

Structural and electrical characteristics of La^{3+} and Ti^{4+} co-doped BiFeO_3

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(Received November 10, 2022, Accepted December 2, 2022)

Abstract: Ceramic materials are widely used as base material for composite film and high frequency resistor because of their better insulating behavior. So, a good and careful study of dielectric and conductivity parameters are required for ceramic material. Polycrystalline ceramic $(\text{Bi}_{0.9}\text{La}_{0.1})(\text{Fe}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (referred as BLaFTO-10 in this communication) was successfully synthesized by traditional solid state reaction method. Structural analysis done with XRD characterization, which confirms the single-phase formation of the compound at room temperature. Scanning electron microscopy is used to examine the morphological study which confirms the polycrystalline nature of the sample. EDX study confirms the formation of compound and presence of all element in the as prepared sample. In this paper focus is made on the study of dielectric measurement, conductivity and impedance analysis in a wide range of frequency (1 kHz to 1 MHz) and temperature ($25^\circ\text{C} - 500^\circ\text{C}$). Ac conductivity follows the universal Jonscher's power law. Dielectric spectrum reveals the high values of dielectric permittivity and low value of tangent loss. These interesting features could be utilized for electronic applications.

1. Introduction

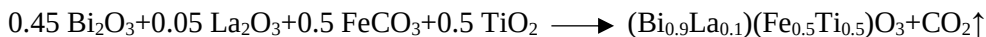
Bismuth ferrite (BiFeO_3 or BFO) is one of the most studied ceramic due to its promising result for device application. Bismuth ferrite shows crystal structure as distorted rhombohedral phase with $R3c$ space group. BFO exhibits perovskite like structure (*i.e.* ABX_3 like structure, A & B are cation with different sizes and X is anion, mostly oxygen is used). Along with excellent properties, BFO also has some drawback like high leakage current density with large amount of energy band gap of 2.8 eV^1 . High leakage current is associated with the oxygen vacancies, which is created by oxidation- reduction of ions for charge compensation^{2,3}. High leakage current

in BFO is present due to different defect in the crystal and also due to presence of some impurity phases (i.e., $\text{Bi}_{25}\text{FeO}_{40}$, Bi_2O_3 , Fe_2O_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ etc.)^{4,5,6}. In the step of reducing the leakage current problem in BFO, researchers are trying by doping or substituting various different ion at different site of BFO or fabricating BFO with other perovskite material^{7,8,9}.

Literature survey shows that, concentration of oxygen vacancies can be reduced by substitution with different atoms (i.e., Zr^{4+} , Sn^{4+} and Ti^{4+}) at Fe site of bismuth ferrite and this doping reduces the conductivity in the ceramic or thin film of BFO^{10,11}. It was reported by Cheng *et al*¹² that, $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ ceramic retain the rhombohedral structure up to $x=0.1$ and changes to orthorhombic structure for $x=0.2$ substitution. With the substitution of La^{3+} , leakage current can be reduced significantly^{13,14}. It was also found that with the doping of rare earth ion on BFO can reduce the impurity phase in BFO. The above discussion motivates for the doping of La^{3+} and Ti^{4+} ion at Bi and Fe site of BFO respectively. There is a lack of literatures on the dielectric and conductivity of lanthanum and titanium doped BFO with modified crystal symmetry. Hence, the aim for this communication is to study and report the structural and dielectric properties of $(\text{Bi}_{0.9}\text{La}_{0.1})(\text{Fe}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ceramic.

2. Method

The sample $(\text{Bi}_{0.9}\text{La}_{0.1})(\text{Fe}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [BLaFTO-10] was synthesized with the solid state reaction method. Starting materials used for synthesis are Bi_2O_3 , La_2O_3 , FeCO_3 and TiO_2 with high purity. Before mixing, stoichiometric amount of the reactant materials were weighed and after weighing, dry grinding was done with the help of agate mortar and pestle for 4 hrs. The reaction involved in the process of formation of BLaFTO-10 sample is:



Homogeneous mixture was obtained and then heat treatment was done. The mixed powder was calcined at 1050°C for 4 hours. Then, calcined powder was mixed with small amount of poly vinyl alcohol (PVA) which was used as a binder and make pallets with the help of KBr press while applying the pressure of $4 \times 10^6 \text{ Nm}^{-2}$ for 4 minutes. The dimensions of the pallet were 2.01 mm in thickness and 5.94 mm in radius. After palletization, pallet was sintered at 1080°C for 4 hours.

