Dielectric, electrical conduction and magnetic properties of multiferroic $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ perovskite compound

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This work focuses on the structural, electrical and magnetic properties of $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramics, fabricated by solid state reaction procedure. XRD forms of the samples at RT exhibited perovskite phase through the hexagonal structure at room temperature. Dielectric studies of the materials with frequency at different temperatures (25–400°C) exhibit two dielectric anomalies, first at 175°C (ferroelectric–ferroelectric transition) and second at around 320°C (ferroelectric–paraelectric transition). The Curie temperature moved towards the low side temperature with the increase in frequency. The less value of activation energy got for these samples could be attributed to the influence of electronic contribution to the conductivity. A significant change in the magnetic studies was observed for $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramic. The impedance analysis confirms the non-Debye type nature of the ceramic and relaxation frequency moved to a higher temperature. The Nyquist plot and conductivity studies showed the NTCR behavior of samples. The highest magnetization field was found at temperature –268.15°C.

Keywords: Lead-free ceramics; X-ray diffraction (XRD); phase transitions; electrical conduction; magnetic properties; multiferroics.

1. Introduction

From a technical point of view, the joint control of electric and magnetic properties is an attractive possibility for recent research.¹ This offers potential applications for new devices of magnetic storage as well as ferroelectric devices.^{2,3} The perovskite materials offer the vast spectrum of electrical properties covering ferromagnetic-(anti-) ferromagnetic, ferroelectric–antiferroelectric, metallic, and semiconductors. Hence, the combination of these perovskite materials opens various routes for achieving the multiferroism in one phase material. Recently, several researchers reported multiferroic perovskite ceramics such as antiferromagnetic–ferroelectric and antiferromagnetic/weak ferromagnetic–ferroelectric systems.^{4,5} As a typical ferroelectromagnetic material, BiFeO_3 (BFO) is the most useful one from the practical application point of view owing to its high Curie ($T_C = 1103$ K) and Neel ($T_N = 643$ K) transition temperatures, and therefore it has involved a great deal of research interest.⁶ Because of the canting of the Fe sublattice moment, BiFeO_3 shows a weak

magnetic moment at room temperature.⁷ The spontaneous magnetic moment was absent in pure BiFeO_3 up to 8 kOe due to the entirely compensated antiferromagnetic ordering.⁸ Preparation of pure BiFeO_3 in the bulk ceramic has been a very difficult task.

$\text{BiFeO}_3\text{-ABO}_3$ systems have attracted great attention as a means to rise structural stability and sinterability.^{9,10} Processing of BiFeO_3 with other perovskite structured materials, such as BaTiO_3 , would prevent the formation of secondary phases^{11,12} and have excellent ferroelectric properties ($T_C = 120^\circ\text{C}$). The overall magnetic behaviors of bulk ReFeO_3 are defined as the result of two contributing magnetic “sublattices”: (i) an antiferromagnetic oxide lattice in which the spins are coupled via a $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ super exchange mechanism; and (ii) a paramagnetic influence from non-coupled ions. Due to spin-canting in the iron containing sub lattice, a minor ferromagnetic moment is detected as a result of the distorted perovskite structure in one particular crystallographic direction.¹³ Terbium ions (Tb^{3+}) possess large atomic weight, smaller size (Radius $\text{Tb}^{3+} = 0.923$ Å) as

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compared to Bi^{3+} Ions (Radius $\text{Bi}^{3+} = 1.032 \text{ \AA}$), and have comparable electronegativity with respect to Bi^{3+} ions, make Tb^{3+} ions the most suitable dopant.^{14–16} Therefore, the big structural distortions would be expected by their substitutions in BiFeO_3 . Furthermore, Tb^{3+} ions possess large magnetic moment; upon their doping, the spiral modulated spin structure of BiFeO_3 could be partially destroyed and the spatial homogenization of spin arrangements could be realized.^{17,18} This results in the improvement of the multiferroic properties of the BiFeO_3 , which is the motivation for the present study.

