ELECTRICAL MEASUREMENT OF La MODIFIED $Bi_4Ti_3O_{12}$ FRAM CERAMIC

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Abstract

Bismuth Layer Structured Ferroelectric (BLSF) ceramic of $La_{0.75}Bi_{3.25}Ti_3O_{12}$, (BLT) abbreviated as future promising ferroelectric random access memory materials was prepared by the conventional solid-state reaction method. Resistivity and dielectric measurements were made as a function of temperature and frequency. The remnant polarization (Pr) is found to be 16 □ C/cm^2. The ferroelectric results were corroborated with the electrical impedance, resistivity and hysteresis properties

Keywords: *Resistivity, Cole-Cole fitting, FRAM, conductivity, impedance*

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1. INTRODUCTION

Bismuth layered structure ferroelectric (BLSF) materials have attracted much attention owing to its scientific and applications point of view [1,2]. Park et al [1] reported that lanthanum modified BLT (Title of the compound) seems to be promising nonvolatile FRAM material. The general formula of the title compound consists of three-layer perovskite units $(Bi_2Ti_3O_{10})^{2-}$ and sandwiched between bismuth oxide layer $(Bi_2O_2)^{2+}$. The inherent ferroelectric properties of these materials are attributed to the layer perovskite-blocks [3]. However these materials are exhibiting low leakage current due to the domain pining effects. The high conductivity nature is attributed on account of defects (oxygen vacancies). In addition to this, the title compound show lower transition temperature and therefore BLT is readily compatible to CMOS technologies [4-6].However the effect of lanthanum role in the layered-perovskite is still not yet understood thoroughly. In view of this, an attempt is made in present investigation.

In present investigation dielectric ferroelectric measurements were made on the sintered cylindrical disks. Impedance analysis is found to be precious tool in separating out several contributions from the total impedance arising from the bulk and interfacial phenomena such as grain, grain boundary contributions. Data can be interpreted in terms of possible formalism, which are connected in the following relations:

Complex impedance $(Z^*) = Z' - iZ'')$ -(1)

Or resistivity $(\rho^* = Z^* \frac{A}{t} = \rho' - i\rho'')$ - (2)

where A is area of electrode and t is thickness of the ceramic .The frequency dependence of the complex resistivity can be expressed by introducing a temperature –dependent factor n into the Debye expression ,i.e, the Cole-Cole expression is as follows

$$\rho^*(w) = \frac{\rho_0}{1+(iw\tau_0)^n}, \tau_0 = \frac{1}{w_0} = \frac{1}{2\pi f_r} - \quad (3)$$

Which is established by considering the material as a parallel circuit of a pure resistor and ideal capacitor .The $w_0 and$ n are the characteristic angular frequency and a temperature –dependent factor, respectively .The factor n may be a function of temperature and take values over the range $0 \leq n \leq 1$.If the factor n is unity, then the relaxation process is a Debye –type process with a single relaxation time. Earlier we have reported that the defects of oxygen vacancies accumulated at grain boundary interfaces [7]. However the effect of La role in these ceramics is not yet understood thoroughly. Therefore an attempt is made in the present investigation and the results were corroborated with resistivity data.

2. EXPERIMENTAL

The BLT ceramics were prepared by using solid state reaction method. The required amount of reactance powder were taken jar and ball milled for2 4 h in acetone media after ball milling the powder were calcinied at 850 C^0 for 2 h .After calcination the powder were crushed and subjected to the cylindrical pellets by applying pressure by using hydraulic process the pellets finally sintered for 1000C^0 for 2h .The pellets were coated with silver paste and complex impedance were made and detail else of the procedure given elsewhere [7].

3. RESULTS AND DISCUSSION

Debye behavior of BLSF materials is being considered to be characteristics future and this phenomenon is being attributed to distribution of relaxation time [6]. The variation of □' and □" with frequency in the temperature region of 390, 410 and 490^{o}C is shown in fig 1. □ "peaks are found to shift towards higher frequencies with increasing temperatures.

