

IMPEDANCE SPECTROSCOPIC STUDIES ON Zr-MODIFIED $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ CERAMICS

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Abstract

Zr- modified Lanthanum Bismuth Titanate, $\text{La}_{0.75}\text{Bi}_{3.25}\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$ (with $x=0, 0.1, 0.3, 0.5, 0.7$ and 1.0), ceramics were prepared by the solid-state reaction method. Impedance measurements were made as a function of frequency (100 Hz - 1 MHz), from RT to 550° C. Complex impedance analysis was used as a tool to analyze the electrical behavior of different micro-elemental regions. Cole-Cole plots showed depressed semicircles, which indicate non-Debye relaxation. Different micro-elemental values, namely grain resistance (R_g), grain boundary resistance (R_{gb}), electrode resistance (R_{el}) and their capacitance values were evaluated, by using Z-view software. The micro-elemental conductivity Vs Temperature plots showed the linear (Arrhenius) nature, and the activation energies were calculated. The multiple activation process, present in the title compound, was corroborated with the DC-conductivity data and our earlier ferroelectric (P vs. E) results.

Keywords: Impedance, Cole-Cole plots, Arrhenius behavior, Non-Debye.

1. INTRODUCTION

The crystal structure of Bismuth layer-structured ferroelectrics (BLSFs) consists with the bismuth oxide (Bi_2O_2)²⁺ layers and pseudo-perovskite blocks, containing BO_6 octahedra. The chemical formula can be expressed as: $(\text{Bi}_2\text{O}_2)^{2+} (\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$. In the above notation, 'A' represents a mono-, bi-, or tri-valent, 'B' denotes a tetra-, Penta-, or hexa- valent ion, and 'm' is the number of BO_6 octahedra of each pseudo-perovskite block ($m = 1, 2, 3, \dots$) [1].

Based on the literature survey, it is concluded that among the A- site as well as A & B-site doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT), the B-site doping have lower coercive field (E_C) [2-4]. If the modified cations have alterable valence, then the modified cations may induce the additional space charges. The substitution of higher valence cations for Ti^{4+} sites certainly reduces fatigue-resistance characteristics, for some extent, in these materials [5]. Since the ionic radius of Zr^{4+} is about 18% larger than that of Ti^{4+} , therefore the substitution of 'Zr' could enhance the relative ionic displacement, which might result into large P_r (remnant polarization) value, compared to lanthanum bismuth titanate. Keeping this view, an attempt was made in our earlier investigation [6]. An interesting and striking feature of our earlier result is that the compound with Zr content with 0.1 concentration was showed the higher P_r value. In the present work, detailed, complex impedance analysis was made to corroborate our mentioned above results.

Impedance spectroscopy is a powerful tool to separate out the contributions of different micro-elemental regions present in a polycrystalline material [7]. The aim of the present work is to characterize the conduction behavior of the samples in order to clarify the influence of Zr substitution for Ti- site on lanthanum bismuth titanate.

2. EXPERIMENT

Polycrystalline materials of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_{3-x}\text{Zr}_x\text{O}_{12}$, with $x = 0, 0.1, 0.3, 0.5, 0.7$ and 1.0 (further these samples are referred as BLT, BLTZ-1, BLTZ-2, BLTZ-3, BLTZ-4 and BLTZ-5 respectively) were prepared through conventional solid-state reaction method. The stoichiometry amounts of AR grade Bi_2O_3 , La_2O_3 , TiO_2 and ZrO_2 fine-powders were taken and these powders were grounded for 24 hours in Planetary Ball Mill (Retch, PM100) using ethanol as a liquid medium. An excess of 5% Bi_2O_3 was added to the reactant mixture before calculation in order to compensate the bismuth loss during high-temperature treatment. The powder was calcined at 850°C for 5 hours. After pre-sintering, the reactant powder was ground in the planetary ball mill to obtain the fine powder. Finally the powder was pressed into circular shaped pellets using PVA as binder, and sintered at 1050°C for 4-5 hours for higher densification. The single-phase formation of crystalline structure was confirmed by the X-ray diffractogram recorded by a Pan Analytical Philips X'pert plus diffractometer with $\text{Cu K}\alpha$ (1.54 Å) radiation and the data was reported in our earlier paper [6].