In the present study, the crystal structure, dielectric and magnetic behavior of the perovskite $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ system have been carried out to examine the ceramic system. This system is a combination of three ternary perovskites (two Ferromagnetic + one Ferroelectric). Electrical properties have been carried out by using complex impedance spectroscopy (CIS) and modulus spectroscopy method,¹⁹ which is a very suitable tool to correlate the structural/microstructural and electrical properties with a polycrystalline ceramics.

2. Experimental Detail

Polycrystalline samples of $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ (BTBFT) were synthesized from high purity oxides, i.e., Bi_2O_3 (99.9%, Aldrich chemicals USA), Fe_2O_3 (99.9%, Aldrich Chemicals, USA), Tb_4O_7 (99.9%, Aldrich Chemicals, USA), BaCO_3 (99.9%, Aldrich Chemicals, USA) and TiO_2 (99.9%, Aldrich Chemicals, USA), by solid-state reaction technique. The constituent compounds in proper stoichiometry were systematically mixed in a ball milling unit for 42 h. The powder was dried at 125°C and calcined at 900°C for 4 h in alumina crucibles. The calcined fine powder was pressed into pellets of 10 mm in diameter and 1.5 mm in thickness using a hydraulic press with a pressure of 50 MPa. These pellets were sintered at a temperature of 1000°C for 3 h. The creation and quality of materials were verified with X-ray diffraction (XRD) process. The XRD of the samples were noted at room temperature using X-ray powder diffractometer (Rigaku Miniflex, Japan) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) in a wide range of Bragg angles 2θ ($20^\circ \leq 2\theta \leq 60^\circ$) at a scanning rate of 2° min^{-1} . Scanning electron micrographs (SEM) of the fractured surface of the specimen was obtained with a JEM-2000FX (JEOL Ltd.) scanning electron microscope worked at 25 kV. The flat polished surfaces of the sintered compound were electroded through the air drying silver paste. Dielectric and impedance properties were determined by the use of PSM1734 Impedance Analyzer in a frequency range from 100 Hz to 1 MHz and samples were heated from room temperature to 400°C . The magnetic data were noted using vibrating sample magnetometer (VSM) (Cryogenic).

3. Results and Discussion

Figures 1(a) and 1(b) show XRD patterns and SEM of the surface of the BTBFT ceramics. The XRD patterns of

$\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramics at room temperature are shown in Fig. 1(a). All patterns match with JCPDS#712494 data and show that the samples have mixed phase with a hexagonal structure at room temperature. All reflection peaks were indexed using observed inter-planar spacing⁷ and lattice parameters of BTBFT by JCPDS database. The higher peak of the compounds are located at approximately $2\theta = 31.84^\circ$, having hkl values $\langle 111 \rangle$ and $\langle 020 \rangle$. Because of the kinetics of formation, another impurity phases are obtained during synthesis. An impurity phase was observed in XRD pattern (shown as * in Fig. 1(a)) and it may be attributed to BaFe_2O_4 (JCPDS#772337). SEM image of the sintered BTBFT ceramic is shown in Fig. 1(b). From the sintered ceramic surface (as-fired), homogeneous grains of various sizes can be clearly seen. All the grains are nearly spherical in shape and their connectivity with neighboring grains suggests grain growth by diffusion. It is seen that the BTBFT with no observable mechanical defects, giving rise to dense, homogeneous, and fine-grained ceramics. The average grain sizes of the ceramic are in the range of $0.5\text{--}12 \mu\text{m}$. Figure 1(c) shows the number of a particle with different particle ranges and it is clear that a maximum number of particle is in the range of 0.5 to $1 \mu\text{m}$.

