramic were studied by solution combustion method and prepared samples were characterized by X-Ray Diffraction (XRD), Transmission Election Microscopy (TEM) and Differential Scanning Calorimetry (DSC). Improved resistivity of $\sim 10^{10}$ ohm-cm were formed by sintering the 400°C , 600°C , 700°C calcined powder at 750°C for 60 min and also there is an improvement in M-H hysteresis loop with cobalt substitution. Room temperature ferromagnetic ordering at nano level is new and intereting on physics and technological point of view in this system.

I. INTRODUCTION

Multiferroic BiFeO_3 (BFO) has been discovered since 1960s [1]. It is still difficult to study its intrinsic ferroelectric properties at room temperature because of its well-known phase impurity and low resistivity [2 – 4]. In bulk form, BFO has a rhombohedrally distorted perovskite structure with space group $R3c$ ($a=3.97\text{\AA}$, $\alpha=89.59^\circ$) [5]. In order to increase the dielectric constant, reduce the leakage current, and hence to improve the ferroelectric polarization in BFO, some attempts have been made including a small doping at the Bi/Fe site BiFeO_3 has a ferroelectric Curie temperature $T_C \approx 830^\circ\text{C}$ and antiferromagnetic (AF) Neel temperature $T_N \approx 370^\circ\text{C}$ [6]. The Co substituted BFO films are shown to have better properties in terms of leakage current density [7]. In the present work, we report the effect of Co substitution (5-25 mol% at the Fe site) on structural, electrical and magnetic properties of BiFeO_3 ceramics [i.e., $\text{BiCo}_x\text{Fe}_{1-x}\text{O}_3$ (BCFO)].

II. EXPERIMENT

The $\text{BiCo}_x\text{Fe}_{1-x}\text{O}_3$ ($x=0.0, 0.05, 0.10, 0.15, 0.20, 0.25$) samples were synthesized by the solution combustion technique with a weighted amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and L-alanine were first dissolved in 2 – methoxy ethanol for 45 min by mean of ultrasonic cleaner. Bismuth nitrate was taken 5mol% excess to compensate Bi loss during sintering process. The solution was refluxed at 80°C for 12h to allow gel formation and dried at 100°C in a dry oven for 36 h. The dried gel was grounded into powder and calcined at 400°C for 2 h, 600°C for 1 h, 700°C for 1 h and 800°C for 30 min. The obtained powders were milled again, and pressed in to 1mm-thick pellets of 15mm in diameter. The pellets were sintered at 750°C rapidly for 60 min. For electric and dielectric measurements, both surface of pellets were polished with silver paste to make electrodes, X-ray diffraction data was collected using a XPERT-PRO diffractometer with $\text{Cu } \alpha$ radiation at step of 0.02 in the range

$2\theta=20^{\circ}$ to 60° . TEM measurements were carried out by Hitachi H7500 with resolving power 2\AA . Differential scanning calorimetry (DSC L 63) was used to study the antiferromagnetic (AFM) to paramagnetic (PM) transition temperature. Room temperature ferroelectric measurements were carried out using loop tracer a frequency of 50 Hz. The magnetic properties were measured by a vibrating sample magnetometer (VSM) at room temperature. Dielectric constant and dielectric loss were performed using precision impedance analyzer Wayne Kerr 6500B over the frequency range from 20Hz-120 MHz.

