

***Chapter 8 Studies on Multiferroic and
Magneto-dielectric response of Co-doped
 $\text{Bi}_{0.5}\text{La}_{0.5}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ multiferroic***

8.1 Introduction

Magnetoelectric multiferroics are a class of materials which possess both ferroelectric and ferromagnetic/antiferromagnetic ordering simultaneously in a single phase. These materials have drawn immense interest in recent years not only for their widespread applications like memory storage devices, spintronics, high-density capacitor, etc. but also for their interesting theoretical aspects. In multiferroics, the cross-coupling between these two ferroic orders i.e. the effect of the external magnetic field used to control or switch polarization and vice-versa is described as ME coupling in these materials [155]. The coupling between these properties opens up a new horizon for their use in technological applications. Unfortunately, there are only a few multiferroics reported in nature because of their chemical incompatibility and simultaneous presence of electric and magnetic ordering.

Among discovered multiferroics, bismuth ferrite BFO is only one which displays high ordering temperature (ferroelectric Curie temperature $T_C = 1103$ K and Neel temperature $T_N = 643$ K) both well above room temperature. BFO is a type-I multiferroic with rhombohedral distorted crystal structure ($R3c$ space group) [39, 156]. BFO exhibits G-type antiferromagnetic arrangement, with a cycloid type spin structure and a long period of 62nm. In BFO, ferromagnetic behavior generally results from the presence of partially filled electrons in the 3d shell of Fe^{+3} ions, while the lone pair electrons in the 6s shell on the Bi-site is responsible for ferroelectricity generation. However, the crystal structure instability, weak ME coupling, a small value of magnetization and high leakage current make it less feasible for its application in technological devices [76, 151]. Since past few years, extensive research work is being carried

out to solve these difficulties by suitable chemical substitution of rare-earth (RE) and transition metal cations on Bi and Fe site of single phase BFO, respectively. For example, suitable chemical substitution of A-site by La^{+3} , Dy^{+3} , Sm^{+3} and replacement of Fe atom with metal (Mn^{+3}) and non-metal dopants (Zr^{+3}) are being carried out for improved multiferroic properties [62, 72, 74]. Moreover, it was observed that the enhancement in magnetization is caused by the suppression or destruction of the cycloid spin structure due to doping. However, intrinsic antiferromagnetic nature of single phase BFO remains intact due to the weak ME effects in the system. Thus, in past years, extensive research has been performed on BFO by various research groups to improve and control ME coupling at room temperature by destroying the cycloid spin structure [108]. Enhancing the ME effect or the MD coupling in BFO still remains a significant ongoing challenge as it is required for practical applications. Hence, a new approach is needed for getting strong ME-effects around room temperature.

The purpose of this chapter is to enhance multiferroic properties and ME coupling near room temperature of the multiferroic Co-doped $\text{Bi}_{0.5}\text{La}_{0.5}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_3$. The study reveals that the Co-substituted BLFMCO multiferroic shows significantly enhanced dielectric constant.

The increase of dielectric constant under the application of a static magnetic field of 1 T throughout the frequency range of investigation confirms experimental evidence of coupling between electric and magnetic ordering in BLFMCO.

8.2 Experimental Techniques

The BLFMCO multiferroic was prepared by standard solid-state reaction route. We have used high purity oxides Bi_2O_3 , La_2O_3 , Fe_2O_3 , CoO , and Mn_2O_3 as initial reagents. Detail of the procedure has been described in Chapter-4 [108]. The formation of single phase BLFMCO polycrystalline sample was analyzed by X-ray diffractometer (Miniflex- $\bar{\text{I}}$, Rigaku, Japan) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at a scan rate of $2^\circ/\text{min}$. The Raman spectra were recorded using a Renishaw micro-Raman spectrometer in the range of 200 cm^{-1} to 800 cm^{-1} . A solid-state laser with an excitation wavelength of 532 nm was used as the excitation source. Magnetic properties were measured with the help of highly sensitivity commercial superconducting quantum interference device [Magnetic Properties Measurement System (MPMS) XL-7, Quantum Design, Inc.]. The E44804 precision LCR meter has been used for dielectric analysis of the sample in a range of frequency (1 KHz-1MHz). The MD measurements were done at 1 T field.