The Impedance measurements were performed as a function of frequency (100 Hz – 1 MHz), using AUTOLAB (PGSTAT 30) low frequency impedance analyzer interfaced to a PC, in the temperature region RT – 550°C. The DC electrical conductivity of the samples was measured in the temperature range of RT - 550°C using Keithley 617 electrometer and Keithley DMM 199 (both were interfaced with a computer using LABVIEW software).

3. RESULTS AND DISCUSSIONS

The complex impedance data of all the samples (BLT & BLTZ), measured at different temperatures, are shown in Fig.1 (a-f) respectively. From the plot, it is observed that the semicircles become small in magnitude with increasing temperature and Zr⁴⁺ concentration. The equivalent circuit, mentioned in the Fig. 2, is found to be well fitted to the experimental data. The data can be divided into three semicircles, consisting of three series connecting sub RC parallel circuit, is as shown in insert Fig. 1 (a-f). The solid line represents the fitting data of the equivalent circuit. A small semicircle observed at higher frequency region indicates the effect of grain, second semicircle at intermediate frequency shows the influence of grain boundaries and the third semicircle at lower frequency is result of electrode effect. The resistance and capacitance of the grain, grain boundary and electrode - interface are estimated in the temperature region 400°C – 500°C, using Z-view stimulation program. The conductivity and the relaxation times were also calculated.

The variation of conductivity of grain, grain boundary and electrode-interface and relaxation time with the inverse of temperature is shown in Fig. 3 and Fig. 4 respectively. Resistance of grain, grain boundary and electrode - interface (R_g, R_{gb} and R_{ei}) (shown in the Fig. 3 (a-f)) are found to decrease with increasing temperature and Zr⁴⁺ concentration. The high resistance of grain, grain boundary and electrode interface of BLTZ-1 is attributed to the highly insulating/dielectric nature of the sample [6, 8]. Since the Zr⁴⁺ ionic radius is 18% greater than Ti⁴⁺ ion inside the BO₆ octahedra, which intern leads to the strong competitive interaction of short - range correlation among the polar domains. This might enhance the resistivity for Bi_{3.25}La_{0.75}Ti_{2.9}Zr_{0.1}O₁₂ (BLTZ-1). It is a known fact that ‘Zr’ can exist in Zr⁴⁺ as well as Zr³⁺ valence state. As ‘Zr’ substitution reaches the solubility limit, it starts entering into the Bi³⁺-site and thus it decreases the resistance of the sample. Moreover, the centers of the three semicircles lie below the real axis, which suggests that the relaxations are of non-Debye type [9, 10].

The conductivity as well as relaxation time plots, shown in the Fig. 3 (a-f) and 4 (a-f), are found to be linear and obey the following Arrhenius relation:

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_a}{KT}\right) \text{ -----(1)}$$

Where the σ_0 is a pre-exponential factor and E_a , K and T represent the activation energy, the Boltzmann constant and absolute temperature respectively. The activation energies for different micro-elemental contributions present in the sample, calculated from the linear fitting the data, are summarized in the Table 1. The estimated activation energies of grain, grain boundary and electrode interface were found to be more than 0.6 e V. These values are found to be similar to the reported activation energy values [11] of three-layered BLSF compound (Bi₄Ti₃O₁₂).