III. RESULTS AND DISCUSSION

The X-ray diffraction patterns of the BiCo_xFe_{1-x}O₃ ($x=0.0, 0.05, 0.10, 0.15, 0.20, 0.25$) nanoparticles are shown in fig 1. XRD study of BiCo_xFe_{1-x}O₃ ($x=0.0, 0.05, 0.10, 0.15, 0.20, 0.25$) shows that for $x=0.0$ (i.e. pure BiFeO₃) composition the powder crystallizes in rhombohedral distorted perovskite (R3c) phases and minor impurity phase Bi₂₅FeO₃₉ was detected [8, 9]. BiCo_{0.05}Fe_{0.95}O₃ (i.e. $x = 0.05$) exhibits the similar rhombohedral perovskite structure (R3c) as BiFeO₃. Small impurity peaks corresponding to Bi₁₂ (Bi_{0.5}Fe_{0.5}) O_{19.5} were observed at the $2\theta=$ (around) 30° . The lattice constants of BiCo_{0.05}Fe_{0.95}O₃ ($a=3.959\text{ \AA}$ and $\alpha=89.48^{\circ}$) are smaller than those of BiFeO₃ ($a=3.976\text{ \AA}$ and $\alpha=89.59^{\circ}$), which is due to the smaller ion diameter of Co³⁺ than that of Fe³⁺ [5, 10]. For the compositions having $x \geq 0.1$ the unit cell parameter (a) decreased with increasing Co additions, while the rhombohedral angle (α) exhibited a small corresponding increase. These changes result from direct substitution of multi-valent Co for the multi-valent Fe within the BiFeO₃ structure. As the ionic radius of Co³⁺ (54.5 pm) is smaller than that for Fe²⁺ (61 pm) or Fe³⁺ (55 pm) ions, a small structure contraction can be expected, giving rise to a slight canting

of the rhombohedral unit cell [5, 11]. A higher level of Co-addition (i.e. $x \geq 0.1$) new peak emerges at $2\theta=$ (around) 27° , which becomes stronger with increasing x . This additional XRD peak can be attributed to the (012) reflection of new secondary phase. It is interesting to note that all the peaks characterizing the crystalline structure of BiFeO₃ are suppressed and those corresponding to secondary phases becomes dominant with a relatively small amount of Co doping when $x \geq 0.1$. Thus the limit of Co substitution in BiFeO₃ must be less than $x=0.1$ [7, 12]. The average grain/particle size has been evaluated from (FWHM) i.e. full width at half maximum of the reflection of maximum intensity (110) in the XRD pattern using the Deby-Scherrer formula [13]

$$d = \frac{k\lambda}{B\cos\theta}$$

Where $B^2 = B_M^2 + B_S^2$, Where d is the particle size in \AA . k is the shape factor (usually taken as 0.9), λ is the X-ray wave length (1.54 \AA). B_M and B_S are the measured peak broadening and instrumental broadening in radian respectively θ is the Bragg's angle in degrees. By using the Scherrer's equation, the calculated average crystallite size for BiCo_xFe_{1-x}O₃ is found to be in the order 9-16 nm.

Fig 2(a, b), shows the TEM image of BiCo_xFe_{1-x}O₃ ($x=0.0, 0.25$) ceramic samples. The mean grain sizes of the nanoparticles were calculated from XRD peak broadening using the Debye-Scherrer formula. The grain size are found to be 10.37, 16.36nm for $x=0.0, 0.25$ respectively. These were further supported by TEM characterization.

Fig 3, show the DSC curve of BiCo_{0.05}Fe_{0.95}O₃ ceramic sample in the 200-500^oC temperature range. As reported in the literature [6], the magnetic order temperature (T_N) of BiFeO₃ is about 370^oC. It is found that the magnetic order temperature (T_N) is

not affected remarkably for BiFeO_3 with Co content $x = 0.05$ and comes out to be 366°C .