8.3 Result and Discussion

8.3.1 X-ray diffraction study

Figure 8.1 displays the room temperature X-ray diffraction pattern with Rietveld refinement of BLFMCO solid solution. In previous articles, it has been shown that replacement of Bi ions by La (20%) suppresses the cycloid spin structure of BFO leading to improved magnetization. This suppression of cycloid spin-structure is coupled to a structural transition from rhombohedral ($R3c$) to orthorhombic ($Pbnm$) [66, 157]. In our previous work, we have also found that multiferroic BLFMO holds orthorhombic structure ($Pnma$) [107]. Rietveld refinement results

confirmed that the solid solution of BLFMCO remained in the orthorhombic crystal structure with ($Pnma$). Thus, 10% doping of Co on Fe -sites does not affect the crystal structure, and the system maintains its native orthorhombic structure ($Pnma$).

All the diffraction peaks obtained in Figure 9.1 are related to the Bragg positions of the orthorhombic structure with no traces of impurities (i.e., $\text{Bi}_{25}\text{FeO}_{39}$, $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{36}\text{Fe}_{24}\text{O}_{57}$, etc.). The lattice parameters and volume of BLFMCO sample obtained from Rietveld refinement are $a=5.5490 \text{ \AA}$, $b=7.8482 \text{ \AA}$, $c=5.5444 \text{ \AA}$, and $V=241.4545 \text{ \AA}^3$ respectively which are very close to Chapter-3 [107]. Hence, XRD analysis has revealed that Co-doping BLFMO sample belonging to the orthorhombic crystal ($Pnma$).

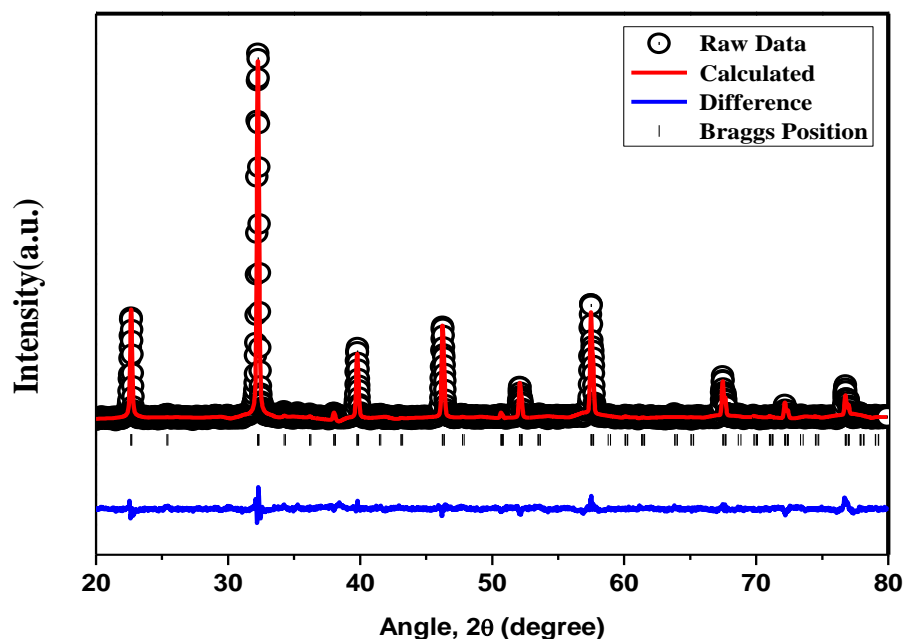


Figure 8.1 Room temperature X-ray diffraction (XRD) with Rietveld refinement pattern of BLFMCO sample. The hollow dots correspond to the observed data (Y_{obs}), solid red lines pass through these dots represents the calculated data (Y_{cal}), and solid blue lines represent the difference between these two, i.e. ($Y_{\text{obs}} - Y_{\text{cal}}$).