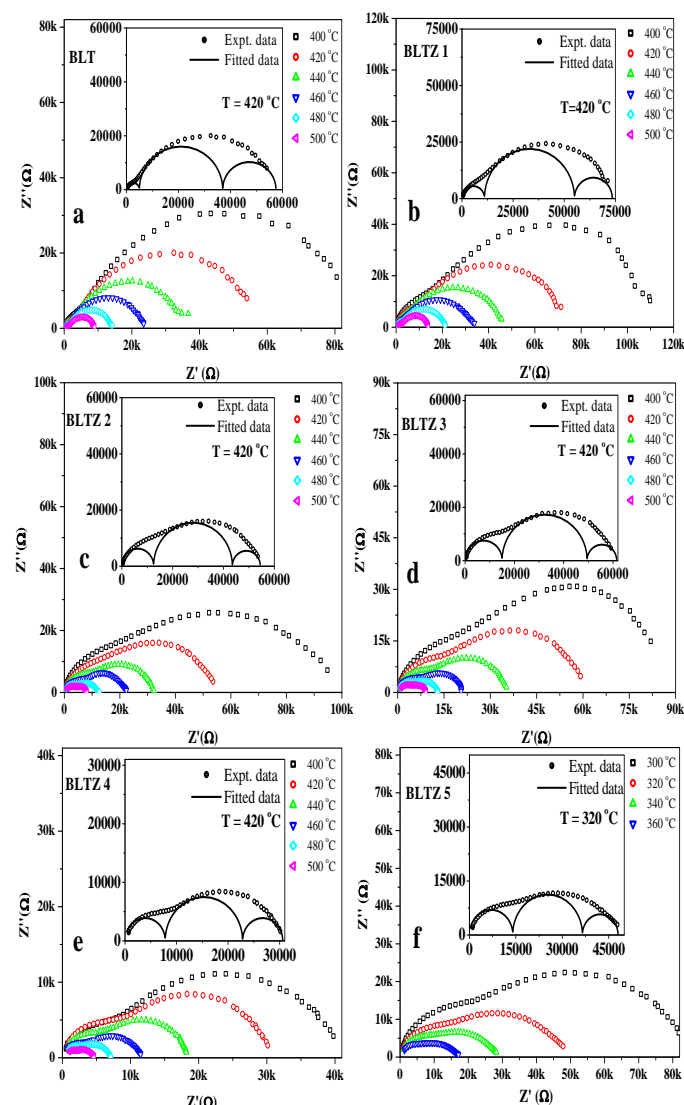


Fig. 1 (a-f). Cole-Cole Plots of BLT & BLTZ ceramics at different temperatures

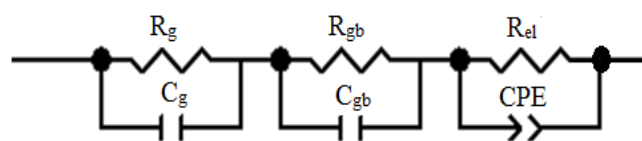


Fig. 2. Equivalent circuit model.