The variation of dielectric constant for $\text{BiCo}_x\text{Fe}_{1-x}\text{O}_3$ ($x = 0.0, 0.05, 0.10, 0.15, 0.20, 0.25$) was studied as a function of frequency at room temperature. The frequency was varied from 20 kHz to 1.1 MHz. The results are shown in fig 4. At low frequency the value of dielectric constant is greater for Co content $x=0.05, 0.10$, than from the value for pure BiFeO_3 ; where as the value of dielectric constant is less for Co content $x=0.15, 0.20, 0.25$ then from the value for pure BiFeO_3 . This variation is observed due to large leakage current developed in samples with Co content $x \geq 0.15$. It is observed that for each sample ($x = 0.05, 0.10, 0.15, 0.20, 0.25$) the dielectric constant decrease with increasing frequency. Further, for each substituted composition the dielectrics constant decreases slowly upto 100 kHz and after that is nearly constant upto 1 MHz. The variation of dielectric constant reveals the dispersion due to Maxwell-Wagner [14, 15] interfacial polarization in agreement with Koops phenomenological theory [16]. Rezlescu et. al [17] have showl that the correlated dielectric polarization and verway type of conduction mechanism between $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ gives local displacement of electrons in the direction of applied field, which induces polarization in multiferrioc. The initial slow decrease in the dielectric constant as predicted by Koops model has not been observe in the present study. This is because the lowest frequency employed in the present investigations is high to observe the initial slow variation of dielectric constrant with frequency. Workers [14, 15] have studied variation of dielectric constant with frequency at low frequencies. The physical reason for the dispersion of dielectric constant can be understood on the basis of hopping of electrons between $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ pairs of ions. The applied electric field displaces

the electrons slightly from their equilibrium positions, thus producing polarization. For all the substituted composition, the dielectric constant decreases with increasing frequency, which is consistent with a combined response of orientational relaxation of dipoles and the conduction of charge carriers [12].

The variation of dielectric loss for $\text{BiCo}_x\text{Fe}_{1-x}\text{O}_3$ ($x = 0.0, 0.05, 0.10, 0.15, 0.20, 0.25$) compositions was studied as a function of frequency at room temperature. The frequency was varied from 20 kHz to 1.1 MHz. The results are shown in fig 5. It is observed that the dielectric loss increases with decreasing frequency with no sign of loss peak [12]. This indicates that our material is homogeneous stoichiometric and has uniform distribution of the grain/particles.

The ferroelectric polarization hysteresis loop at room temperature is shown in fig 6. Due to relatively large leakage current in the samples, only low field electric hysteresis loop of $\text{BiCo}_{0.05}\text{Fe}_{0.95}\text{O}_3$ ceramic sample is shown. The loop is not really saturated and represents a partial reversal of the polarization [18]. However the fig 6. show a much improved saturation than in the case of BiFeO_3 , resulting in some value of remanant polarization P_r , although its value is still far less than the expected value of bulk BiFeO_3 samples ($95 \mu\text{C}/\text{cm}^2$ predicted by the theory [12, 19]. But workers [7] shown that in the case of BiFeO_3 thin films ferroelectricity can be improved by adding small amount of cobalt. Addition of 3 at. % cobalt to BiFeO_3 films increased the remanant polarization from 49 to $72 \mu\text{C}/\text{cm}^2$.

The M-H hysteresis loops of $\text{BiCo}_x\text{Fe}_{1-x}\text{O}_3$ ($x = 0.0, 0.05, 0.10, 0.15, 0.20, 0.25$) ceramic samples at 300 K are shown in fig 7. In pure BiFeO_3 , the magnetization varies nearly linearly with the applied magnetic field confirming that sample is antiferromagnetic having a G-type magnetic structure [20] and having a

residual magnetic moment due to canted spin structure (weak ferromagnetic). The magnetic field dependent magnetization of $\text{BiCo}_x\text{Fe}_{1-x}\text{O}_3$ for ($x = 0.05, 0.10, 0.15, 0.20, 0.25$) exhibits a clear hysteresis loop at 300 K. The saturation magnetization $M_s = 1.97$ emu/g, remanant magnetization $M_r = 0.65$ emu/g, and coercivity $H_c = 566.4$ Oe i.e. for $x=0.05$ are much larger than those of BiFeO_3 prepared under similar conditions $M_s = 0.03$ emu/g, $M_r = 0$ emu/g, $H_c = 35.948$ G, respectively [10, 21]. Further these value increases for concentration $x = 0.10, 0.15, 0.20$ & 0.25 with causing magnetic anisotropy of cobalt