Temperature dependence of permittivity and dielectric loss of the BLT at different frequencies is shown in fig2. The broad dielectric loss peaks observed in the region I and region II (shown in the fig 2a, as doted lines) indicates the thermally active conduction, associated with dipole reorientation. The inset of fig 2b shows the variation of dielectric constant vs. temperature. From the plot the transition temperature is found to be 440^{o}C. The typical hump-like behavior in dielectric loss variation could be consequence of ion jump relaxation effect. It is known that bismuth oxide compounds loose oxygen traces at sintering temperatures, as per the following Korger and Vink mechanism [7]:

$$O_o \rightarrow \frac{1}{2} O_2 + V_{\ddot{o}} + 2e$$

The electrons releases in the above process may capture either by Ti^{4+} ion to form Ti^{3+}. However, the exponential dependent conductivity nature shows that the conduction occurs due to the transport of oxygen charge carriers. To pinpoint more about the conduction mechanism Complex impedance analysis is studied.

Complex impedance plots (Cole-Cole plot) are found to be precious tool to separate out the various contributing factors such as grain, grain boundary and electrode effects [8]. Moreover these contributing elements are connected in parallel combination network with capacitance (C) and resistance(R). In the present investigation, Cole -Cole plots are shown in the fig 3(a-c). The resistance and capacitance of grain (r_g , c_g) and grain boundaries (r_{gb} , c_{gb}) are calculated, by using Z-view software fitting and are the proposed equivalent circuit is depicted in the fig 3. Appearing broad semicircular peaks in the variation of resistivity vs. frequency plots, associated with both grain(g) and grain boundary (gb) effects (shown as solid curves in the fig 1) with in ferroelectric domains mainly due to the domain polarization, which is partially reversible. Cole-Cole plot yields to two semicircles; this is due to the diffuse of oxygen vacancies that are generally present in the bismuth oxide materials. The variation of ac-conductivity with frequency is plotted and shown in fig 3d. The ac-conductivity is found to be independent of temperature and depends significantly on frequency and at high temperatures. Increasing the ac-conductivity values is due to the increase the conductivity of the sample. The substitution of La for Bi may cause depressive stressing the perovskite unit cell, as a result leading to the distortion in the structure. In addition to this, the different subsistent with different ionic radii of La/Bi and stress of TiO_6 octahedra buckle, the sample showed a kind of diffused nature. Earlier we have reported that the cation displacement with regards the Bi_2O_2 layers in BLT might contribute large polarization (ferroelectric properties) in the materials [7]. In other words, the displacement of Bi ions in the ab-plane is dominant rather than the displacement of the Ti ions in ab-plane. The hopping mechanism is confirmed from the variation of ac-conductivity with frequency plot by observing different slopes in frequency domain.

From the Cole-Cole fitting, the depressed angle values (n_g and n_{gb}) show that they are almost temperature dependent and less than 1. The grain and grain boundary parameters are given Table 1. This indicates that there exist a hopping mechanism between Ti^{3+} states and Ti^{4+}, as mentioned earlier [7].

Fig 4 shows P-E hysteresis loop of BLT ceramic. The hysteresis loop was measured a driven electric field of 80 kV/cm at room temperature. The remnant polarization value (Pr= 16 □ C/cm^2), which is almost same value as reported in the literature [9]. The coercive field E_c = 60 kV/cm. The perfect loop attributed to the minimized domain pinning behavior. The oxygen vacancies generated due to the Bi cation vacancies would assemble at domain boundaries during the sintering condition. The vacancies form complex dipoles with electron and hence defects significantly reduced thereby domain pinning effect can be minimized. This is intern responsible for well hysteresis loop for BLT and hence becomes promising characteristic of the material.

Table 1. Cole-Cole Plot fitting parameters

S.No	**Temperature**	**Series resistance (R_s)**	**Grain (g) parameters**	**Grain Boundary (gb) parameters**
1	340^{0}c	1.4047E-1 **Ω**	r_g = 10726 □ CPE_g= 8.74E-10 F n_g = 0.93708	r_{gb} = 35509 □ CPE_{gb}= 6.91E-08 F n_{gb} = 0.72563
2	410^{0}c	5.0771E-1 **Ω**	r_g = 1346.7 □ CPE_g=3.22E-09 F n_g= 0.9263	r_{gb} = 7031.8 □ CPE_{gb}=2.73E-07 F n_{gb} = 0.66969
3	490^{0}c	10.402 **Ω**	r_g= 535.63 □ CPE_g= 6.35E-10 F n_g=0.98856	r_{gb} = 2348.8 □ CPE_{gb}=8.2718E-07 n_{gb}=0.61649