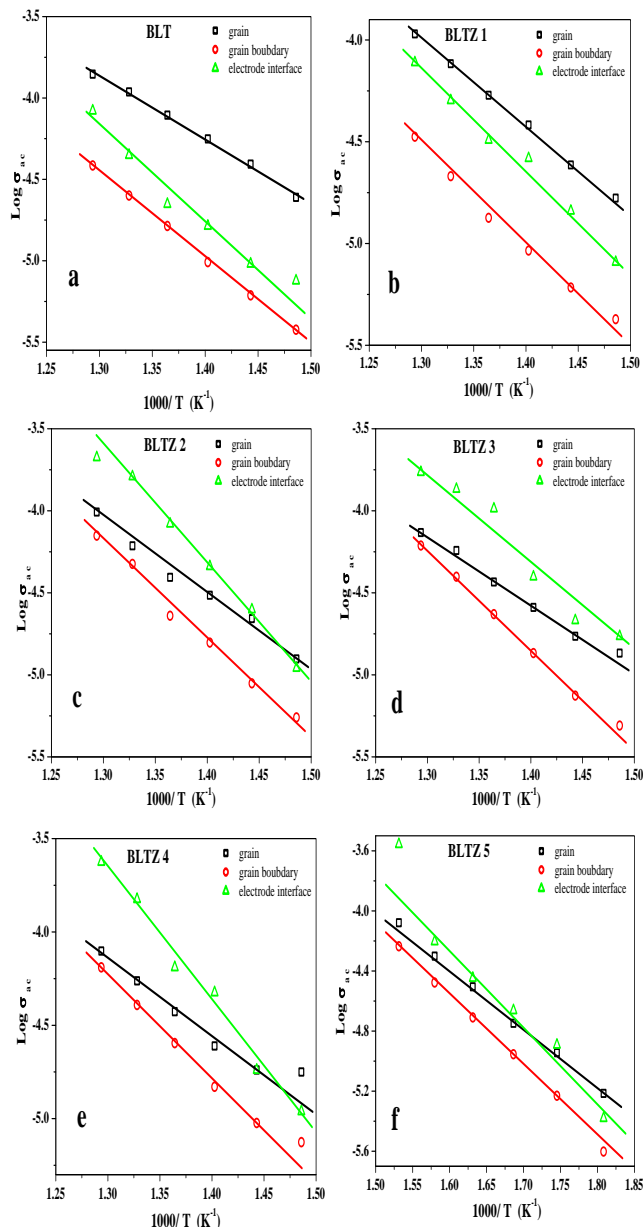


Fig.3 (a-f): Log σ_{ac} of grain, grain boundary and electrode interface Vs $1000/T$ of BLT & BLTZ ceramics.

Fig.5 (a-f) shows the variation of the imaginary part of the impedance (Z'') and frequency for all the samples. Z'' plots show broad peaks and the broadness of the peaks increases with increasing the temperature. This indicates the presence of a multiple relaxations phenomenon (non Debye). It is also observed that the peak maxima found to shift towards the high frequency side with increasing the temperature. This type of behavior is commonly observed in many ferroelectric materials with different cations occupying 'A' or 'B' sites. This behavior is being attributed to the cationic disorder due to the random distribution of heterovalent ions at cation sites [12]. A noteworthy aspect forms the plot is

that the Z'' values are found to merge into the single vale at higher frequency region. This indicates the minimizing the space-charge effects, which are present in the sample.

Based on the above study, the non-Debye type behavior of the title compounds and the dispersion observed in the spectroscopic data, at intermediate frequency region, is attributed to the chemical heterogeneity present in ceramics, which are due to random distribution of cations of both 'A' and 'B' site of ABO_3 perovskite units [9-11]. Due to slow diffusion of ions in the thermo mechanical process, during solid-state sintering of the constituent oxides, the resultant material would have micro- heterogeneities. These heterogeneities may be due to disorder, resulting from random occupation of La^{3+} and Bi^{3+} in 'A' sites and Zr^{4+} and Ti^{4+} in 'B' sites of the ABO_3 perovskite lattice. In this compound each unit cell contains three units of ABO_3 structures. Each set of three ABO_3 perovskite units is separated by $(Bi_2O_2)^{2+}$ layers. Because of the random occupation of equivalent sites by different ions, there are fluctuations in the structure. This might result into multiple-relaxation phenomena in the similar ceramics as we reported earlier [6, 9, 10].

