



Multiferroic Investigations of Dy and Tb doped (Bi,Pb)(Fe,Ti)O₃ Ceramics

Monika Mishra^{*a}, Dr. Rizwan Arif^b

^aDepartment of Physics, School of Basic and Applied Sciences, Lingaya's Vidyapeeth, Faridabad

^bDepartment of Chemistry, School of Basic and Applied Sciences, Lingaya's Vidyapeeth, Faridabad

*Corresponding Author

Ms. Monika Mishra

Department of Physics, School of Basic and Applied Sciences

Lingaya's Vidyapeeth, Faridabad-Haryana

Email: Monikamishra@lingayasvidyapeeth.edu.in

Phone NO.: +91-9582580679

Abstract

Polycrystalline samples of Bi_{0.8}A_{0.1}Pb_{0.1}Fe_{0.9}Ti_{0.1}O₃ (where A = Dy and Tb) ceramics have been prepared through high temperature sintering technique. X-ray diffraction analysis showed that the ceramics possess perovskite phase with hexagonal crystal symmetry. Dielectric and electrical properties indicate that the Curie temperature shifted to higher temperature with Dy doping. AC conductivity of the sample increases with increase in temperature which confirms the negative temperature coefficient of resistance (NTCR) behaviour of material. Substitution of Dy and Tb ions at A-site suppress the spiral spin structure of BiFeO₃ which is further responsible for the appearance of weak ferromagnetism at room-temperature. Induced destruction of the spin cycloid due to the Dy and Tb substitution, these multiferroic properties are attributed because of the enhanced magneto-electric interaction.

Keywords: Ferroelectric; Ceramics; Multiferroics, Perovskite, Dielectric, Impedance, NTCR

1. Introduction

Multiferroics have simultaneous electric and magnetic ordering, thereby also referred to ferroelectromagnets (FM), magneto-electrics (ME) and/or ferroelastics. These multiferroics have gained much attention for their potential applications and rich fundamental physics. Magneto-electric effect denotes the coupling between the magnetic and the electric properties of a material. The small coupling between the electric and magnetic properties of the system in multiferroic provides an additional degree of freedom for device fabrication [1, 2]. BiFeO₃ (BFO) and Bi₅FeTi₃O₁₅ (BFTO) are few such examples of multiferroic systems [3, 4]. The ferro-electromagnetic property of sulphide spinels and oxide perovskites have been also reported [5]. Those materials possessing ABO₃ type structure offers a broad range of magnetic and electrical properties which mainly covers anti-ferroelectric, anti-ferromagnetic properties in metals, semiconductor, and insulator. Hence by making a composition of these perovskite materials opens new ways to achieving the multiferroic properties in a single phase system. In latest researches, several composite groups for the synthesis and characterization of multiferroic perovskite systems such as [BiFeO₃ (BF) – BaTiO₃ (BT)] anti-ferromagnetic-ferroelectric [6], anti-ferromagnetic/weak ferromagnetic-ferroelectric [(BF)–PrFeO₃ (PF)–PbTiO₃ (PT)] [7] and BiDyFeO₃ (DF)–BaTiO₃ (BT)] systems have also been reported [8].

As per the intensively reported studies in recent years, BiFeO₃ has come out to be a perovskite structure exhibiting several magneto-electric properties at room temperature. BFO is a ferroelectric material with a Curie temperature of about 1103 K and anti-ferromagnetic with a Neel temperature (T_N) of 643 K [9]. BiFeO₃ has been synthesized by deploying several synthesis techniques such solid state, sol gel method and hydrothermal process etc. In the solid state technique, Bi₂O₃ and Fe₂O₃ are made to react within the temperature range of 800–830 °C and the remaining unreacted secondary phases Bi₂O₃/Bi₂Fe₄O₉ phases are removed by washing with HNO₃. The disadvantage of this process is that there is the necessity of leaching

the unwanted phases during synthesis by using an acid and effectively providing the coarser powder & reproducibility of the process is also poor [10]. To synthesize pure BiFeO_3 , some attempts were already made but small traces of $\text{Bi}_{46}\text{Fe}_2\text{O}_{72}$ was found while the sintering of ceramics is done [11]. Therefore, utilization of BiFeO_3 - ABO_3 solid solution systems is one of the ways to increase the sinterability and stability of structure of composite material. Moreover, another major issue reported for BFO-based ceramics is that their insulating resistance is very low which creates difficulty in measurements of ferroelectric, dielectric quantity and magneto-electric coupling at room temperature.

RMO_3 (where R is a rare-earth ion and M is a transition metal atom), DyFeO_3 and TbFeO_3 also belong to this class of perovskite oxides. Just like BiFeO_3 , DyFeO_3 is also having centre of inversion exhibiting orthorhombic structure [12]. Magnetic field induced ferroelectricity in DyFeO_3 and TbFeO_3 crystal can be controlled by magnetic field and the ferroelectric state can be reversible by varying the material in magnetic field which confirms the strong magneto-electric coupling present in such systems [13]. Ferroelectricity was also induced in these systems by epitaxial strain due to the result of structural distortion in the structures of multiferroic systems [14]. Solid solution of bismuth ferrite and rare earth ferrites strongly infers the several interesting properties for magneto-electric applications. Because of the high electric conductivity of BiFeO_3 , synthesis of pure polycrystalline sample of BiFeO_3 (BFO) is quite challenging because there is always the formation of secondary stable thermodynamically phase of $\text{Bi}_2\text{Fe}_4\text{O}_9$. Other ferroelectrics such as PbTiO_3 with perovskite structure were introduced to form solid solutions with BiFeO_3 in order to stabilize the perovskite phase. PbTiO_3 also helps in reducing electrical coercive field by forming a morphotropic phase boundary (MPB) with BiFeO_3 [15]. Phases of different symmetries are separated by this morphotropic phase boundary (MPB) arising from PbTiO_3 and BiFeO_3 sides [16, 17]. Structural, magnetic and morphological properties as a function of composition