8.3.2 Raman study

To get further confirmation of the phase transition of BLFMCO sample, Raman spectra were recorded at room temperature. From the first principle calculations it has been shown that at room temperature, pure BFO in R3c coordination shows only 13 Raman active optical phonon modes: $\Gamma_{R3c} = 4A_1 + 9E$. [158]. It is found that low-frequency Raman modes (**A**) are associated with the vibration of Bi-O bond whereas higher frequency **E** modes are related to the Fe-O vibration. Here, we have studied the Raman spectra of BLFMCO along with pure BFO polycrystalline sample in the range of 200cm^{-1} to 1000cm^{-1} which are shown in insets of Figure 8.2. In contrast to pure BFO, Co-doped BLFMO multiferroics exhibit quite different Raman spectrum which shows only three intense Raman modes at ~ 630 , 430 and 230cm^{-1} . The change from pure BFO in the Raman spectrum is understood to be due to the phase transition from rhombohedral (pure BFO) to orthorhombic (BLFMCO) structure. The transition is attributed to the John-Teller (JT) distortion in $(\text{Mn/Fe})\text{O}_6$ due to the presence of JT active ions (Mn and Fe) and the lattice distortion due to Co doping. Chem. et al. also showed that Mn, Ho, and Mn, Ho co-doped BFO went through structural phase transition from rhombohedral to a dual phase consisting of tetragonal and orthorhombic phases [158]. Further, the obtained modes are slightly shifted towards the higher wavelength which confirms the successful substitution of Fe sites by Co ions in BLFMO lattice [159]. Hence, Raman spectra also confirmed that on doping of Co ions, the BLFMO lattice retains its structure ($Pbnm$) and does not go through any structural transition.

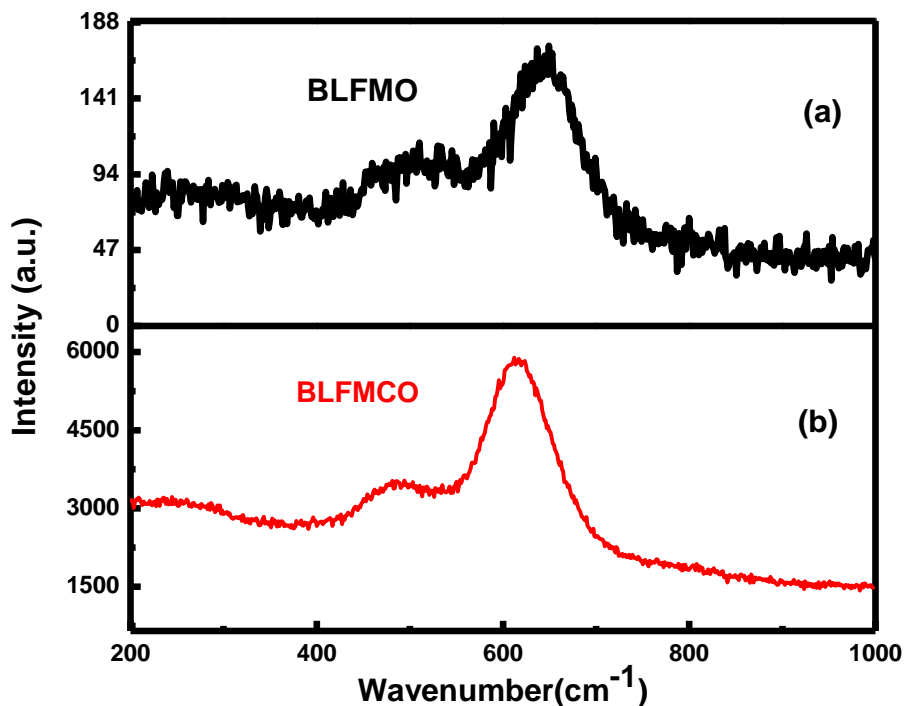


Figure 8.2 Characteristics Raman spectra measured at room temperature for polycrystalline (a) BLFMO (b) BLFMCO samples.