Figure 2 shows the variation of ε with the temperature at frequencies 1–100 kHz for BTBFT. The observed peaks in the dielectric constant can be correlated to the two phase transitions from Ferro to Ferro (T^1) and ferroelectric to paraelectric (T^2) at temperatures 175°C and 320°C , respectively.²⁰ These two peaks are due to three different types of ferroelectric compounds present in the system.²¹ These two peaks are due to different phase transitions of BiFeO_3 and BaTiO_3 and the dielectric peak is shifted towards the low-temperature side on the increasing frequency. It is due to the occurrence of electromagnetism effect in the $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ material. In the case of $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$, a second peak observed near 315°C that may be related to the magnetic transition in the BiFeO_3 materials. These type of two peaks has been observed in samples due to the high percentage of dopant ion ($>5\%$).^{20–24} With the increase in temperature, the dielectric constant rises up to 170°C and then decreases up to 235°C . After 235°C , dielectric constant increases again up to 320°C . The two maximum values of dielectric constant ($\varepsilon_{\text{max}}^1$ and $\varepsilon_{\text{max}}^2$) with two transition temperatures at different frequencies (1–100 kHz) are shown in Table 1.

Figure 3 shows the variation of $\log \sigma_{\text{ac}}$ (s/m) versus $1/T$ (K^{-1}) of BTBFT ceramics at 1–100 kHz frequencies in the temperature range from 325°C to 345°C . The ac electrical conductivity was obtained from the impedance data using the formula $\sigma = \omega \varepsilon \varepsilon_0 \tan \delta$, (where ε_0 is the vacuum dielectric constant, ω is the angular frequency and k_B is the Boltzmann constant). The value of activation energy was calculated in the paraelectric region from the plot of $\ln(\sigma_{\text{ac}})$ versus $1/T$ using the conductivity relation $\sigma = \sigma_0 \exp(-E_a/k_B T)$ ^{25,26} as shown in Table 1. It is observed that σ_{ac} increases with increasing temperature confirming the NTCR behavior. At high

Fig. 1. (a) XRD patterns of sintered Bi_{0.8}Tb_{0.1}Ba_{0.1}Fe_{0.9}Ti_{0.1}O₃ ceramics, (b) SEM micrographs of sintered surface of Bi_{0.8}Tb_{0.1}Ba_{0.1}Fe_{0.9}Ti_{0.1}O₃ ceramics and (c) range of different particles size with number of particles of Bi_{0.8}Tb_{0.1}Ba_{0.1}Fe_{0.9}Ti_{0.1}O₃ ceramics.

Fig. 2. Variation of dielectric constant (ϵ) as function of temperature of Bi_{0.8}Tb_{0.1}Ba_{0.1}Fe_{0.9}Ti_{0.1}O₃ ceramics at different frequencies (1–100 kHz).

Table 1. Details of the physical parameters of Bi_{0.8}Tb_{0.1}Ba_{0.1}Fe_{0.9}Ti_{0.1}O₃ ceramics.

Composition	Freq.	T^1 (°C)	$\epsilon_{\max}^1$	T^2 (°C)	$\epsilon_{\max}^2$	E_a (eV)
Bi _{0.8} Tb _{0.1} Ba _{0.1} Fe _{0.9} Ti _{0.1} O ₃	1 kHz	175	7298	315	2338	1.46
	10 kHz	170	2101	320	920	1.37
	100 kHz	170	722	310	384.5	1.06

temperature, the donor cations have a major part in the conduction process and activated with small energy which is called activation energy. The activation energy at different frequencies was found to be low in the paraelectric region. The inset graph of Fig. 3 gives the activation energy with different frequencies of ceramic. This may be due to ionic solids having a narrow number of mobile ions being trapped

Fig. 3. Variation of AC conductivity ($\ln \sigma_{ac}$) as a function of absolute temperature ($1/T$) for $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramics at different frequencies (1–100 kHz).

in relatively stable potential wells during their motion over the solid. Because of the increase in temperature, the donor cations are taking a major part in the conduction process. The donors have produced a level (i.e., band-donor level), which is much closer to the conduction band. So, only a less amount of energy is essential to activate the donors. Furthermore, a slight alteration in stoichiometry in multi-metal complex oxides, a large number of donors or acceptors ions can be formed, which makes donor or acceptors like conditions in the vicinity of conduction or valence bands. These acceptors or donors may also be activated with less energy.²⁷