of $(1-y)(\text{BiFeO}_3)-y(\text{PbTiO}_3)$ solid has been reported by many researchers. Investigations revealed that availability of mixed crystals with a $\text{BiFeO}_3\text{-PbTiO}_3$ (BF-PT) in ratio of 50:50 ultimately favours the formation of chemically ordered micro-regions where the spiral spin modulation is found to be decreased [18]. In addition to this, it was observed that the substitution of Ti at B-atomic site i.e. in place of Fe results in increase in magnetic properties of compounds [19, 20]. Hence, the overall magnetic behaviour of bulk REFeO_3 (RE-Rare Earth) can be summed up as the result of two contributing magnetic ‘sub lattices’: (i) an antiferromagnetic iron oxide lattice in which the spins are coupled through a $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ super exchange mechanism; and (ii) a paramagnetic contribution which are due to essentially non-coupled ions. A small ferromagnetic moment is observed in the iron containing sub lattice due to spin-canting. Spin canting is a phenomenon through which the spins are tilted by a small angle about their axis. This ferromagnetic moment is observed because of the distortion caused in perovskite structure in one particular crystallographic direction [21]. In this study, the investigations of the crystal structure, dielectric and magnetic properties of the ternary perovskite system $\text{Bi}_{1-x}\text{A}_x\text{Pb}_y\text{Fe}_{1-y}\text{Ti}_y\text{O}_3$ (where $\text{A} = \text{Dy, Tb}$, $x=0.1$ and $y=0.1$) (which is a combination of three ternary perovskite, Ferroelectric and Ferromagnetic) have been carried out. Radii of Dy and Tb are just similar to each other (Atomic radii of $\text{Tb} = 225\text{pm}$ and $\text{Dy} = 228\text{pm}$) and used to substitute at the A site of samples which further helps in decreasing the amount of oxygen vacancies and Bi volatilization.

2. Experimental procedure

Polycrystalline samples of $\text{Bi}_{0.8}\text{A}_{0.1}\text{Pb}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ (BPFT) ($\text{A} = \text{Dy}$ and Tb) were synthesized from high purity oxides (Bi_2O_3 (Aldrich chemicals USA), Fe_2O_3 (Aldrich chemicals, USA), Dy_2O_3 (M/S Aldrich chemicals, USA), Tb_4O_7 (M/S Aldrich chemicals, USA), PbO (M/S Aldrich chemicals, USA) and TiO_2 (Aldrich chemicals, USA), through high temperature solid-state methodology. The reagents of sample compounds were mixed in a unit

of ball milling machine thoroughly for almost around 48 hours taken in suitable stoichiometry. The powder was first kept for drying completely at temperature 125 °C in order to remove its moisture. Before being cold pressed, the powder is calcined at 800 °C in alumina crucibles for a time period of around 4 hours. Then a hydraulic press is used to make cylindrical pellets of the calcined fine powder, pressed with a pressure of 50 MPa to make pellets of order of 10 mm in diameter and 1-2 mm in thickness. These pellets were embedded in the same composition then sintered at 850 °C for 4-5 hours. The XRD patterns were recorded at room temperature using X-ray powder diffractometer (Rigaku Miniflex, Japan) with CuK α radiation of wavelength ($\lambda = 1.5405 \text{ \AA}$) at a scanning rate of around $1/2^\circ \text{ min}^{-1}$ in a wide range of Bragg angles 2θ ($20^\circ \leq 2\theta \leq 60^\circ$) to confirm the pure phase formation and compound quality at room temperature. The sintered pellets were firstly ground and then polished with silver paste on opposite faces of coated pellets before making the dielectric measurements. The value of dielectric constant (ϵ) and loss tangent ($\tan\delta$) of the compounds were also calculated (RT) and as a function of frequency in a home-based furnace within a frequency range of (10^2 - 10^6 Hz) in a temperature range of RT -400 °C using a HP 4284A Precision LCR meter. The magnetic studies were recorded by deploying Cryogenic vibrating sample magnetometer (VSM).

3. Results and Analysis

3.1. Phase and structural characterization

The XRD patterns of $(\text{Bi}_{0.8}\text{A}_{0.1}\text{Pb}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3)$ ($\text{A} = \text{Dy}$ and Tb) ceramics at room temperature is given in **Fig. 1a**. It is observed that all the samples have a single phase at room temperature and exhibits a hexagonal structure (JCPDS#742497 $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{Fe}_{0.8}\text{Ti}_{0.2}\text{O}_3$). An observed inter-planar distance d is marked and further used to index all the reflection peaks of compounds (**Table 1**). Least-squares refinement method is performed to evaluate the lattice constants of $\text{Bi}_{0.8}\text{A}_{0.1}\text{Pb}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$. The observed and calculated d values of all diffracted lines (reflections) of the above compounds strongly

indicated that as we increase or decrease the doping concentration in compound, no change in the parent hexagonal structure of crystal. During synthesis, BFO is found to compose of two or more distinct phases one is dispersed phase along with matrix phase impurity because of the kinetics of the formation, The observed impurity phase attributed to the presence of $\text{Bi}_2\text{Fe}_4\text{O}_9$ (Secondary phase) is shown as in **Fig. 1a**. When we move from Dy doped BPFT to Tb doped BPFT, this secondary phase is disappeared. As it is discussed for BiFeO_3 , it has never been an easy task to synthesize a pure quality compound of BFO. Reported studies revealed that there is always a small concentration of impurity present along with major phase. [22]. **Fig. 1b** shows the (020) and (120) diffraction peaks of the compounds which confirm no peak shifts has been occurred. The intensity increases as we move from Dy doped BPFT to Tb doped BPFT which is due to the substitution of these ions at A atomic sites.