X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive XRD (EDX), dielectric and conductivity measurement were done for the sample. XRD pattern was recorded by Rigaku Powder X-ray diffractometer at room temperature. $\text{Cu-K}\alpha$ radiation was used as incident beam with wavelength 0.154nm and XRD pattern was recorded at wide range

of bragg's angle (20° to 80°). Morphological studies were done by scanning electron microscope and energy dispersive XRD at room temperature. Phase sensitive meter (PSM-1735, Newton4th Ltd, UK) with impedance analyzer was used in the measurement of dielectric and conductivity parameter with a wide range of frequency and temperature.

3. Results and Analysis

3.1. Structural analysis

Structural analysis of the sample BLaFTO-10 was done with XRD analysis. XRD pattern of the tested sample was recorded at room temperature by Rigaku powder X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda=0.154 \text{ nm}$). Fig.1 shows the XRD pattern of the sample BLaFTO-10. Analysis of the obtained XRD data was done with "POWDMULT" Software¹⁵ in which data is fitted according to least standard deviation. Sharp peaks in the pattern suggest that sample has good crystalline nature. Based on best agreement between observed and calculated interplanar distance data, suitable unit cell for the compound was confirmed as monoclinic phase with the lattice parameters: $a=4.0981 \text{ \AA}$, $b=21.3207 \text{ \AA}$, $c=16.4901 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 94.308^\circ$. All peaks from XRD pattern are indexed with the help of "POWDMULT" software.

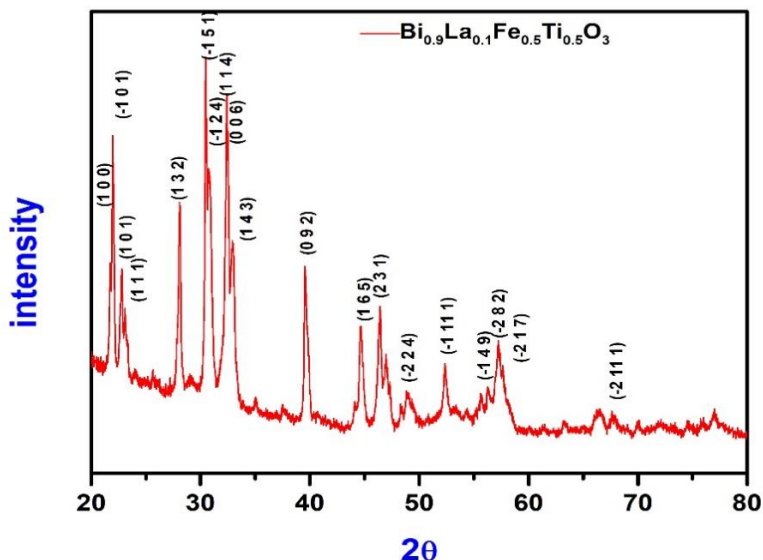


Figure 1: XRD pattern of BLaFTO-10 sample recorded at room temperature

3.2. Morphological analysis

For microstructural and morphological study, scanning electron microscopy is used. Figure 2 shows the SEM image of the sintered sample BLaFTO-10, and the SEM was recorded at room temperature. The image shows the grains are formed and are of same dimension but with different shape and size.