IV CONCLUSION

In summary, $\text{BiCo}_x\text{Fe}_{1-x}\text{O}_3$ ($x = 0.0, 0.05, 0.10, 0.15, 0.20, 0.25$) nanoparticles have successfully been prepared by solution combustion method. The microstructure of BiFeO_3 ceramics can be modified dramatically by small amount of Co doping and for the XRD pattern is concerned; the limit of Co substitution must be less than 10 mol% before the peak of a new phase is observed. Electric hysteresis loop (P-E loop) in Co substituted BiFeO_3 was not really saturated, which requires the measurement at low temperature. It was found that due to Co substitution at Fe results an improvement in ordering of dielectric constant and dielectric loss and further enhanced magnetic properties of $\text{BiCo}_{0.25}\text{Fe}_{0.75}\text{O}_3$ with saturation magnetization, remanant magnetization and coercivity ($M_s = 20.8$ emu/s, $M_r = 5.09$ emu/g, $H_c = 566$ Oe) were found.

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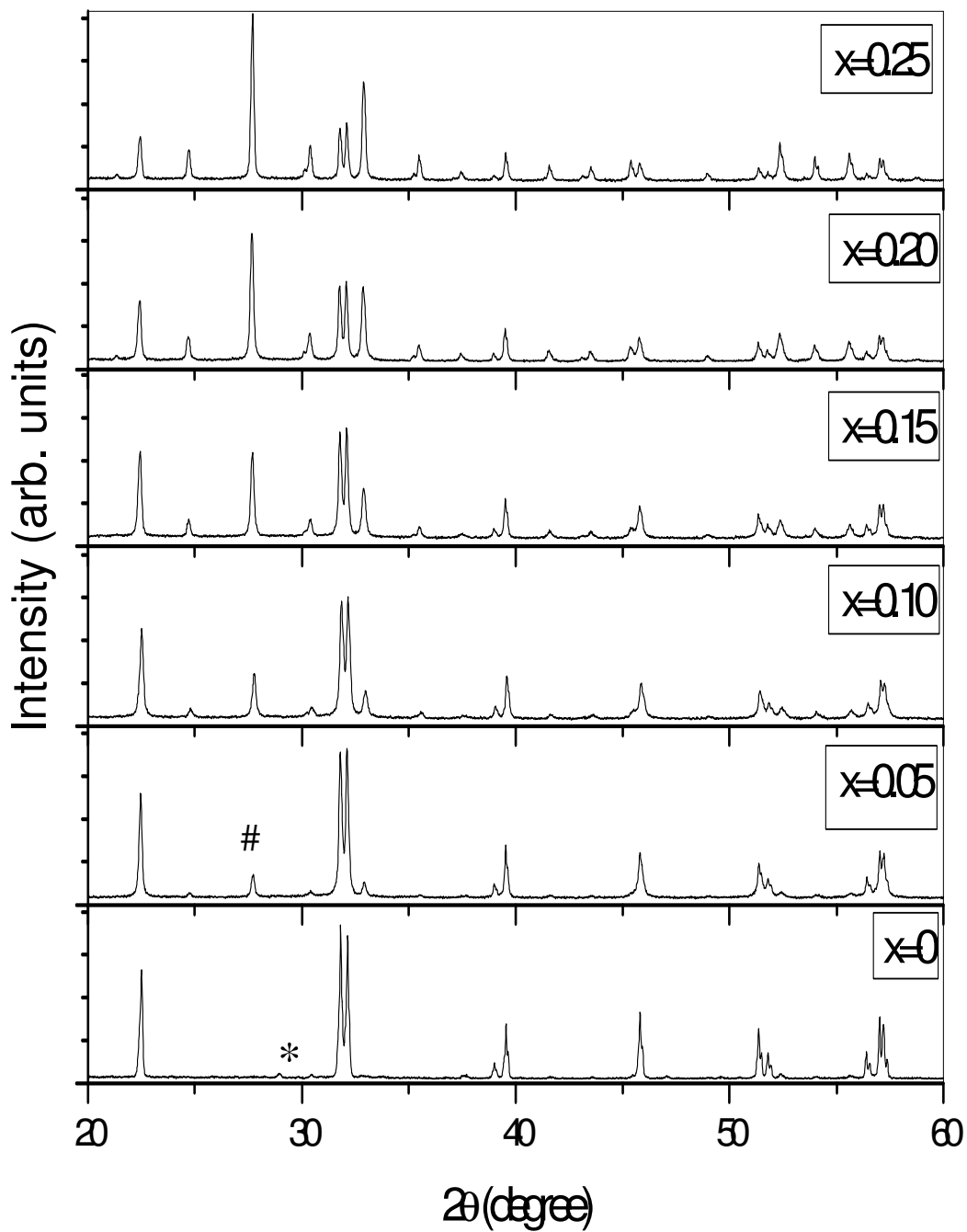
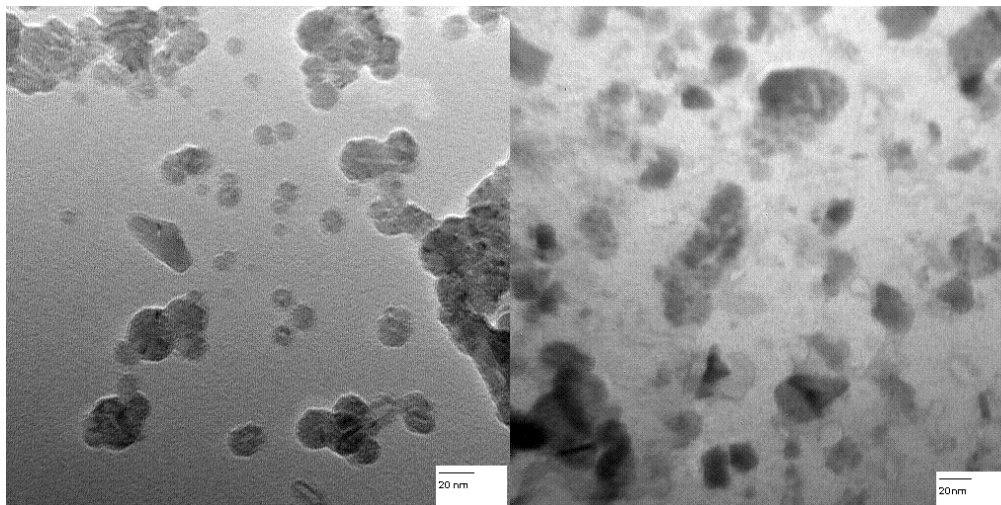