The electrical properties of BTBFT ceramics were studied by the CIS method. It is essential to alter the dielectric and electrical data in different kinds of formalism and evaluate them to get a true picture of the material. The use of function Z'' is mostly suitable for the resistive and/or conductive examination of the samples where the long-range conduction dominates, while the ϵ^* and M^* functions are appropriate after localized relaxation dominates. Therefore, the plotting of data in terms of impedance and electric modulus gives a complete assignment of the physical processes taking place in the material. The variation of real (Z') and imaginary (Z'') part of impedance with frequency at various temperatures (from 225°C to 325°C) for BTBFT ceramics is shown in Figs. 4(a) and 4(b). The pattern shows a sigmoid variation as a function of frequency in the low-frequency area followed by a saturation area in the high-frequency area. This recommends the existence of mixed nature of polarization behavior in the material, as electronic, dipolar and orientation polarization. A reducing trend of Z' with the rise in temperature recommends the presence of negative temperature coefficient of resistance in the samples in the low-frequency area but then again tends to merge in the high-frequency area at all temperatures. This rise in ac conduction with temperature may be due to the contribution of defects similar to oxygen

(a)

(b)

Fig. 4. (a) and (b) Variation of real (Z') and imaginary (Z'') part of impedance with frequency at different temperatures of $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramics.

vacancies. Generally, the contribution due to oxygen vacancies is extra prominent in perovskite structures at higher temperatures. Therefore, these results indicate an increase in ac conductivity with increase in temperature due to the release of space charge and reducing in the barrier properties of the material.

With the rise of frequency, the imaginary part of impedance (Z'') increases initially, attains a peak (Z''_{max}) and then decreases with frequency at all measured temperatures as shown in Fig. 4(b). At higher frequency side, all the curves are merged because of the decrease in space charge polarization with the rise in frequency. The peak shifts near to higher frequency side with increasing temperature causing

Fig. 5. (a) and (b) Variation of real and imaginary part (Z' and Z'') of impedance and (b) Fitted graph of real and imaginary part (Z' and Z'') of impedance with different temperatures of $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramics.

the resistance of the bulk material to reduce. Also, the magnitude of Z'' decreases with increasing temperature. This implies that dielectric relaxation is temperature-dependent.

Figure 5(a) shows the temperature-dependent spectra (Nyquist plot) (semi-circular arcs) of BTBFT ceramics. As the temperature increased, the slope decreased and was set up to curve towards the major (Z') axis forming semicircular arcs. The radius of curvature was obtained to decrease with rising in temperature, which shows the increase in conductivity of the sample with temperature. Normally, the existence of semicircle arcs depends upon the power of the relaxation and experimentally existing frequency range. In the Nyquist plots, the intercept to semi-circular arc on real axis (Z') provides the value of bulk resistance (R_b) of the materials which found to decrease with rising in temperature. In the present case, two semicircle arcs are observed at 250°C, 275°C and 300°C which shows two contributions, i.e., bulk and grain boundary effects.²⁸ But at 325°C, a single semicircular arc observed which signifies only one influence, e.g., bulk property of the material. Generally, the relaxation time for grain boundary area is much larger than that of the grains and, then, its response relaxes at low frequencies. Thus, the low-frequency arc in the Nyquist plot links to the grain boundary properties and the high-frequency arc to the grain/bulk effect of the sample. This electrical behavior can be signified in terms of an equivalent circuit or the fitting of the Nyquist plot for BTBFT ceramics by using commercially available software ZSimp WIN Version 2 is shown in Fig. 5(b). It is observed that with the rise in temperature, the slope of the lines decrease and the lines bend towards real (Z') axis and at higher temperatures (250°C, 275°C, 300°C and

325°C); a semicircle could be traced, showing the rise in conductivity of the sample. It also shows that the peak maxima of the plots reduce and the frequency for the maximum moves towards higher values with the rise in temperature. This may be because of the presence of distributed elements in the sample electrode system.^{19,29} The bulk resistance of the material reduces with the rise in temperature representing a typical semiconducting property, i.e., negative temperature coefficient of resistance behavior. An equivalent circuit is being used to provide a whole picture of the sample and establish the structural property relationship of the materials. Here, it has also been observed from the Nyquist plots that the effect of grain size on the inter grain resistivity rises with decreasing grain size. In the fitting of the Nyquist plot for the semicircular arc with the real axis (Z') providing us an estimate of the bulk resistance (R_b) for higher temperature is given in Table 2.