8.3.3 Magnetic analysis

Figure 8.3(a) depicts the field cooled (FC) and zero-field cooled (ZFC) dc magnetization M - T curves of BLFMCO sample under the application of 500 Oe field in the temperature range 2-300 K. A large bifurcation between FC and ZFC plots can be seen in BLFMCO sample near room temperature which is a signature of spin glass behavior or super paramagnetism (SPM) blocking [141, 160]. The spin-glass behavior is generally associated with intense magnetic frustration, random positions of magnetic ions, and deformed lattice structure [160]. A significant bifurcation in ZFC-FC curves was also reported in BLFMO sample in our previous report [107], and the substitution of Co on BLFMO enhances it. The massive bifurcation in the plot can be understood to be due to increase in the competing magnetic interaction between ferromagnetic

(Mn-spin) and antiferromagnetic (Fe-spin) cluster in the sample due to the presence of Co ions [161, 162], as previously observed in Co-doped BFO and $\text{BiFe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ thin films [162]. Further, the ZFC magnetization curve of BLFMCO decreases gradually with decreasing temperature and shows a magnetic upturn due to re-orientation of spins below 120K (see insets Figure in 8.3(a)).

This signature of spin-reorientation transition (T_{SR}) can arise due to a change in the magnetic interaction between ions and variation in octahedral angles [161]. The observed spin reorientation transition temperature (T_{SR}) 120K is consistent with that observed in BFO single crystal [30].

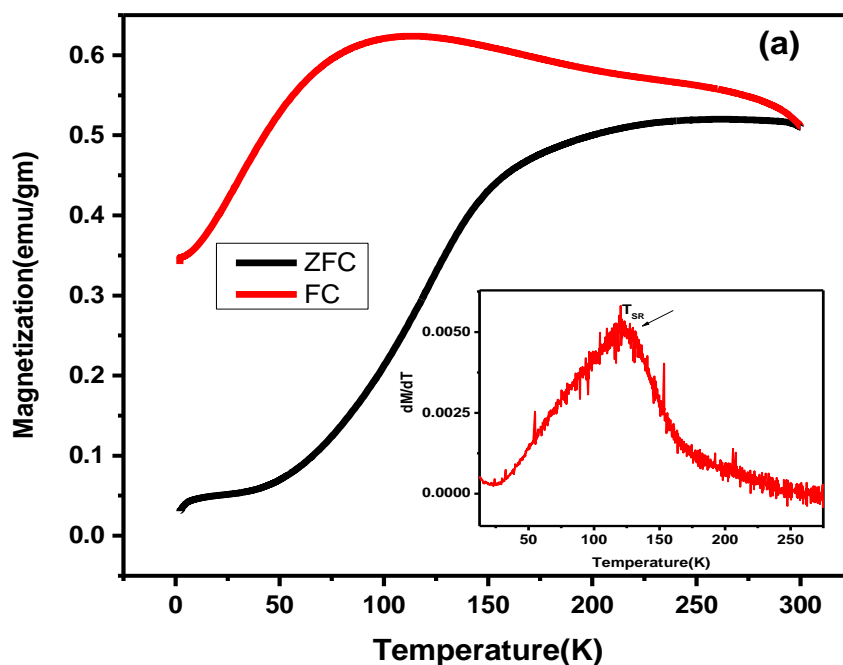


Figure 8.3 (a) Temperature dependence of magnetic moment (M-T curves) of BLFMCO sample measured under an applied field of 500Oe under field cooling (FC) and Zero-field cooling (ZFC) conditions.

Figure 8.4 and 8.5 show the magnetization (M) vs. magnetic field (H) hysteresis loops (magnetic field ± 3 T) of multiferroic BLFMCO measured at different temperatures. A weak ferromagnetic behavior (soft ferromagnetic) was observed at 300 K which is entirely from that observed in BLFMO [ref...Own Paper.]. The enhancement in the magnetic properties by substitution of Mn ions by Co ions (10%) can be assigned to the direct ferromagnetic interaction between Fe-O-Co ions and other possible super-exchange interaction between mixed valancies of Fe and Co] [162, 163]. Y. Chiang et al. have shown improvement of ferromagnetic characteristics of Co-doped BFO to be due to super-exchange interaction between mixed valancies of Fe and Co ions.