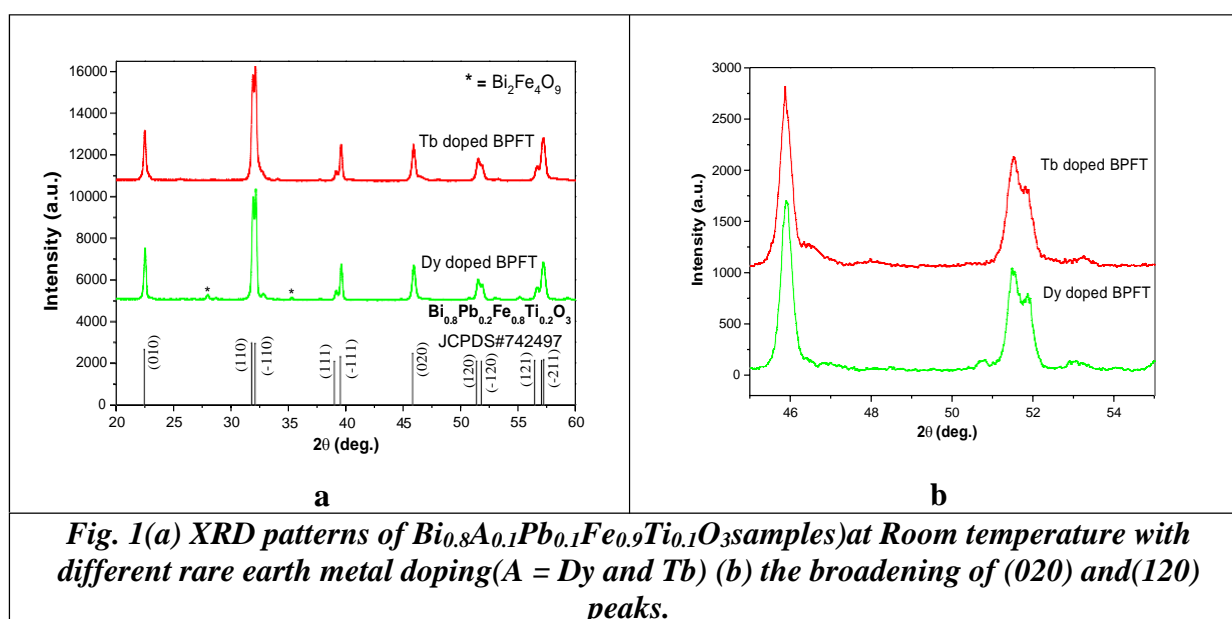
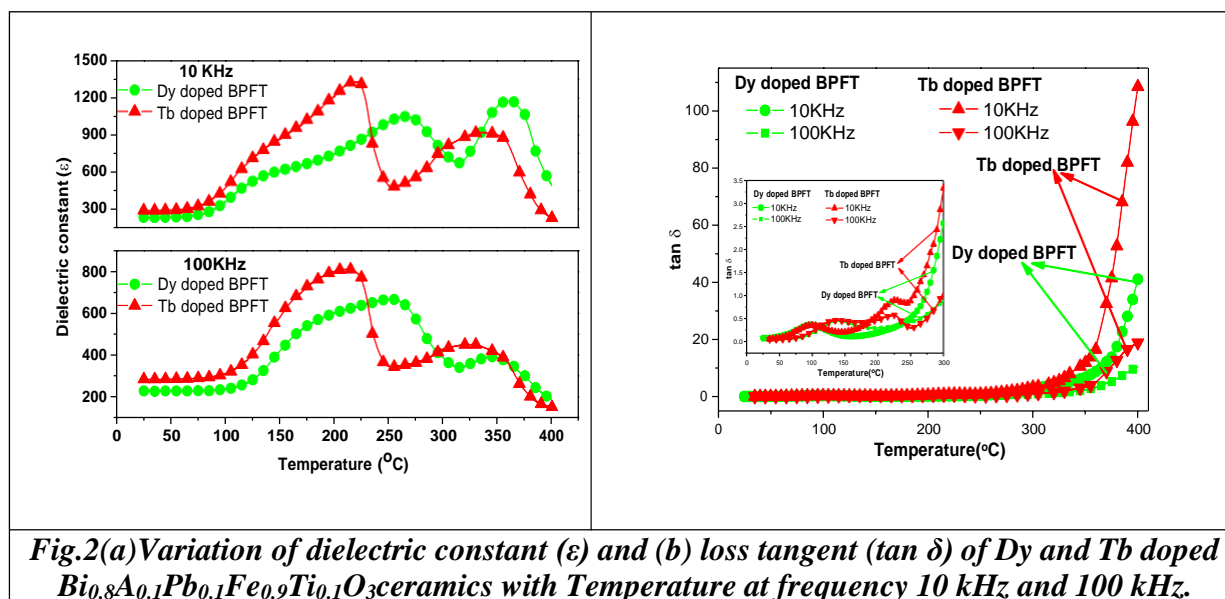


Table 1: Lattice parameters of Dy and Tb doped $\text{Bi}_{0.8}\text{A}_{0.1}\text{Pb}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramics.