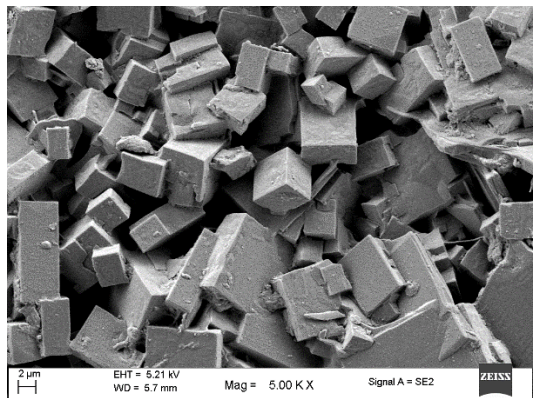


Figure 2: microstructural image of BLaFTO-10 sample by FE-SEM

Presence of uneven size of grains of microstructure confirms the polycrystalline nature of the sample. With the grains, few voids with irregular sizes are also present in the SEM image, which can be due to the oxygen vacancy, evaporation of carbon dioxide. Many important features like conductivity, dielectric nature, toughness, yield strength etc. are directly related to the microstructure of the sample. Figure 3. is the energy dispersive XRD (EDX) pattern of the tested sample, which shows the presence of all component (*i.e.* Bi, La, Fe, Ti, O) with presence of no foreign element in the sample.

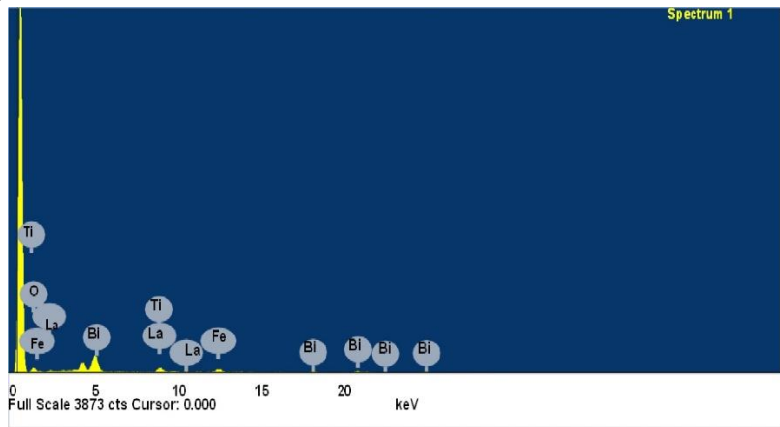


Figure 3: EDX pattern of Sample BLaFTO-10

Formation of required compound has been confirmed by compositional analysis from EDX. Atomic percentage also confirms the formation of compound which is given in Table 1.

Table 1: compositional Element with atomic percentage present in the sample BLaFTO-10

Element	Atomic percentage
Bi	10.53
La	2.79
Fe	8.40
Ti	8.17
O	70.11
Total	100.00

3.3. Effect of variation of Frequency and Temperature on Dielectric property

There are two important basic parameters of dielectric analysis are used in dielectric measurement. One is dielectric constant and other is dielectric tangent loss¹⁶. The first one, dielectric constant is used to measure the how much amount of energy can be stored and tangent loss talks about energy loss in the material. In this analysis part we will discuss the variation of dielectric constant and dielectric loss with respect to frequency and temperature. Dielectric measurement has been done in wide range of frequency (1kHz-1MHz). Fig.4 (a) represent the tangent loss of the material BLaFTO-10 with respect to varying frequency at few selected temperatures. From figure 4(a), it can be seen that in lower frequency region, $\tan\delta$ shows higher values as compared to higher frequency region. In lower frequency region, value of $\tan\delta$ is higher for high temperatures. As in low frequency region, grain boundary effect is more as compare to grain effect. Mostly grain effect occur at high frequency region. Conduction at grain boundary require high energy as they possess high resistance¹⁷, that is the reason behind high energy loss at low frequency region. Representation of dielectric constant with varying frequency is shown in Fig. 4(b). Dielectric constant of a dielectric material can be expressed as $\epsilon_r = Cd/\epsilon_0 A$, where C is the capacitance of the material, d represents the thickness, ϵ_0 is the absolute permittivity and A is the cross-sectional area of the sample. From fig. 4(b) it can be state that, dielectric constant decreases with increasing frequency. In lower frequency region dielectric constant depends on temperature and for higher temperature, dielectric constant is also high. There are various kind of dipolar polarization (i.e., ionic, orientational, electronic, etc.) acts at lower frequency region, that is the reason behind high dielectric constant. As the frequency increases,

contribution from electronic polarization remains only, and dielectric constant become temperature independent.