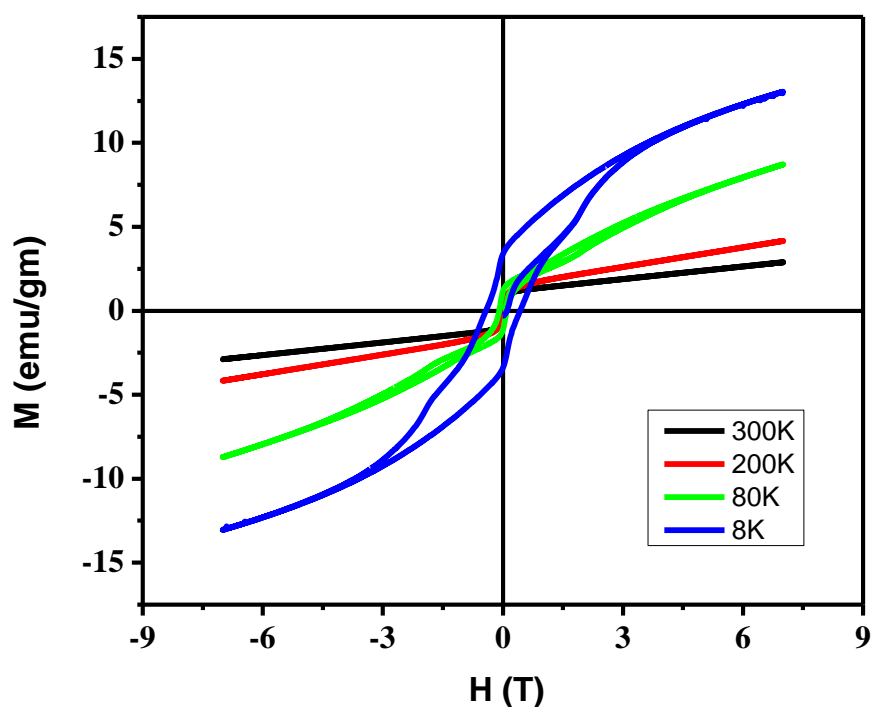


Figure 8.4 Magnetization(M) vs. magnetic field(H) hysteresis loops measurement of sample BLFMCO obtained at different temperatures (i) 300K (ii) 200K (iii) 80K (iv) 2K. (Inset shows the enlarged view of M-H curves)

Interestingly, the M-H hysteresis loop of BLFMCO obtained at 80K displays the wasp-waisted shape of the hysteresis loop which is a very rare phenomenon in BFO based systems. The wasp-waisted type M-H loops are widely reported in geological metals, cobalt-doped ferrites and metal alloys [ref,.....]. The obtained wasp-waisted hysteresis loop in BLFMCO sample can be understood to be due to the presence of two different magnetic phases, i.e., AFM and FM in the sample [38]. The peculiar wasp-waisted hysteresis loops with coercive field $\sim 900\text{Oe}$ without field cooling are useful to derive novel and multifunctional devices.