Sample	Crystal System	Particle size	Lattice Parameter	d_{obs}	d_{cal}	Hkl
BDPFT BTPFT	Hexagonal	~30-40nm	a = 5.5728 Å c = 6.9257 Å	3.9586	3.9596	(010)
				2.8133	2.8135	(110)
				2.7868	2.7864	(-110)
				2.3081	2.3085	(111)
				2.2789	2.2787	(-111)
				1.9799	1.9798	(020)
				1.7775	1.7777	(120)
				1.7640	1.7640	(-120)
				1.6295	1.6297	(121)
				1.6137	1.6139	(-121)
1.6088	1.6087	(-211)				

3.2. Dielectric properties

As well known, the Dielectric constant is inversely proportional to temperature. **Fig. 2 a, b** shows the variation of dielectric constant (ϵ) and $\tan\delta$ with temperature for both compositions between the frequency range of 10 kHz and 100 kHz. The presence of these two phases confirms the presence of two different ferroelectric compounds i.e. BiFeO_3 and PbTiO_3 in the ceramic system [24-26]. Ferroelectric-ferroelectric phase transition is indicated by first and second peak which correspond to the ferroelectric–paraelectric phase transition [23]. As observed at both the frequencies (10 kHz and 100 kHz), the value of Tb doped BPFT is much larger than the dielectric constant of Dy doped BPFT. In **Fig. 2b**, it is represented that up to 275 °C, the dielectric loss gradually increases in a smooth manner. Doping effect is contributed by even very small impurities segregated to boundaries. This doping may cause the transformation of dielectric into a semiconductor. So, the problem of synthesizing pure BFO still persists as there is spontaneous change of the oxidation state of $\text{Fe}^{3+}/\text{Fe}^{2+}$ [27, 28].



Above Curie temperature, the dielectric permittivity of an ideal ferroelectric follows the Curie-Weiss law given in **Eq. (1)**,

$$1/\epsilon = (T-\theta)/C, (T>\theta). \dots\dots\dots \text{Eq. (1)}$$

Where C is Curie-Weiss constant, θ represents Curie-Weiss temperature. It is observed in the paraelectric phase only at blocking Temperature (T_B). **Fig. 3a-b** shows the inverse of ϵ as a function of temperature at 10 kHz & 100 kHz and the fitting of the experimental data to Curie-Weiss law. From the figure, a deviation from Curie-Weiss law starting at T_B has been observed. The parameter ΔT_m is often used to show the degree of deviation from the Curie-Weiss law. ΔT_m is the temperature where the ferroelectric transition can occur defined by $\Delta T_m = T_B - T_m$. T_B is determined from the Curie-Weiss law [29].