Figure 6(a) shows the variation of real part of the electric modulus (M') with frequency towards higher temperatures between 250°C and 325°C for BTBFT ceramics. It is studied by a low value of M' in the low-frequency area by a continuous

Table 2. Resistance of bulk and grain boundaries of $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramics after Nyquist plot fitting.

Composition	T (°C)	R_g (ohm-cm ²)	R_{gb} (ohm-cm ²)	CPE (Q)
$\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$	250	234	81350	2.041E-8
	275	1.416E-4	25180	1E-5
	300	2.29E-5	89.91	1.596E-8
	325	1.025E-7	0	2.126E-7

Fig. 6. (a) and (b) Variation of real (M') and imaginary (M'') part of modulus with frequency at different temperatures of $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramics.

dispersion with the rise in frequency. It was observed that M' values saturated to a maximum (M_∞ — the asymptotic value of M' at higher frequencies) in the high-frequency area for all temperatures. The asymmetric plot of M' is due to the stretched exponential nature of relaxation time of the compound. Monotonous dispersion on rising frequency at lower temperatures may be due to the reason of short range mobility of charge carriers. These results may be probably related to a lack of restoring force leading the movement of the charge carriers below the action of an induced electric field. M' decreases with rising in temperature in the observed frequency range.

Figure 6(b) shows the variation of imaginary part of the electric modulus (M'') with frequency at higher temperatures for BTBFT ceramics. By these graphs, we found that the position of the peak M''_{max} shifted to higher frequencies as the temperature was increased. Actually, the peak in the imaginary part of the electric modulus describes the regions where the carrier can transfer at long distances. The carriers are confined to potential wells and being mobile on short distances at a frequency above peak maximum. The peaks are asymmetric and broader than the ideal Debye curve. Also, a peak in the M'' imaginary part shows a dielectric relaxation process in the solid, and the frequency to the maximum shows the mean relaxation time of this method. As can be seen, the imaginary part of the electric modulus shows a very well defined peak. The frequency range where the peaks rise is symbolic of transition from long range to short range mobility.^{30,31} Two peaks in graph confirm the coexistence of two systems.²⁰ The complex electric modulus spectrum M' versus M'' for the sample is shown in Fig. 7. Two arcs are observed at different temperature ranges (225°C, 250°C and 275°C) in our samples. The first arc is due to the contribution

of grain while the second arc is due to the contribution of grains.³² The patterns are studied by the presence of little asymmetric and depressed semicircular arcs, the center does not lie on M' axis.

The behavior of electric modulus spectrum is expressive of the temperature-dependent hopping type of mechanism on behalf of electric conduction (charge transport) in the sample and non-Debye type behavior of dielectric relaxation. In relaxation system, one can determine the possible relaxation time (τ) from the position of the loss peak in the Z'' as well as M'' versus $\log f$ plots according to the relation: $\tau = 1/\omega = 1/2\pi f$ (f is the relaxation frequency). We found double semi circular arcs in the complex modulus plots, a small semicircle at the high-frequency area and a large semi-circular arc at the

Fig. 7. Variation of real (M') and imaginary part (M'') of modulus with different temperatures of $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramics.

Fig. 8. Scaling behavior of (a) ($Z''/Z''_{\max}$) and (b) ($M''/M''_{\max}$) versus $\log(f/f_{\max})$ of $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramics.

low-frequency region. The modulus spectrum shows a marked variation in the shape with the rise in temperature signifying a possible change in the capacitance value as a function of temperature. Figures 8(a) and 8(b) shows the scaling nature of the sample was studied by plotting the normalized plot of $M''/M''_{\max}$ and $Z''/Z''_{\max}$ as a function of the normalized frequency at different kind of temperatures for BTBFT ceramics. The normalized plot joins on a single master curve at different temperatures. The modulus scaling behavior shows an insight into the dielectric processes occurring inside the material.^{33,34} The value of FWHM calculated by the normalized spectrum is greater than $\log \frac{2+\sqrt{3}}{2-\sqrt{3}}$, and this indicates about behavior of non-Debye type which is well supported by complex impedance plot. The peaks shift and broadening were found at higher frequencies with increasing temperature. The presence of temperature-dependent peaks ($Z''_{\max}$ and $M''_{\max}$) at frequency ($\omega_{\max} = 2\pi f_{\max}$) shows the presence of relaxation process, which is temperature-independent.³⁵ These relaxation processes may be due to the existence of defects which became mobile at high temperature and immobile species at low-temperature.