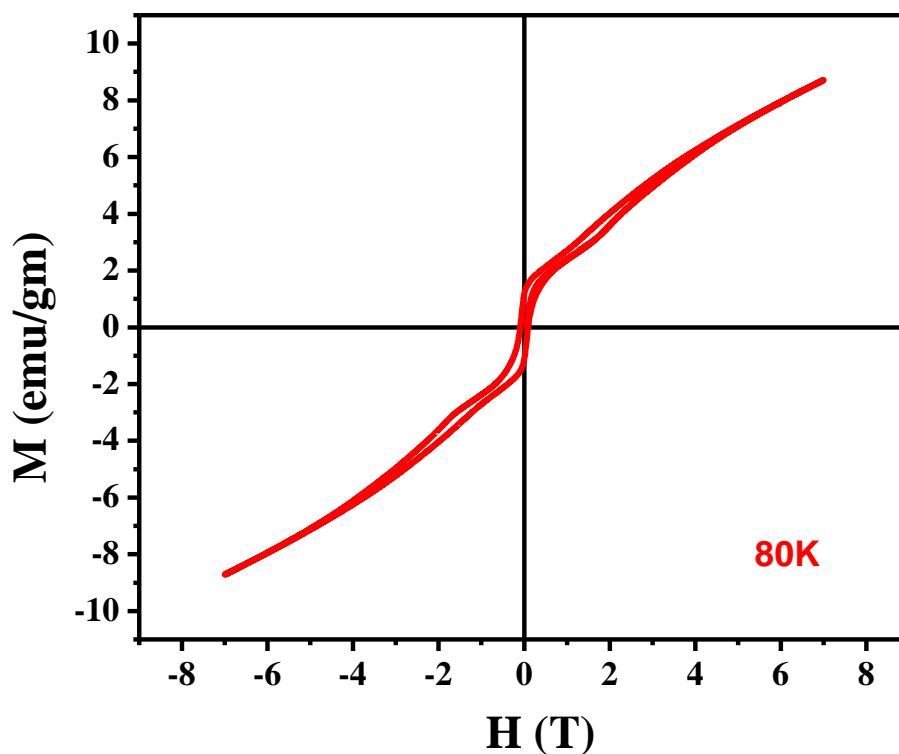


Figure 8.5. Meta- Magnetic hysteresis loop of sample BLFMCO at 80K.

8.3.4 Dielectric analysis

The temperature dependence of the relative dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) measured at different frequencies (1 KHz, 10KHz, 50KHz, 120KHz, and 1MHz) of the BLFCMO sample is shown in Figure 8.6. Co doping in BLFCMO can be seen to modify the value of ϵ_r from $\sim 8.5 \times 10^3$ (for BLFCMO) to 2.8×10^4 (for BLFCMO) at 1KHz at room temperature making it useful for capacitor applications. This sharp increase in ϵ_r can be understood on the basis of the inter-wall hopping mechanism. Co-doping in BLFCMO sample increases the defects near the grain boundary which increases the rate of inter-wall hopping. The increment in the rate of inter-wall hopping is considered responsible for large dielectric constant [107]. Moreover, BLFCMO sample exhibits nearly constant ϵ_r value up to ~ 165 K and then increases sharply with increase in temperature. Such behavior is often linked to the dipolar relaxation mechanism. At low temperatures frozen electric dipoles cause a decrement in electric constant under the application of applied electric field, but at higher temperatures, electric dipoles get thermally excited leading to a sharp enhancement in ϵ_r .

Moreover, it is observed that BLFCO shows large ϵ_r for frequency 1KHz, followed by continuously decrementing in ϵ_r with increasing frequency from 10KHz to 1MHz. This can be explained by the Koop's phenomenological theory in conformity with Maxwell-Wagner theory according to which at low frequency the electric dipoles have sufficient time to align themselves in the direction of the applied field, while at higher frequencies there is less time for orientation of dipoles in the field direction causing the depolarization in the sample [148]. The same behavior can also be observed in the value of dielectric loss for BLFCNO sample. Further, it can

be seen that dielectric loss exhibits peaking behavior which shifts towards higher temperature as frequency increases from 1 KHz to 1MHz.