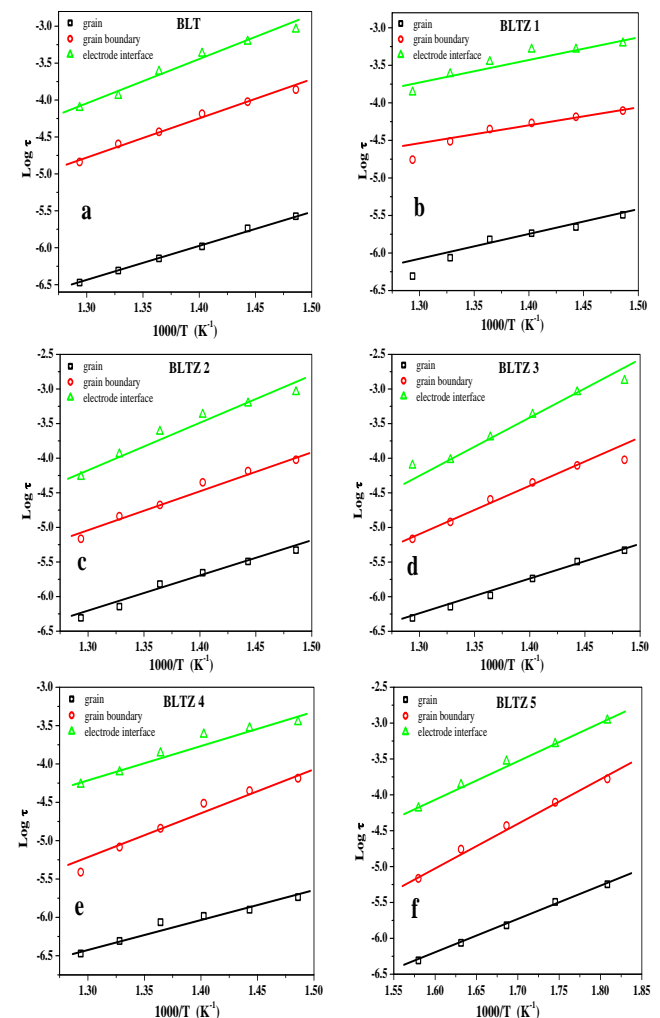


Fig.4 (a-f): log τ of grain, grain boundary and electrode interface Vs $1000/T$ of BLT & BLTZ ceramics.