Fig. 1-XRD pattern of $\text{BiCo}_x\text{Fe}_{1-x}\text{O}_3$ ($0 \leq x \leq 0.25$) ceramic samples (*, # indicates the presence of impurity phases)



(a) (b)
 Fig. 2-(a)TEM image of BiFeO_3 powder calcined at 800°C , (b) TEM image of $\text{BiCo}_{0.25}\text{Fe}_{0.75}\text{O}_3$ powder calcined at 800°C .

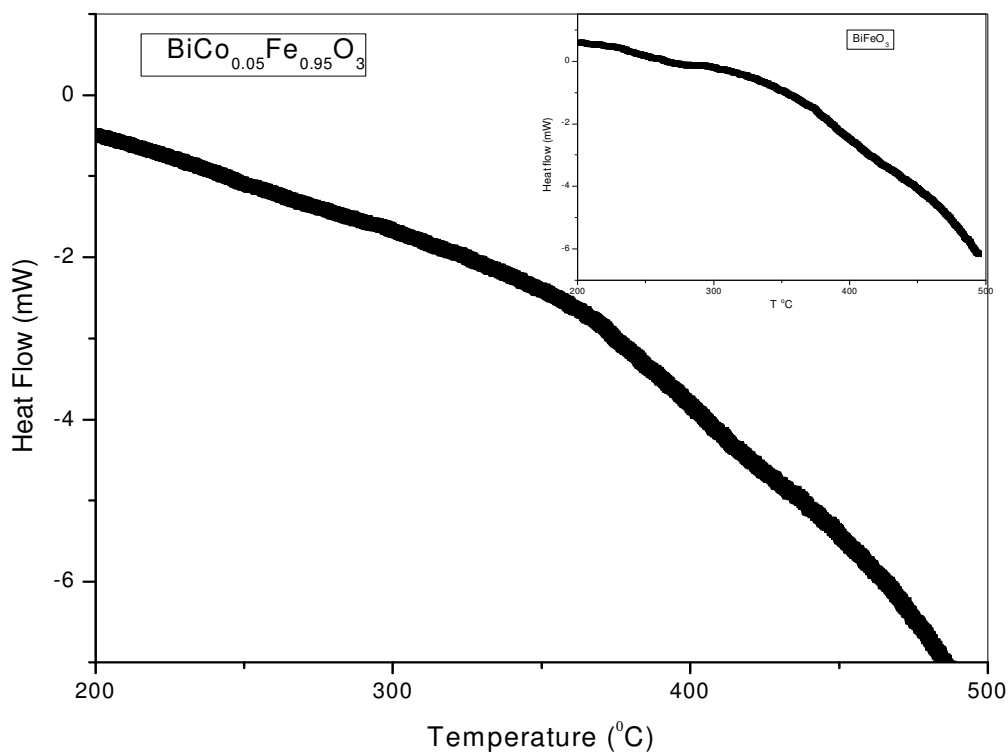


Fig. 3- DSC curve obtained for $\text{BiCo}_{0.05}\text{Fe}_{0.95}\text{O}_3$ ceramic, BiFeO_3 (inset) showing the changes in the magnetic ordering (T_N) temperature.

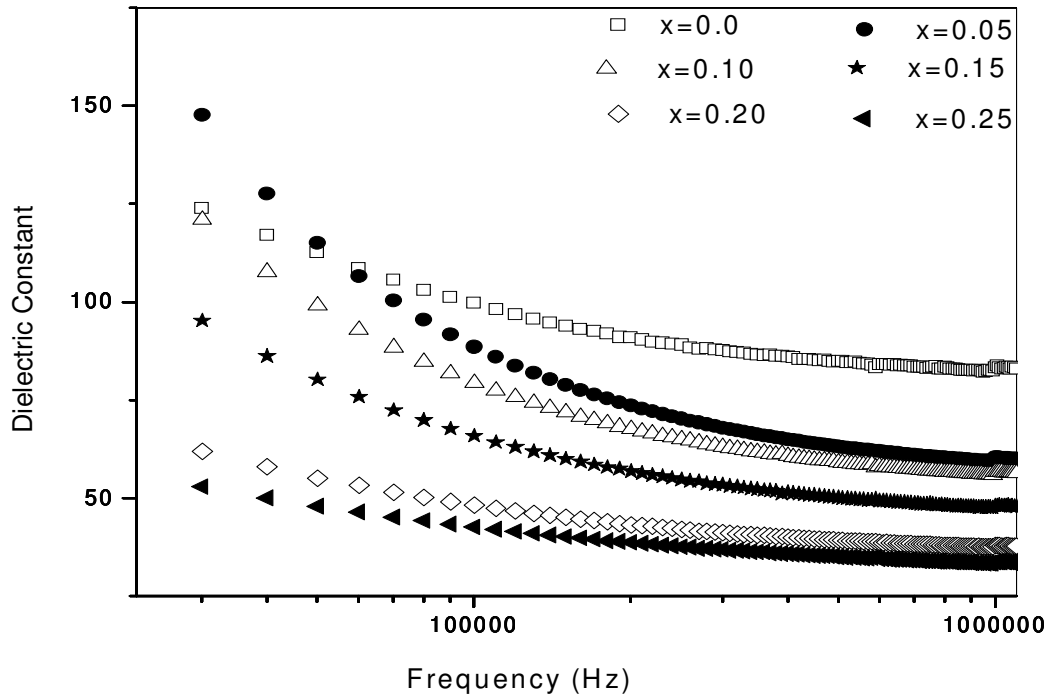


Fig. 4- Dielectric constant as a function of frequency for the samples of $\text{BiCo}_x\text{Fe}_{1-x}\text{O}_3$.