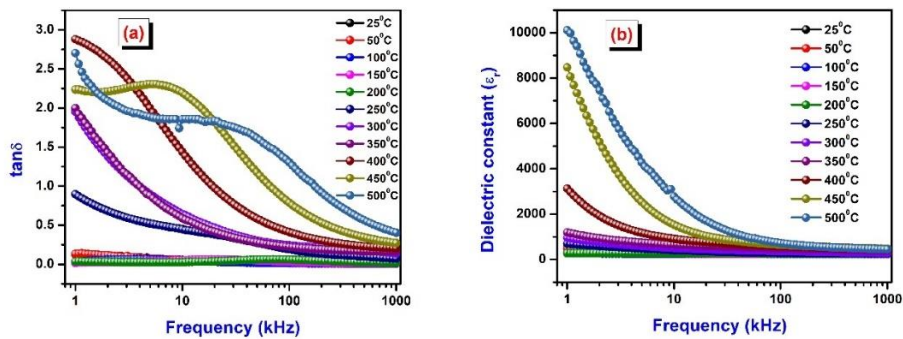


Figure 4: (a) dielectric loss (b) dielectric constant variation with frequency for BLAFTO-10 sample

In another way dielectric measurement were recorded as function of temperature (25⁰C-500⁰C) at some selected frequencies (10, 50, 100, 500 and 1000 kHz). Fig. 5(a) shows tanδ variation with temperature. Rate of change of value of tanδ in lower temperature range is very small but as we move toward higher temperature region, tanδ variation is significant. For 10 kHz frequency, tanδ shows maximum value at around 430⁰C and the start decreasing, while for other frequency tanδ shows continuous increasing trend up to 500⁰C. presence of any defect and scattering of charge carrier due to increase in temperature could be the reason behind high value of dielectric loss (tanδ) at higher temperature region. Fig. 5(b) shows dielectric constant variation with respect to temperature. Dielectric constant also follows the same trend as tanδ. In low temperature, dielectric constant value is low and after 250⁰C dielectric constant increases gradually for all frequencies.

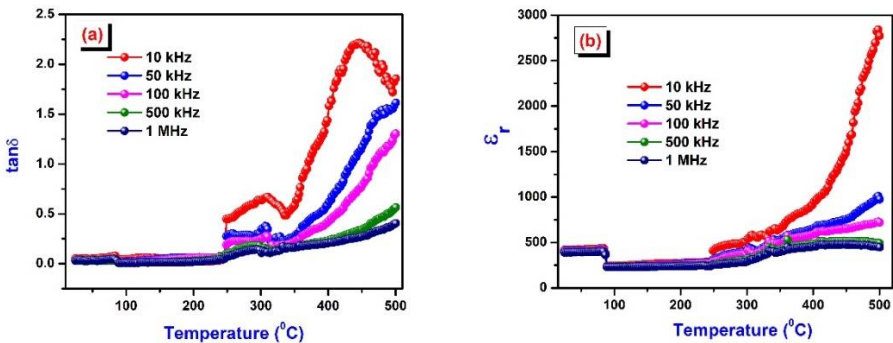


Figure 5: (a) dielectric loss (b) dielectric constant variation with temperature for BLAFTO-10 sample

As the temperature increases, agitation of the molecules also increases, thus the mobility of the polar molecules increases, which shows higher dielectric value of dielectric constant at higher temperature region. Variation in dielectric parameters is useful to find the phase transition in structure of the sample¹⁸. As for the this tested sample, phase transition point could not be achieved in the temperature range from 25⁰C to 500⁰C.

3.4. Impedance analysis with varying frequency -

Complex impedance analysis¹⁹ is widely used technique in Dielectric material as well as in ionic material. Impedance analysis talks about different process like, bulk and grain boundary effect, interface effect in frequency domain. With the help of impedance analysis microstructure of the dielectric material can be correlates with the electrical properties²⁰. Complex impedance is given by the formula-

$$Z^* = Z' + jZ''$$

where Z' is real and Z'' is imaginary component of impedance²¹.

$$Z' = \frac{R}{1+(\omega RC)^2} \quad \text{and} \quad Z'' = \frac{-\omega C R^2}{1+(\omega RC)^2}$$

Fig.6(a) is the representation of Z' with the varying frequency. This data has been collected with wide range of frequency from 1kHz-1MHz at different selected temperature ranging from 25-450⁰C. From graph it is seen that in lower frequency region dispersion in the values of Z' is clearly visible while as we go toward higher frequency region, all values of Z' seems to be merged together irrespective to different temperature. So, it can be concluded that Z' becomes temperature independent at higher frequency region from temperature dependent at lower frequency region²².