The magnetic moment with a temperature between -268.15°C and 26.85°C in zero-field cooled (ZFC) and field cooled (FC) conditions through an applied magnetic field of 0.1 T is given in Fig. 9. The magnetic moment (M) versus temperature (T) curves of BTBFT sample under the ZFC and FC conditions exist a systematic change. The magnetization value at the low-temperature suggests the existence of uncompensated anti-ferromagnetic spins (Fe^{3+}).³⁶ Initially, magnetization reduces with the rise in temperature and then increases as shown in Fig. 9. As temperature goes down further from 26.85°C to -268.15°C , the magnetization rises rapidly, checking that there is a magnetic phase transition. The magnetic phase transition is proposed to be a change of iron (Fe) sublattice from anti-ferromagnetic to antiferromagnetic

at low-temperature.³⁷ The variation of $M-T$ curves with BTBFT sample may be attributed to different factors like (i) variation in the oxygen stoichiometric and doping at A and B sites, (ii) decrease in particle size and (iii) change in the magnetic anisotropy.³⁸ The saturation of magnetization is not reached for all samples with an applied magnetic field up to 10 T .

Figure 10 shows the magnetic hysteresis loops measured at -268.15°C , -263.15°C , -123.15°C and 26.85°C . The magnetization curves of the $M-H$ loop at low magnetic field are not collinear and this shows a weak ferromagnetic nature of samples, which could be further examined by the nonzero remnant magnetization and coercivity as shown in the partially enlarged curves in the inset of Fig. 10. The more magnetization, coercive field, and $M-H$ loop area were found

Fig. 9. Variation of magnetic moment with temperature of $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramics for FC and ZFC.

Fig. 10. M-H loops of $\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramics at (a) -268.15°C , -263.15°C and (b) -123.15°C , 26.85°C .

for 268.15°C compared to -263.15°C , -123.15°C and 26.85°C . The enhancement of magnetization in this ceramic is always recognized to the size effects of the suppression of helical order,³⁹ i.e., incomplete rotation of the spins along with the direction of the wave vector, growing in spin canting because of surface strain and oxygen defects. On the other hand, oxygen defects could also increase the magnetization by introducing Fe^{2+} into the ferromagnetic order across $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{2+}$.⁴⁰ Furthermore, during the high-temperature annealing process, the canting angles in samples were further⁴¹ modified by the interaction between the external magnetic field and the uncompensated spins in the canted antiferromagnetic order, which may be the main reason causing the net magnetization to increase.

4. Conclusions

$\text{Bi}_{0.8}\text{Tb}_{0.1}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ (BTBFT) solid solution ceramic was prepared using solid state reaction method. Studies of temperature-dependent dielectric properties of a sample exhibit two dielectric anomalies one at 175°C and another about 320°C . At higher temperatures, the detected double semi-circles in electric modulus plots check about the creation of samples in single phase and show the presence of both bulk and grain boundary contributions. Impedance analysis shows the most bulk (grain) resistive contribution in the samples at high temperatures whereas complex modulus plots indicate the existence of grains as well as grain boundary influences in

the materials. Both impedance and modulus analysis indicate the behavior of negative temperature coefficient of resistance (NTCR) of the samples. They also check the existence of a non-Debye type of relaxation phenomenon in the samples. In the case of magnetization, the coercive field was found to be decreased with temperature -268.15°C , -263.15°C , -123.15°C and 26.85°C . A minor loop traced for all these samples shows an antiferromagnetic behavior with weak ferromagnetism.

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