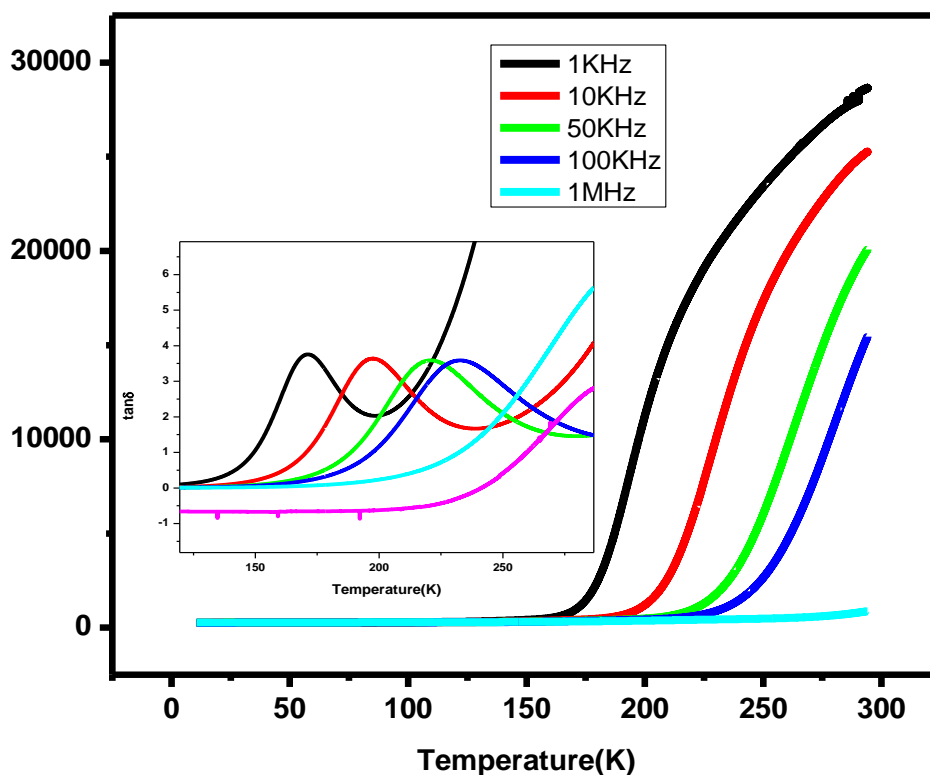


Figure 8.6 Dielectric constant vs. temperature plots of BLFMCO samples. (The corresponding loss tangent is presented in the inset of Figure 8.6)

8.3.5 Magneto-dielectric (MD) analysis

The presence of Magneto-electric (**ME**) coupling in the material can be directly determined by switching the polarization **P** (respectively, magnetization **M**) by the application of the external magnetic field (respectively, electric field). However, due to the different origin of **P** and **M** in BFO, it shows weak coupling between ferroelectric and magnetic orders have restricted it for application point of view. The signature of ME coupling, indirectly, can also be studied by

changing the dielectric permittivity under the application of magnetic field [77, 164]. This tuning of dielectric constant induced by an external field defined as magneto-dielectric (MD) coupling. Quantitatively, the presence of MD coupling in the sample is measured in terms of the magneto-dielectric coefficient (MD %) characterized as the following formula.

$$\text{MD\%} = \frac{\varepsilon(H,T) - \varepsilon(0,T)}{\varepsilon(0,T)} \times 100$$

Where, $\varepsilon(H, T)$ and $\varepsilon(0, T)$ are the value of the dielectric constant in the presence and absence of external magnetic field (H) at temperature T respectively. For BLFMCO sample, we studied the switching dielectric constant measurement as a function of the field at different temperature at frequency 1 KHz. From the Figure 8.7, it is clearly seen that the magnitude of MD% directly increases with field and becomes stable at the higher field at all temperature signifying a positive MD coupling. This outcome shows the present of MD coupling in the sample near room temperature by the second criterion. It is reported that the increment or decrement in dielectric permittivity with applied field depends on the pair co-relation of nearest-neighbor spin product and the coupling constant [67]. A. S. Priya et al. also found positive MD behavior in single phase BFO and (Dy, Cu) – co-doped BFO composite at room temperature [43]. We obtain here a significant increase in MD% around 6.3% at 250K for 1 KHz frequency near room temperature. This result is clear experimental evidence of coupling between electric and magnetic ordering at room temperature. This strong enhanced in MD coupling is basically related to spin fluctuations of a sample. It was reported that large spin fluctuations suppressed the spin cycloid structure, resulting for change in dielectric permittivity on the application of the magnetic field [67, 165]. This result demonstrates that the present of MD coupling in the sample near room temperature.