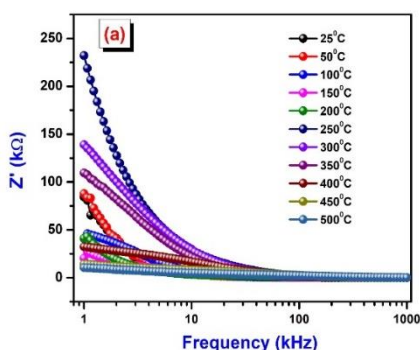


Figure 6(a): variation in real part of impedance with varying frequency

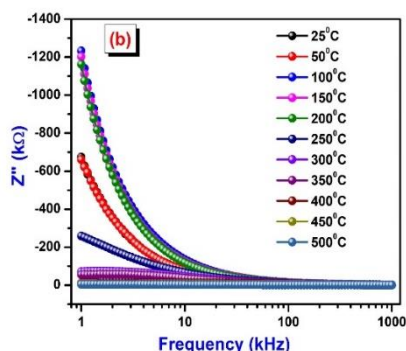


Figure 6(b): variation in imaginary part of impedance with frequency

Values of Z' are also decreasing with increment in temperature which shows that grains resistance is decreasing. So here, this sample BLaFTO-10 shows negative temperature coefficient of resistance (NTCR). In the initial stage of frequency or lower frequency region, reason behind decrease in Z' values with varying frequency could be the slow dynamic relaxation process which is may be present due to space charge which got released at higher frequency region and real component of Z' got decreased²³. Fig.6(b) shows the imaginary component of Z (i.e., Z'') with varying frequency. At different temperature Z'' shows different values at particular frequency. There are different maxima for Z'' for each different temperature. Peak position is also different for each temperature data which shows the variation in relaxation time in the tested sample. Different broadening size of peaks is the indication of presence of electrical phenomena with a spreading of relaxation time in the material.

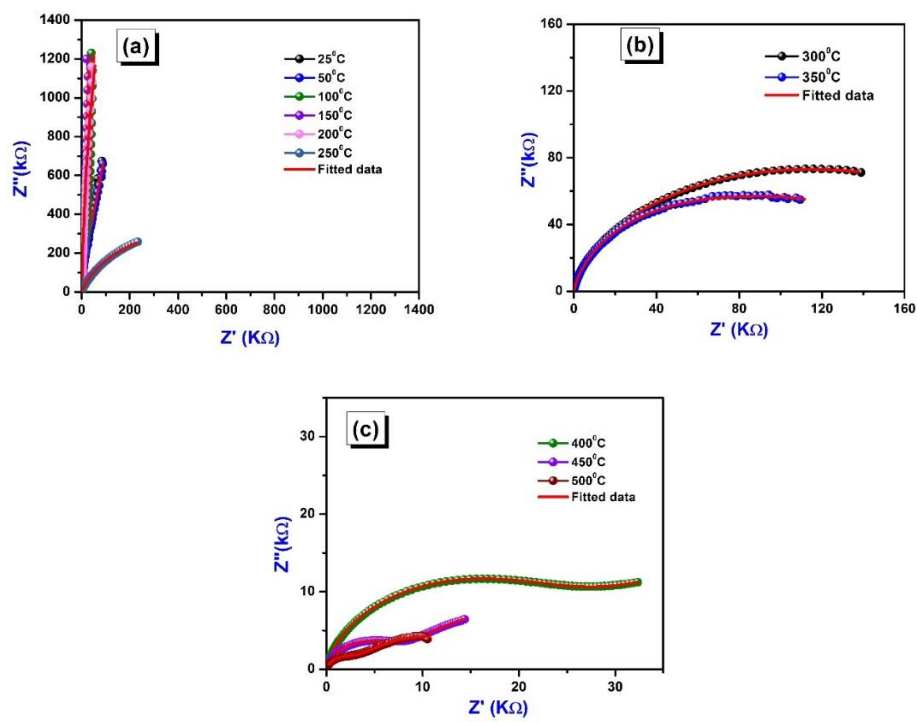


Figure 7 (a), (b) and (c) Nyquist plot for sample BLaFTO-10 at different temperature