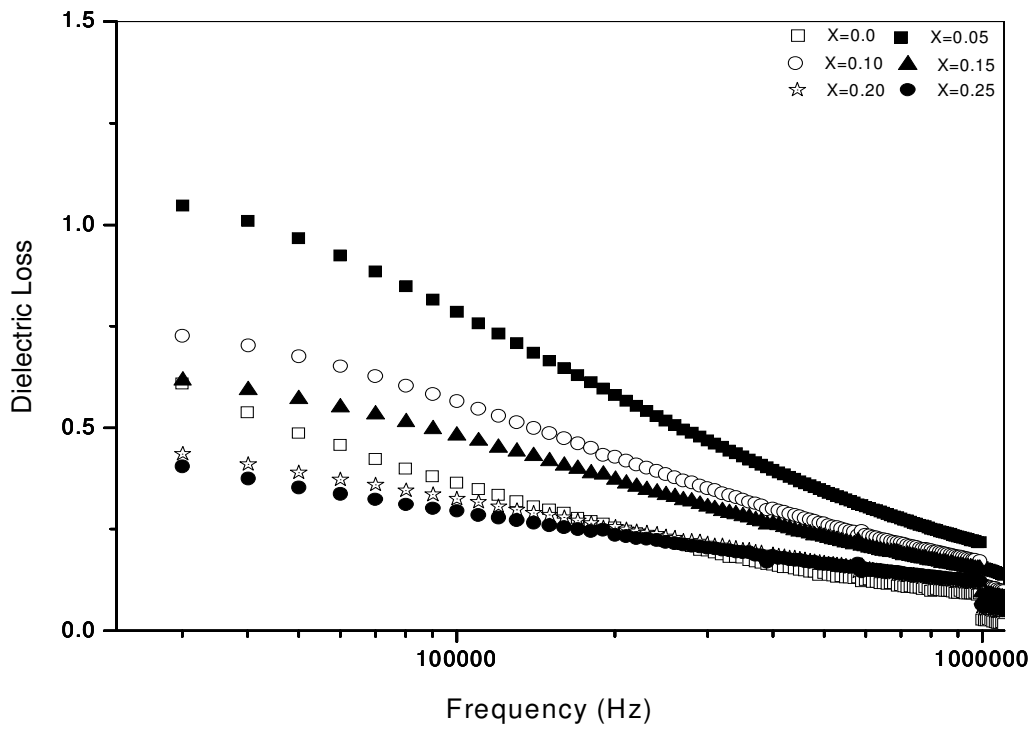


Fig. 5- Dielectric loss as a function of frequency for the samples of $\text{BiCo}_x\text{Fe}_{1-x}\text{O}_3$.