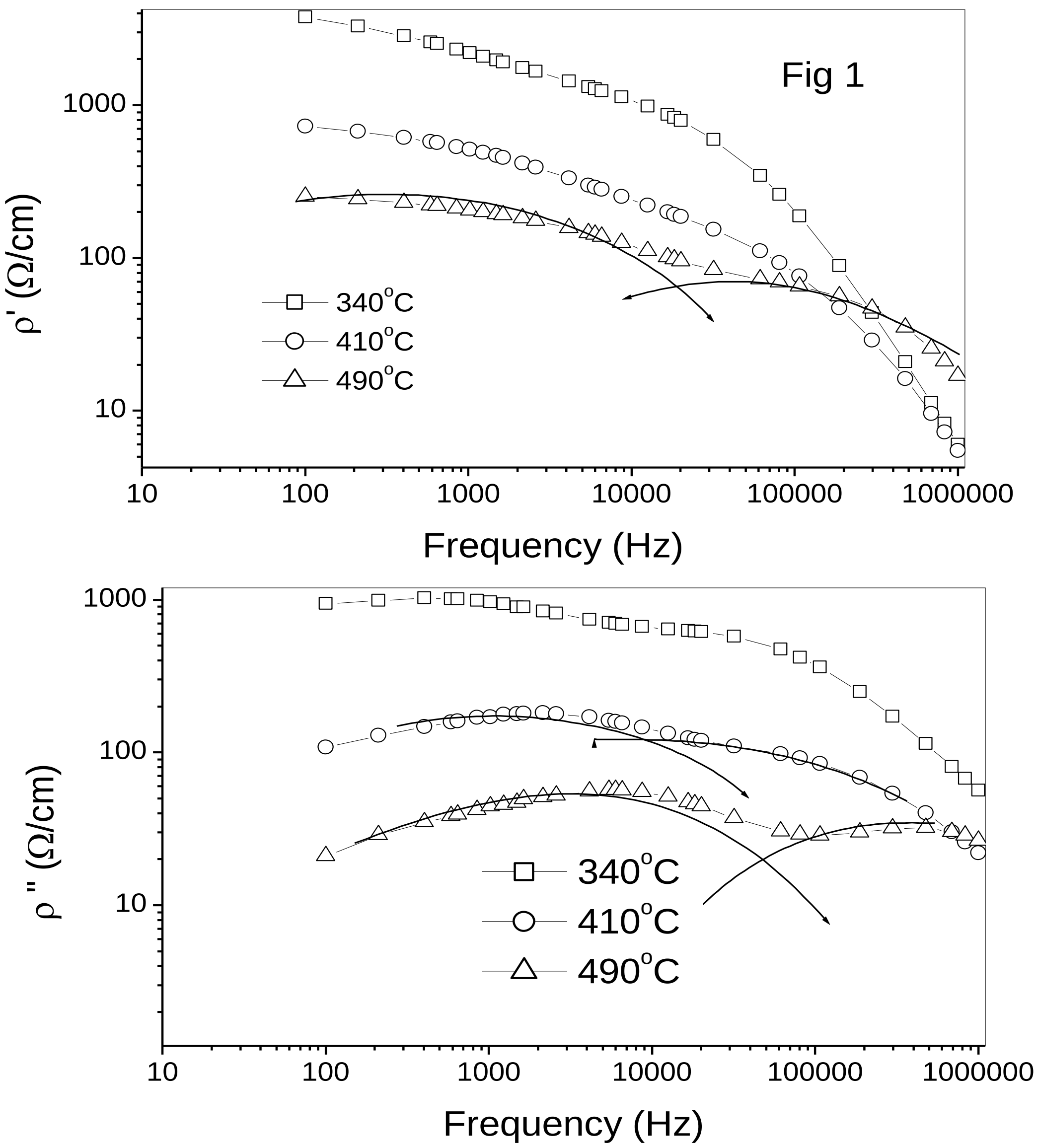

Fig 1 (a-b) variation of □’ and □” with frequency