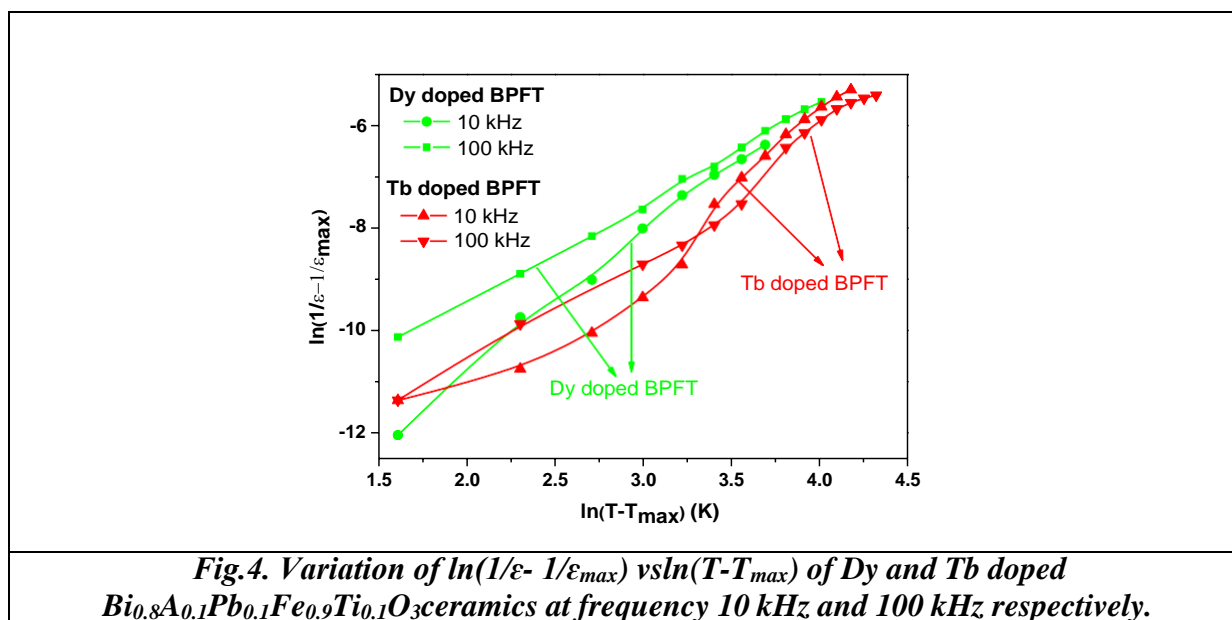
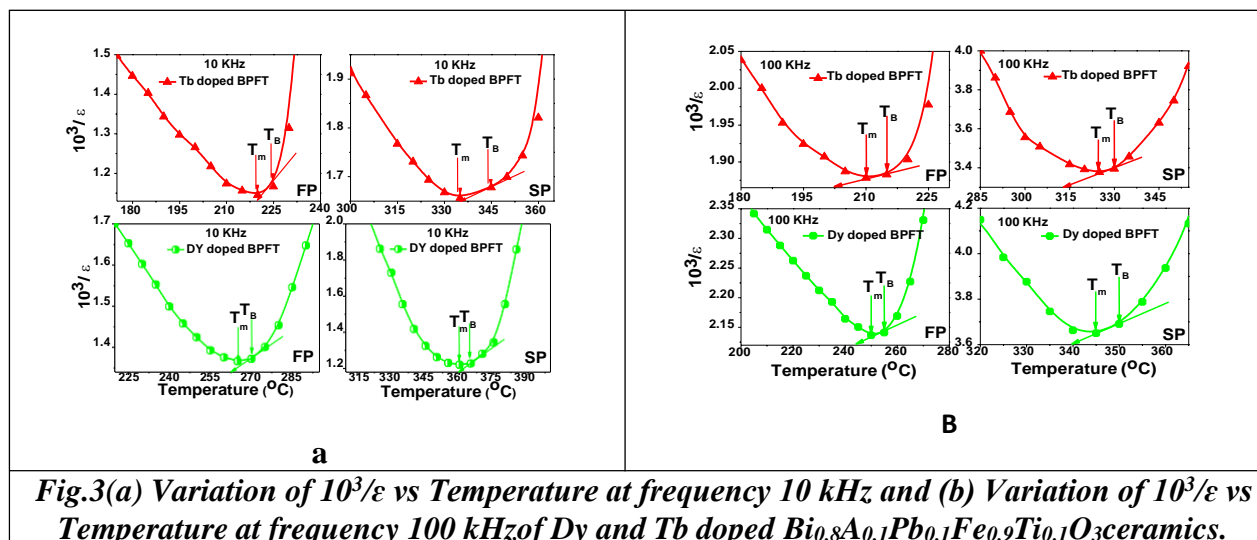
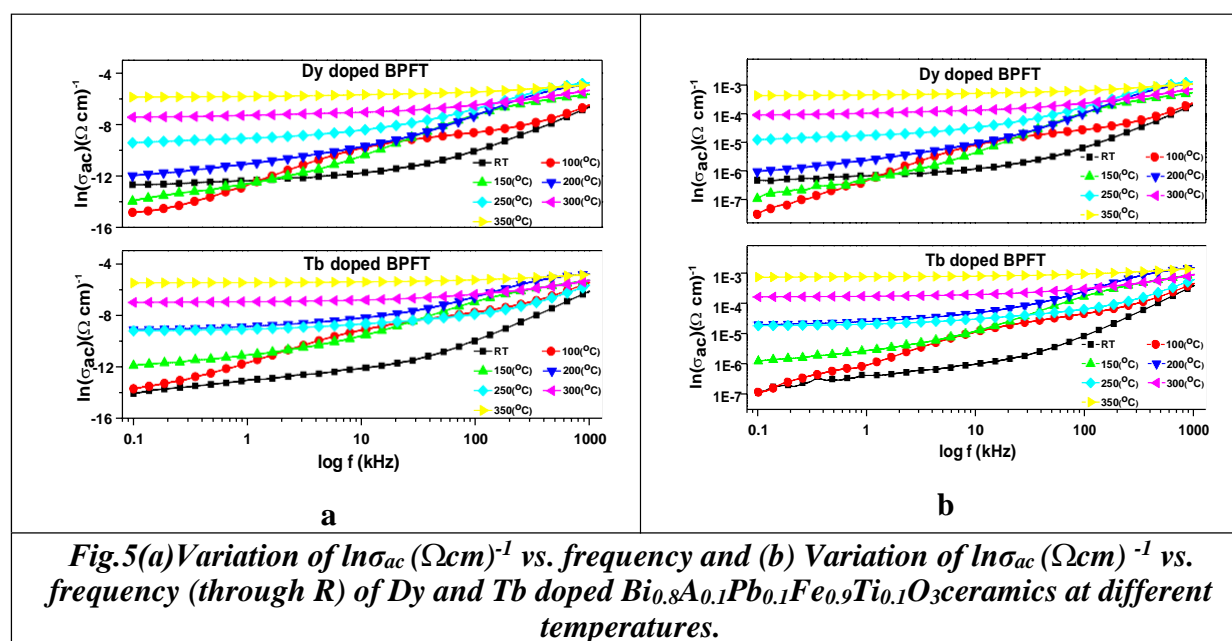


Fig.4. represents variation of $\ln(1/\epsilon - 1/\epsilon_{\max})$ vs $\ln(T - T_{\max})$ of Dy and Tb doped $\text{Bi}_{0.8}\text{A}_{0.1}\text{Pb}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramics at frequency 10 kHz and 100 kHz respectively. The graphs between $\log \sigma_{\text{ac}} (\Omega\text{cm})^{-1}$ vs $10^3/T (\text{K}^{-1})$ of Dy doped BPFT and Tb doped BPFT at frequency 10 kHz and 100 kHz in the temperature range from 320°C to 400°C are drawn and given in **Fig. 5**. Impedance data collected from the LCR meter. The AC electrical conductivity was calculated using the formula:

$$\sigma = \omega \epsilon \epsilon_0 \tan \delta$$

Where ω is the angular frequency, ϵ is the vacuum dielectric constant, and k_B is the Boltzmann constant. At Curie temperature(T_c), there is usual change in slope only at higher frequencies is observed. Activation energy was calculated by using the slope of $\ln(\sigma_{ac})$ vs $10^3/T$ in paraelectric region by using the conductivity relation $\sigma = \sigma_0 \exp(-E_a/k_B T)$ [30].