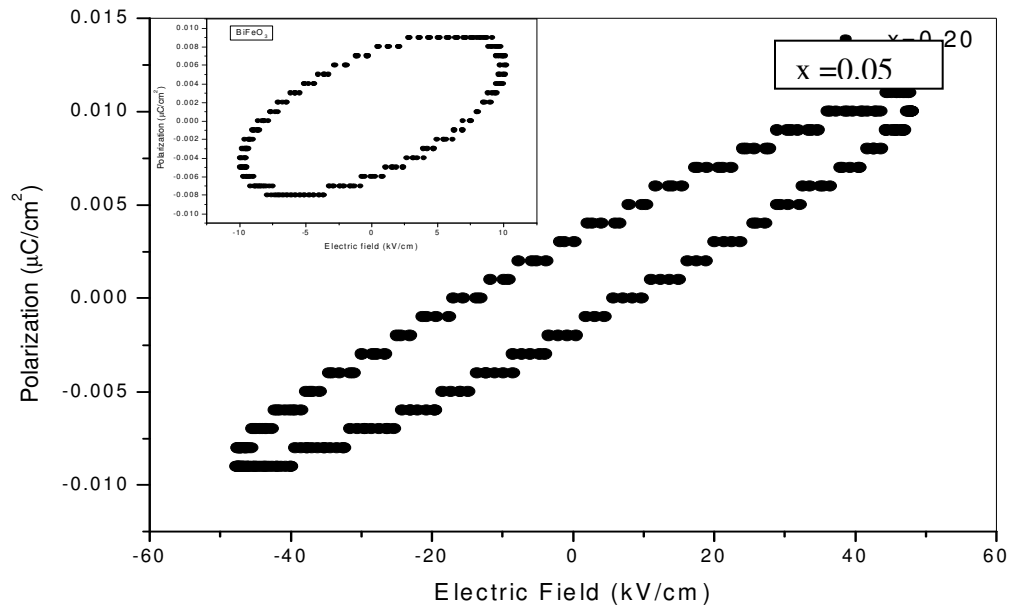


Fig. 6- P-E hysteresis loops of $\text{BiCo}_{0.05}\text{Fe}_{0.95}\text{O}_3$, BiFeO_3 (inset) ceramic as a function of applied field

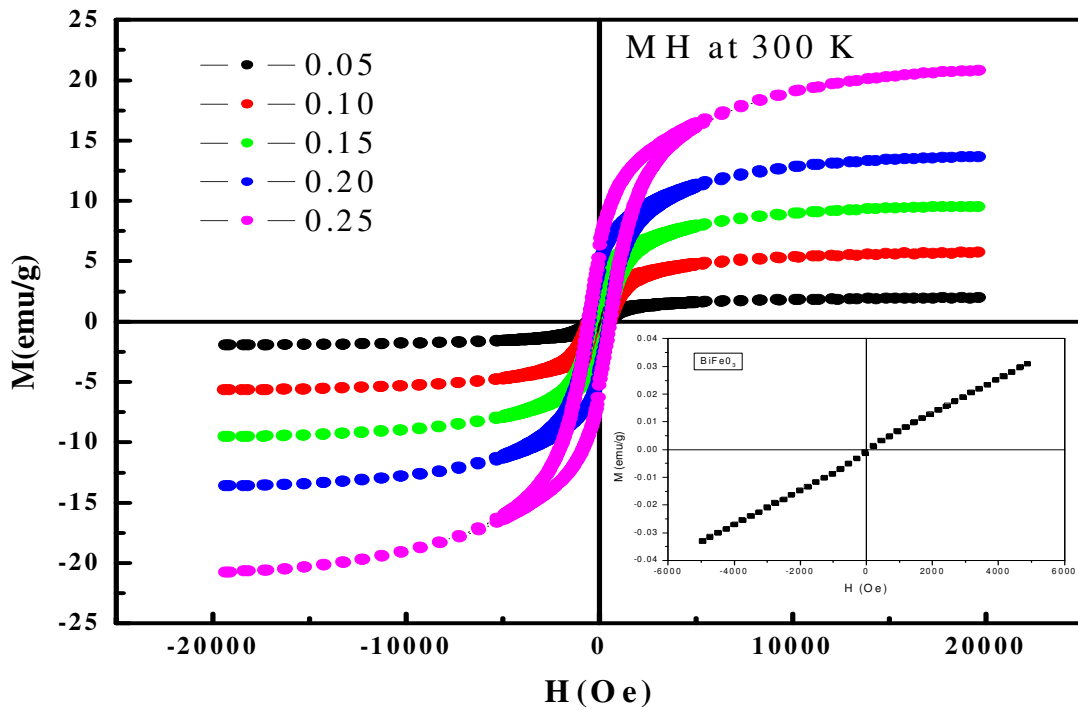


Fig. 7- The Magnetic hysteresis loops of $\text{BiCo}_x\text{Fe}_{1-x}\text{O}_3$ ($0.05 \leq x \leq 0.25$) ceramic samples, (M-H of BiFeO_3 ceramic in the inset) at 300 K