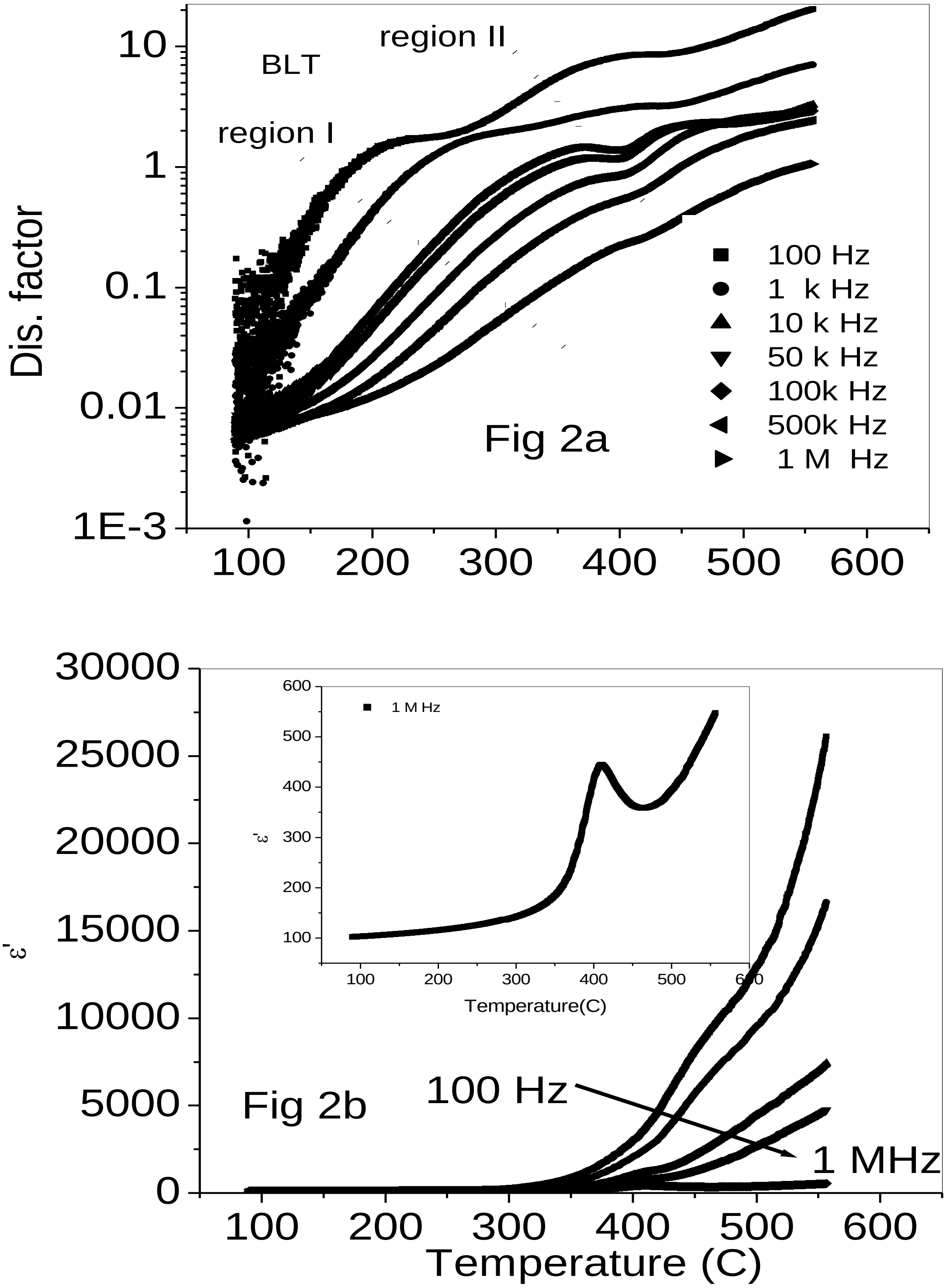

Fig 2 (a-b) Variation of dielectric loss and dielectric constant with temperature.