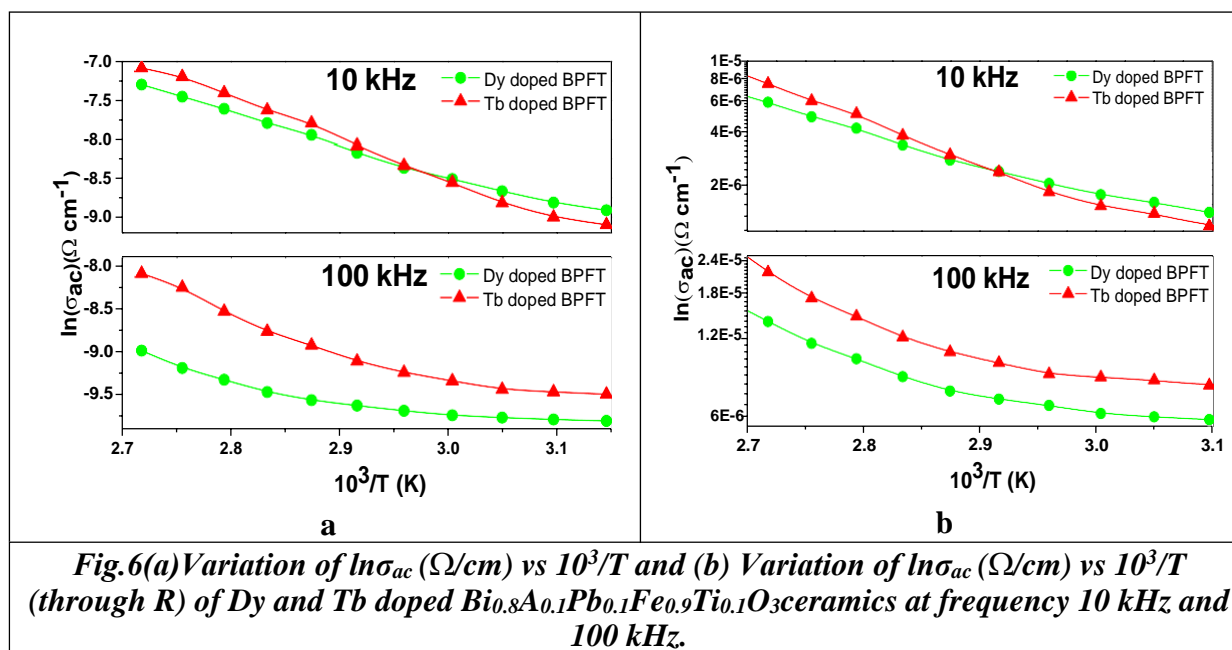


The value of activation energy is indexed in **Table 2**.

Table 2: Details of the physical parameters of Dy and Tb doped BPFT ceramics							
Sample Name	Frequency (kHz)	T^1_{max}	ϵ^1_{max}	T^2_{max}	ϵ^2_{max}	γ	Ea (eV)
BDPFT	10	265	1044	360	1168	1.9496	0.34
	100	250	667	345	390	2.7090	0.15
BTPFT	10	220	1330	335	920	2.3096	0.43
	100	210	811	325	451	2.7032	0.29

The frequency spectrum of the conductivity at different range of temperatures for the samples is shown in **Fig. 6**. Low frequency dispersion obeying the power law feature (Joncher law) has been observed to change its slope governed by n. At higher frequency, the hopping takes place by charge carriers through trap sites that minimize the effects of unintentional

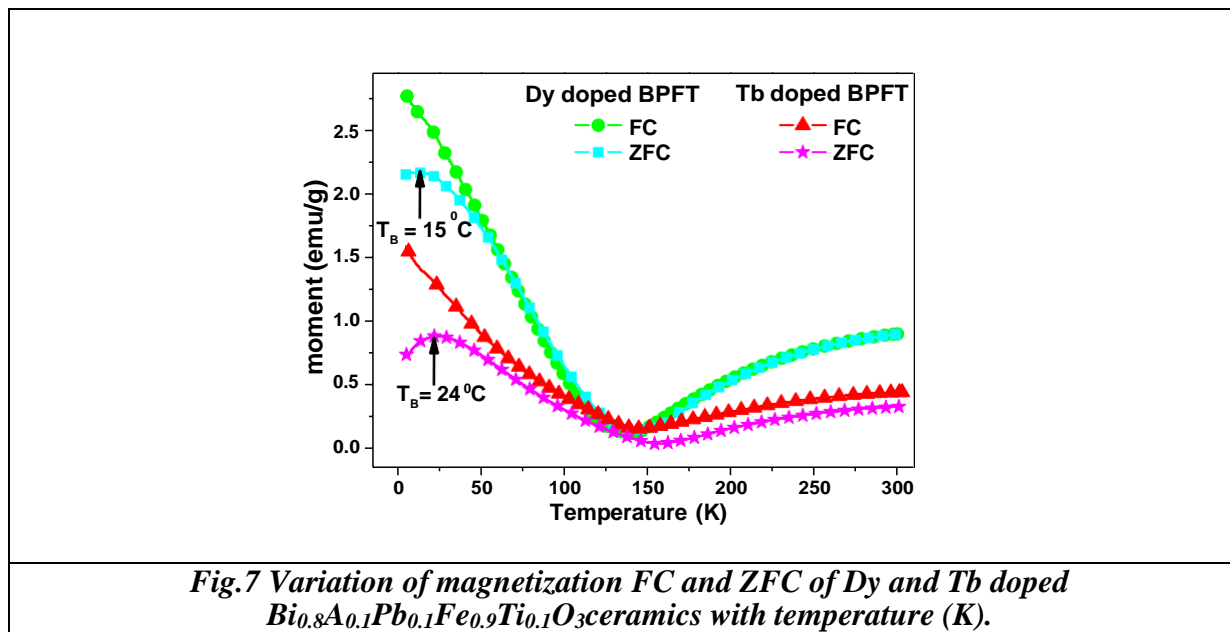
interference. The conductivity is lower at low frequency which is attributed because of the numbers of charge carriers which have high relaxation time due to higher energy barriers respond in low frequency region might be less in numbers. The potential height is reduced as the thermal energy of the charge carriers is increased at higher temperatures. A low frequency dispersion region is shown by the conductivity spectrum which is further followed by a high frequency plateau region. DC conductivity is caused by the frequency independent plateau region and low frequency region corresponds to the AC-conductivity. Due to presence of space charge, the dispersion behaviour may be observed while the space charge becomes less active in the plateau region at higher frequency domain. At lower temperatures σ_{ac} linearly varies with frequency and non-linearity occurs in the high frequency region. This behaviour indicates the role of hopping phenomenon is so prominent in conduction process at low temperature region.