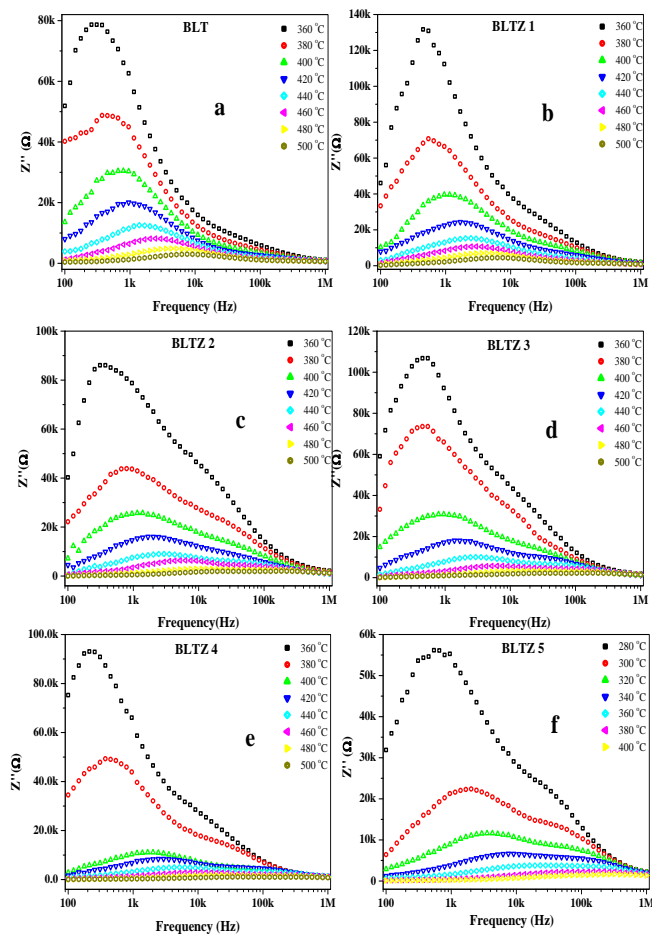


Fig. 5 (a-f), Z'' Vs Frequency plots of BLT & BLTZ

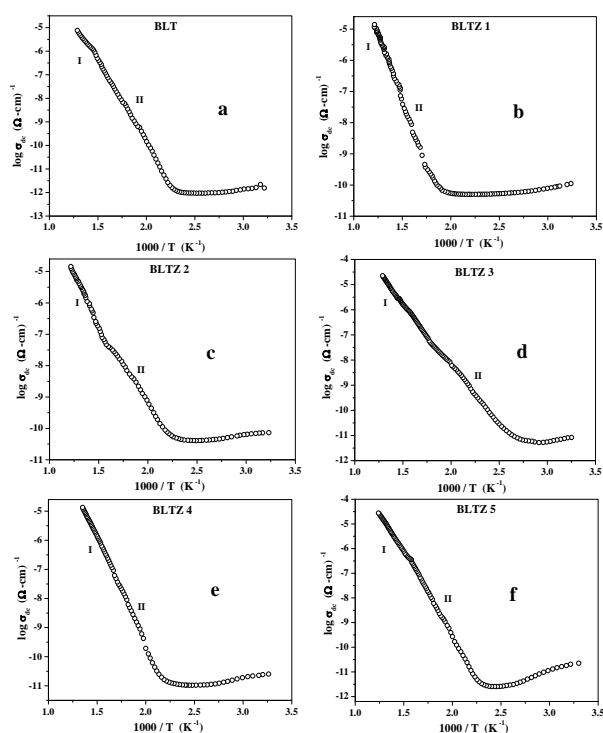
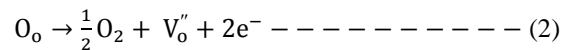


Fig.6 (a-f), σ_{dc} Vs $1000/T$ plots of the BLT & BLTZ

In the present materials, the oxygen vacancies are considered to be one of the mobile charge carriers. This phenomenon is attributed to the volatility of ‘Bi’ during high temperature sintering process. Bismuth oxide compounds are expected to lose some traces of oxygen during a high temperature sintering process, which can be defined by the following Kroger and Vink notation [9, 12, 13]:



In the present Ti-based materials, Ti^{4+} can be expressed in the form of $Ti^{4+}+e^- \rightarrow Ti^{3+}$. The formation of oxygen vacancies can be explained in the following two different charge states:

- (i) Neutral charge state (V_o^x): This state can able to capture two electrons and it will be neutral in the lattice.
- (ii) Single and double ionized state (V_o' and V_o''): These states cannot trap any electron it is positively twofold. These are thermally activated and enhance the conduction process. However, double charge oxygen vacancies are considered to be more mobile charges and play important role in the conduction process.

Sample	A.C. Conductivity Activation Energy (eV)			A.C. Relaxation Activation Energy (eV)			D.C. Activation Energy (eV)	
	E_g	E_{gb}	E_{el}	E_g	E_{gb}	E_{el}	Region - I	Region - II
BLT	0.78 ±0.02	1.05 ±0.01	1.08 ±0.10	0.94 ±0.02	1.01 ±0.05	1.14 ±0.09	0.97 ±0.020	1.41 ±0.008
BLTZ-1	0.84 ±0.01	0.92 ±0.04	0.98 ±0.05	0.79 ±0.10	0.63 ±0.10	0.64 ±0.09	1.58 ±0.020	1.73 ±0.040
BLTZ-2	0.87 ±0.05	1.16 ±0.05	1.35 ±0.06	1.03 ±0.08	1.18 ±0.09	1.26 ±0.13	1.37 ±0.016	0.96 ±0.014
BLTZ-3	0.80 ±0.04	1.16 ±0.03	1.16 ±0.12	1.05 ±0.04	1.23 ±0.11	1.39 ±0.10	1.01 ±0.005	0.91 ±0.006
BLTZ-4	0.71 ±0.08	1.00 ±0.07	1.41 ±0.08	0.73 ±0.08	1.27 ±0.11	0.88 ±0.10	1.35 ±0.005	1.54 ±0.020
BLTZ-5	0.80 ±0.02	0.96 ±0.02	1.16 ±0.13	0.94 ±0.03	1.19 ±0.06	1.05 ±0.04	1.17 ±0.008	1.44 ±0.005