Fig. 7 (a-c) is the representation of Nyquist plot at different temperature. The effect of different region like grain, grain boundary and electrode effect can be understood on the basis of Nyquist plot. Contribution of different region

and their resistive and insulating properties can normally be explained by an equivalent electronic circuit. Normally symmetric semi-circular arc (i.e., whose center lies on real axis), supports Debye type of relaxation. Asymmetric arc arises in the sample due to imperfection in the creation of sample or any defect present in the sample, and this type of arc represents the non-Debye type of relaxation. For our tested sample, from Nyquist plot it can be seen that non-Debye type relaxation is found in the sample. Table 2 shows the calculated values of capacitance, resistance and phase constant of grain and grain boundary.

Table 2: capacitance, resistance and phase constant value at grain and grain boundary for the sample BLaFTO-10

Temp (°C)	Model	C _G (F)	R _G (Ω)	Q _G	C _{GB} (F)	R _{GB} (Ω)	Q _{GB}
25	(CRQ)(CR)	1.711E-010	2.374E+007	1.625E-010	1.866E-009	5.097E+004	-
50	(CRQ)(CR)	1.054E-010	1.915E+007	1.981E-010	1.517E-009	6.694E+004	-
100	(CRQ)(CR)	1.152E-010	4.123E+015	3.662E-011	1.250E-009	2.942E+004	-
150	(CRQ)(CR)	6.120E-010	9.465E+003	3.218E-009	1.330E-010	6.138E+007	-
200	(CRQ)(CR)	7.747E-010	2.147E+010	3.186E-005	1.367E-010	2.726E+007	-
250	(CRQ)(CR)	1.254E-010	9.544E+005	6.462E-009	9.053E-010	6.267E+003	-
300	(CRQ)(CR)	1.566E-010	4.223E-008	2.757E+005	7.289E-010	3.892E+002	-
350	(CRQ)(CR)	9.734E-011	1.012E+005	1.901E-009	3.214E-009	6.267E+004	-
400	(CRQ)(CR Q)	7.180E-018	4.659E+004	2.865E-007	2.462E-010	2.740E+004	3.263E-008
450	(CRQ)(CR Q)	2.517E-010	7.731E+003	4.674E-008	7.175E-020	2.812E+004	3.181E-007
500	(CRQ)(CR Q)	2.675E-010	3.212E+003	3.959E-007	6.471E-022	1.506E+004	2.570E-007

3.5. Modulus analysis

Hodge highlighted that with impedance, modulus analysis will also give better information about different electro region of the material²⁴. With the combination of these two, impedance and modulus formalism, contribution of different active region toward the relaxation process can be determined²⁵.

Modulus analysis is used to study the rate of hopping of charge carrier and relaxation phenomena in the sample. Electric modulus in the sample can be expressed as^{26,27}

$$M = M' + M''$$

$$\text{where } M' = B \left[\frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \right] \quad \text{and} \quad M'' = B \left[\frac{\omega \tau}{1 + \omega^2 \tau^2} \right]$$

Fig. 8(a) shows the variation of M' (real component of modulus) and 8(b) is the representation of M'' (imaginary component of electric modulus). In M' versus frequency curve, M' tends to lower values at low frequency region for higher temperature, which represents the non-existence of electrode effect. As the frequency increases, M' also increases and try to saturate at higher frequency region. Conduction phenomena and short range of mobility of charge carrier can be reason behind this trend. This implies that there is a lack of restoring force of flow of charges under the influence of study electric field²⁴. For Fig. 8(b), there is a peak associated with each M'' data, that is known as $M''_{\max}$. As the temperature increases, these $M''_{\max}$ values shift to higher frequency side. This implies that there is hopping mechanism is taking place, which dominates for higher temperature. There is asymmetric broadening of peaks is also present in the sample which shows presence of various relaxation time constant. The spread of relaxation time constant in the sample shows the non-Debye type of nature²⁸.