3.3. Magnetic properties

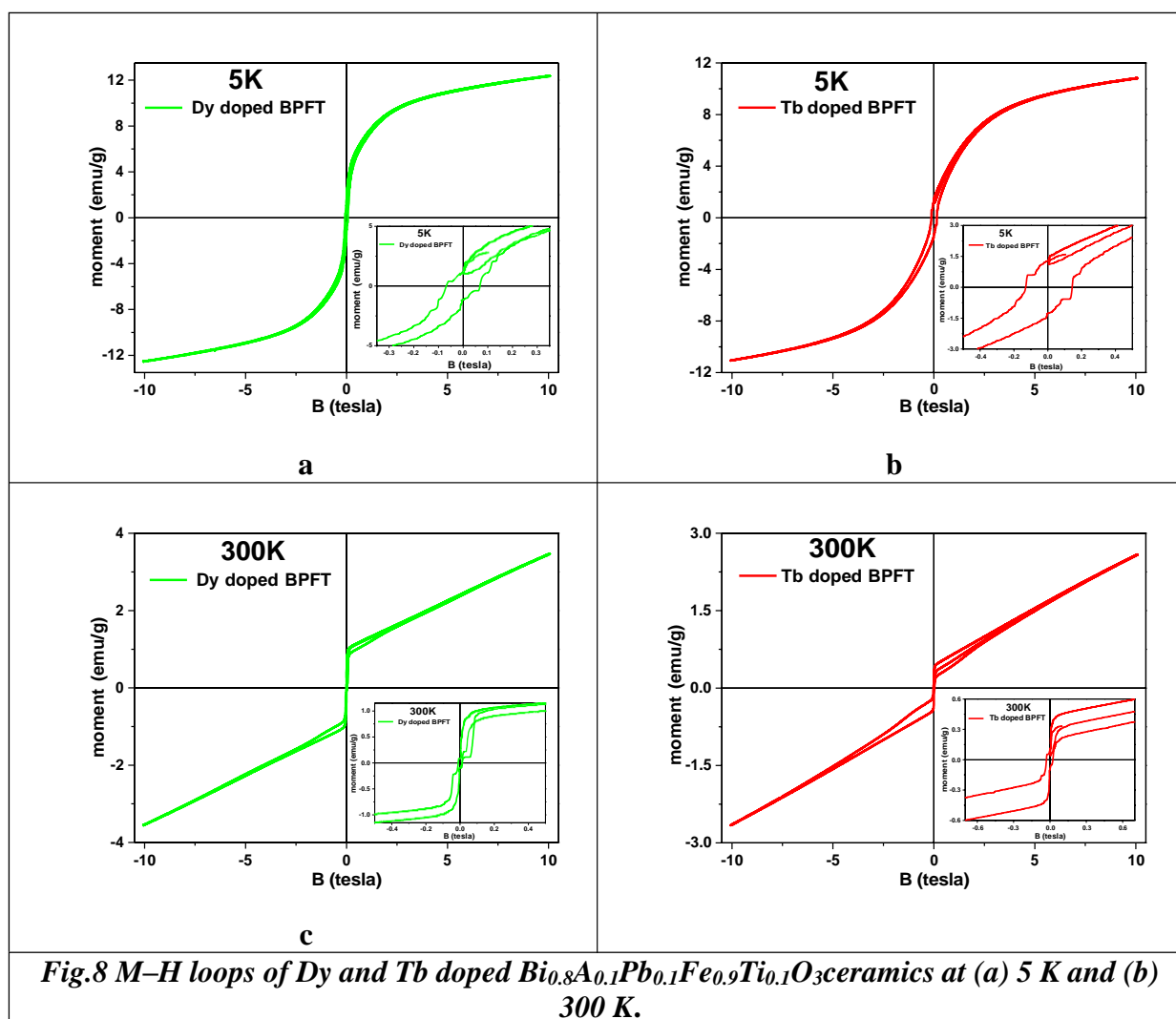
Fig. 7 is showing the magnetic moment as a function of temperature under zero-field cooled (ZFC) and field cooled (FC) conditions with an applied magnetic field of 1 Tesla between 5 and 300 K. By cooling the sample in zero-field, then warming within the field of 1 Tesla and simultaneously measuring the magnetization while increasing the temperature (from RT- 5 K,) the field cooled (FC) magnetization is obtained. Here, the transition temperature is defined as the temperature at which the Zero Field Cooled (ZFC) and Field Cooled curves (FC) get bisected. From the figure 6, it has been concluded that on increasing the temperature, initially the value of ZFC magnetization increases, reaches its maximum and then decreases at blocking temperature (T_B) which is defined as the temperature at which the nano-particle moment gets blocked (do not relax). Below this T_B , the material shows the slow rate of relaxation of magnetization. These spins can flip only above this Blocking temperature (T_B). The Zero Field Cooled (ZFC) magnetization coincides with the Field Cooled (FC) magnetization at this point. The magnetic moment (M) vs. temperature (T) curves of Dy doped BPFT and Tb doped BPFT samples under the ZFC and FC has been presented which shows a systematic change under specific conditions. The high value of magnetization at the low temperature range strongly infers that there is presence of uncompensated anti-ferromagnetic spins (Fe^{3+}). As shown in **Fig. 7**, initially the value of saturated magnetization decreases with an increase in temperature and then increases. This behaviour is attributing the presence of either some paramagnetic spins that are not depending upon the anti-ferromagnetic ordering or uncompensated magnetic spins, which results in superparamagnetic ordering as in case of anti-ferromagnetic domains [24, 31, 32]. In this phenomenon, the magnetic materials showing the properties similar to that of paramagnetism even when the temperatures are below the Curie temperature or the Neel temperature. The phenomenon, where the energy required to change the direction of the magnetic moment of a particle is comparable to the ambient thermal energy, is a small length-scale phenomenon. The rate at