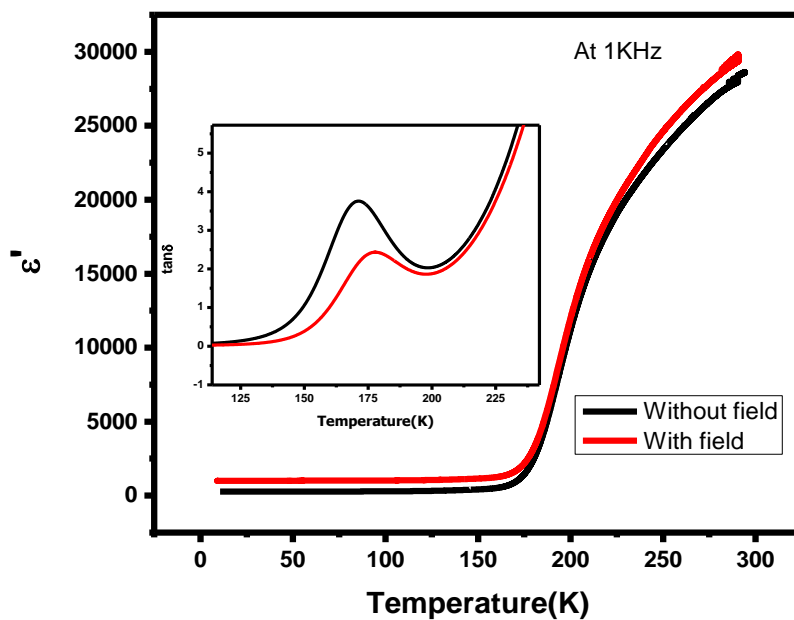
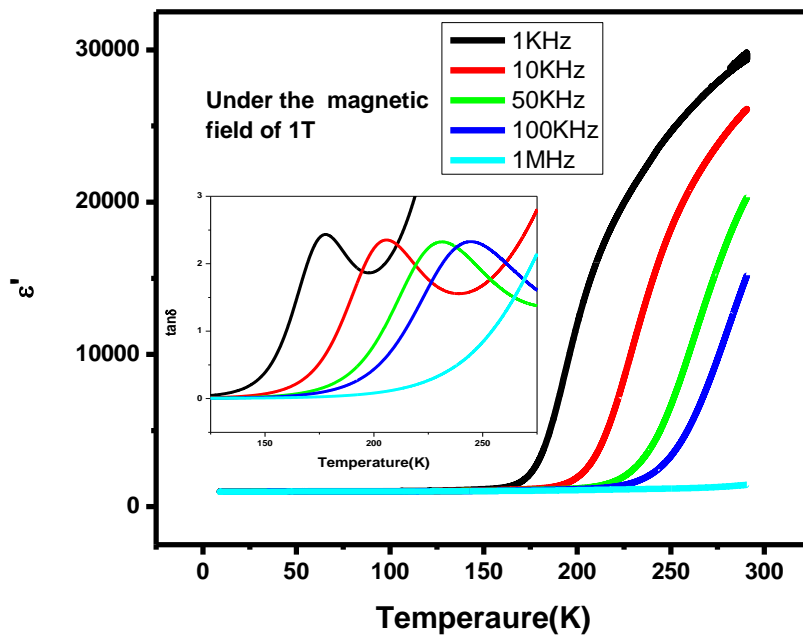


Figure 8.7 Dielectric constant vs. temperature variation of BLMCO sample under the magnetic field of 1T. (The corresponding loss tangent is presented in the inset of Figure 8.7.)

8.4 Conclusion

In this chapter, we have successfully prepared BLFMCO sample by solid state route. The XRD with Rietveld refinement shows that BLFMCO sample is formed in a single phase (*Pnma*). Raman study also reveals that there is no structural transition occurring with Co doping in BLFMO. The introduction of Co at Fe-site induced ferromagnetism due to magnetic interaction between Fe-O-Co ions. Further, multiferroic BLFMCO exhibits large spontaneous exchange bias which shows maximum at low temperature ($H_{SEB} = 332.05\text{Oe}$ & $H_{SC} = 2301.03\text{Oe}$) and continues to decrease with increasing temperature. Rarely reported spontaneous ‘wasp-waisted’ hysteresis loop obtained at 80K making it more beneficial for new improved applications. Temperature-dependent dielectric constant measurement shows that substitution of Co at Mn site enhanced the dielectric properties which might be due to Maxwell –Wagner effect. The result on MD response confirms high MD coupling of BLFMCO sample, quantitatively measured to be ~5% (at 1KHz frequency) near room temperature at low magnetic field 1T.