Table 1: AC conductivity, Relaxation and DC conductivity activation energy values

Fig. 6 (a-f) shows the DC conductivity of the BLT & BLTZ ceramics as a function of temperature. The DC conductivity plots can be distinguished into two regions: one at high temperature (paraelectric phase) and another at a low temperature region (ferroelectric phase) with different slopes in different temperature regions. A significant dispersion is observed at lower as well as higher temperature regions in the relaxation time (τ) plot (fig 5). It indicates that the samples have more oxygen vacancies [14, 15-17].

According ion-jump model, at low temperatures, the conduction is through hopping of charged particles from one localized state to another, resulting in to the long-range translational motion of charge carriers [18]. Activation energies calculated from the $\log \sigma_{dc}$ Vs $1000/T$ plots (fig 6)

are summarized in the Table 1. Typically, the activation energies for the conduction behavior of oxygen vacancies in the octahedral perovskite structure are around 1eV and that of cation vacancies is higher activation energy value (more than 1 e V) [19, 20]. A change in the temperature-dependence of DC (bulk) conductivity is possibly associated with ferroelectric-paraelectric phase transition around transition temperature (T_c). However, sudden changes observed at far below the transition temperature in the DC-conductivity data is attributed to the abrupt changes in the defect concentration. A change in the conductivity around the transition temperature is attributed to paraelectric-ferroelectric phase transition phenomenon [9]. High conductivity values and nearly 1 e V activation energy values, compared to the PZT [10] clearly indicates that the high defect concentration or high-defect mobility nature of these materials.

The high ionic conductivity and high activation energy of BLTZ-1 indicates the presence of more oxygen vacancies. This might lead to more fatigue-resistance, compared to the other compositions. This is clearly confirmed by observing higher grain conductivity for BLT and BLTZ-1, compared to the other material (fig 5). This indicates that BLTZ-1 has more mobility and higher charge carrier concentration than other compounds in the study. The overall electrical properties of BLTZ-1, at higher frequency region were influence of grain rather than grain-boundary and electrode-interface. In addition, the elimination of defects, trapped in the grain boundary and electrode-interface significantly reduces the influence of domain pinning. In other words, the oxygen vacancies can easily released out when switching the field is applied. Consequently, no space charge built up and hence the BLTZ-1 compound showed promising ferroelectric property [see ref 6 of our earlier work on same compounds].

4. CONCLUSION

Complex impedance measurements were studied on the Zr substituted Lanthanum modified Bismuth titanate ceramics, in order to understand the role of Zr on BLT. The Cole-Cole plots showed three semicircles. The different micro-elemental regions have a random distribution of La^{3+} and Bi^{3+} in 'A' site and Zr^{4+} and Ti^{4+} in 'B' site of the ABO_3 perovskite units. DC conductivity studies indicate the presence of multiple activation process, which are due to the oxygen vacancies and 'A' site cation vacancies. Defects, such as oxygen vacancies are considered to be the most mobile charges and play an important role in polarization. The results can be corroborated to our earlier hysteresis loop measurements [6]. From the activation-energy and the conduction results, the conduction is thought to be dominated by charge carriers such as oxygen vacancies. Probably, double charged oxygen vacancies are the most mobile charges which are playing important role in the conduction mechanism. On account of its characteristic nature (easy recovery of oxygen vacancies from the trap sites) BLTZ-1 is considered to be future promising FRAM materials, as we have reported earlier [6].

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