which the particles randomly reverse their direction becomes significant at this point. The anomalous magnetization could be affected by the fluctuation of Fe valance ions that goes from 3^+ to 2^+ . The variation of M–T curves with doping composition might be due to the reduction in particle size, doping at A and B sites, variation in the oxygen stoichiometry and due to the change in the magnetic anisotropy[33].

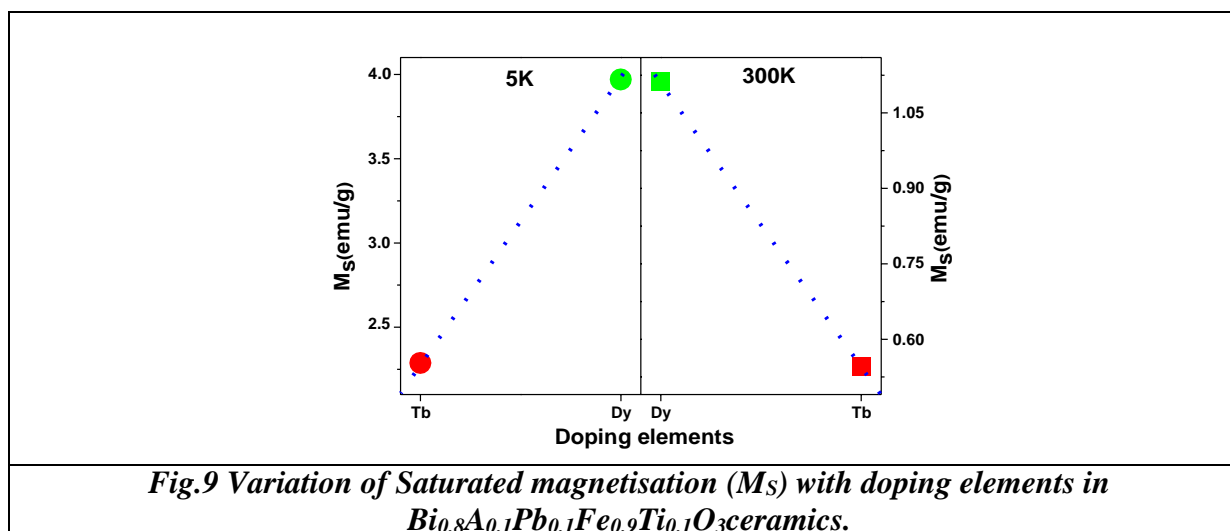


This set of magnetization curves known as M–H hysteresis curves of ferromagnetic material measured at temperatures 5 K and 300 K is shown in **Fig. 8**. The Magnetic-Hysteresis loops depicts that the magnetization curves of the loop at low field are not collinear hence the sample is a weak ferromagnetic material. **Fig. 8** confirms the ferromagnetic nature of samples as there is nonzero remnant magnetization and coercivity as shown in the partly enlarged curves. In these samples, an increment of magnetization is observed which is always ascribed because of the incomplete rotation of the spins along the direction of the wave vector i.e. size effects of the suppression of helical order hence contribute for increase in spin canting due to surface strain and oxygen defects[34, 35]. The net magnetization will be enhanced by the uncompensated spins and this cycloid spin structure could be suppressed, the canting of

spin due to surface strain as well[36]. On the other hand, magnetization could be increased by oxygen defects as they introduce Fe^{2+} into the ferromagnetic order across $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{2+}$ [34, 37]. During the high temperature annealing process, the canting angles in samples were modulated because of the interaction between the external magnetic field and the uncompensated spins in the canted anti-ferromagnetic order. This modulation of canting angles is assumed to be one of the causes for the increase in net magnetization of the sample.



The effect of doping on saturated magnetization is given in **Fig. 9**. Both magnetic hysteresis loops are measured at temperature range of 5 K and 300 K which shows that value of saturated magnetization is higher for Dy doped BPFT than that of Tb doped BPFT.



4. Conclusion:

Solid solutions of $(Bi_{0.8}A_{0.1}Pb_{0.1}Fe_{0.9}Ti_{0.1}O_3)$ ($A = Dy$ and Tb) confirms the hexagonal structure at room temperature. The dielectric constant measured at frequency = 10 kHz shows Ferroelectric–Paraelectric phase transition at temperature 150–350 °C. It is observed in paraelectric phase only above Blocking temperature (T_B) i.e. at temperature much higher than T_m . AC conductivity of the material increases with rise in temperature, confirming the Negative Temperature Coefficient of Resistance (NTCR) behaviour of material. The transformation of paramagnetism into relatively weak anti ferromagnetism in $(Bi_{0.8}A_{0.1}Pb_{0.1}Fe_{0.9}Ti_{0.1}O_3)$ ($A = Dy$ and Tb) ceramics due to the influence of the uncompensated anti-ferromagnetic spin. For all these samples, the minor loop traced indicates very weak ferromagnetism associated with anti-ferromagnetic nature.

5. Conflict of Interest

Authors declare no conflict of interest.

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