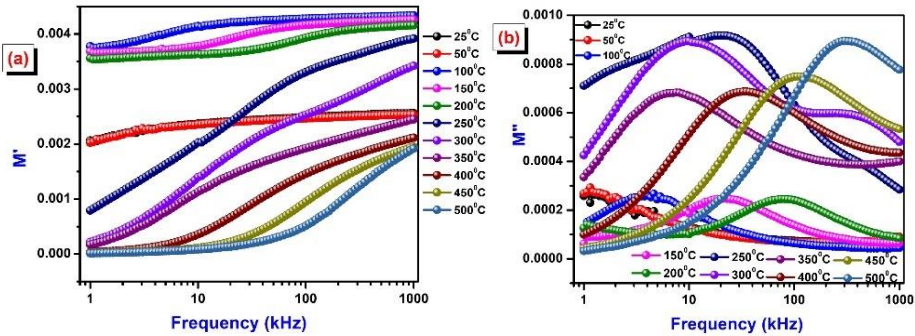


Figure 8: variation of electric modulus (a) real part (M'), (b) imaginary component (M'') of the sample BLAFTO-10 with changing frequency

3.6. Conduction of the sample with frequency

Ac conductivity analysis is used to provide information about hopping ion dynamics or electrical transport in the sample. Ac conductivity in a Dielectric material is determined by $\sigma_{ac} = \epsilon_0 \epsilon_r \omega \tan \delta$, where symbol has their usual meaning. Fig 9 illustrates the frequency dependent ac conductivity of the

sample BLaFTO-10 at some different selected temperature. Frequency dependent ac conductivity generally expressed by Jonscher's universal power law, that is given as²⁹

$$\sigma_{ac} = \sigma_{dc} + A\omega^n$$

Frequency dependent conductivity generally show a flat or constant ac conductivity in lower frequency region, which refers as dc part of conductivity, that is pure dispersive component of ac conductivity. As for higher frequency region, conductivity shows increasing nature with increasing frequency (*i.e.* $A\omega^n$). Here A is the temperature dependent constant, which represents strength of polarizability and n is the temperature dependent frequency exponent, which tells about conduction mechanism. The value of n lies between 0 and 1. Where 0 represents the random hopping and value approaches toward 1 shows the correlation between charge carrier increases. Figure 8 shows that ac conductivity increases with increasing frequency for most of the temperature and for some temperature like 300°C, 350°C and 400°C, ac conductivity remains constant in low frequency region and for higher frequency region ac conductivity depends on frequency and increases with increasing frequency. Frequency dependent ac conductivity plot try to merge at higher frequencies, which suggest the NTCR nature in the sample BLaFTO-10.

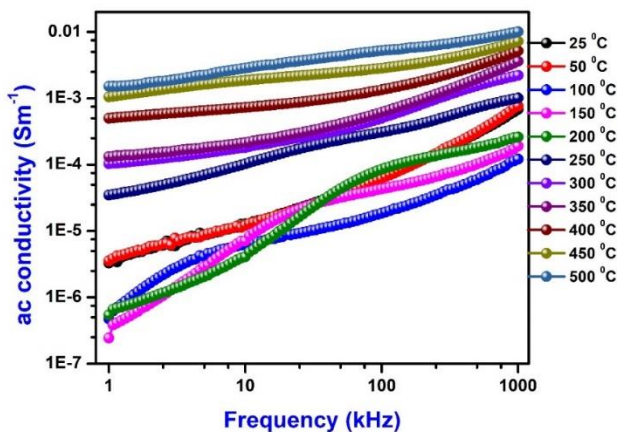


Figure 9: Ac conductivity of the sample BLaFTO-10 with the variation of frequency

4. Conclusion

(Bi_{0.9}La_{0.1})(Fe_{0.5}Ti_{0.5})O₃ ceramic is successfully synthesized with high temperature solid state reaction route. XRD pattern confirmed, single phase formation of the sample with monoclinic phase. Microstructural analysis was done with scanning electron microscope (SEM), which shows polycrystalline

nature of sample with different shape and size of grains. Frequency dependent ac conductivity follows Jonscher's power law. The Negative Temperature Coefficient of Resistance (NTCR) nature is also present in the as prepared sample. Further, electrical characteristics of the ceramic may be used to select the material for potential electronic applications.

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