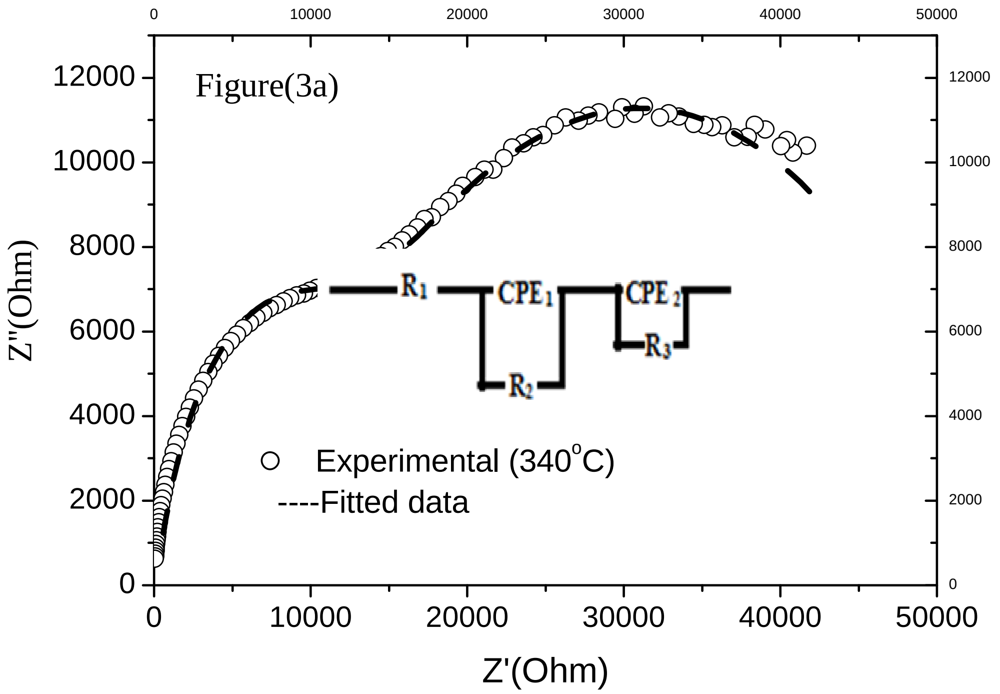

Fig 3a Z” vs. Z’ at 340^{o}C (Inset fig: equivalent circuit)

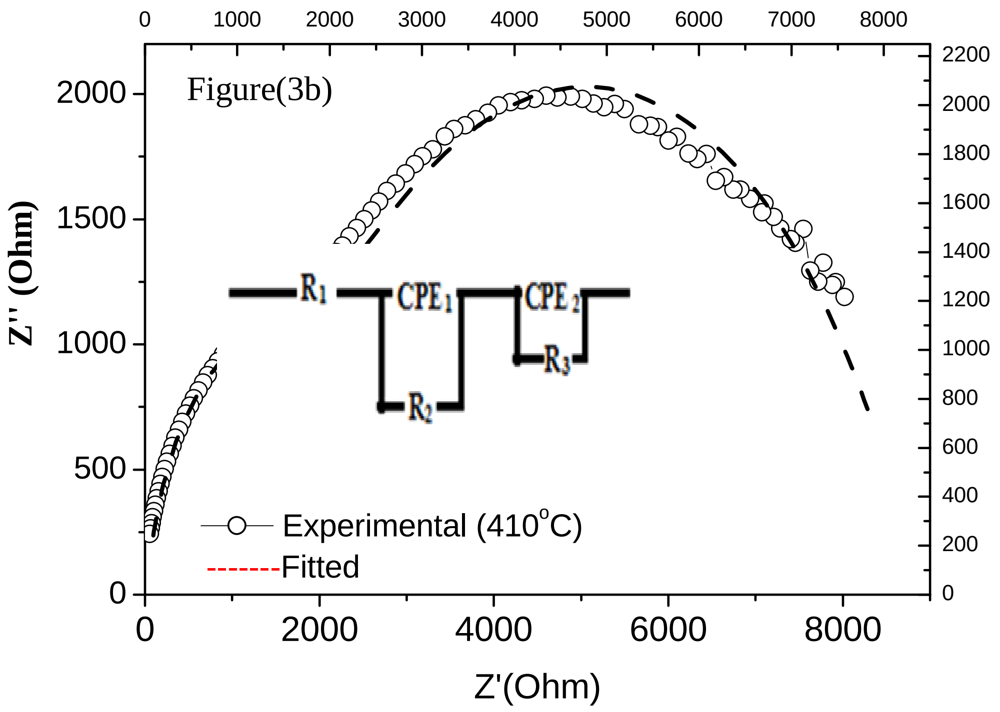

Fig 3b Z” vs. Z’ at 410^{o}C (Inset fig: equivalent circuit)

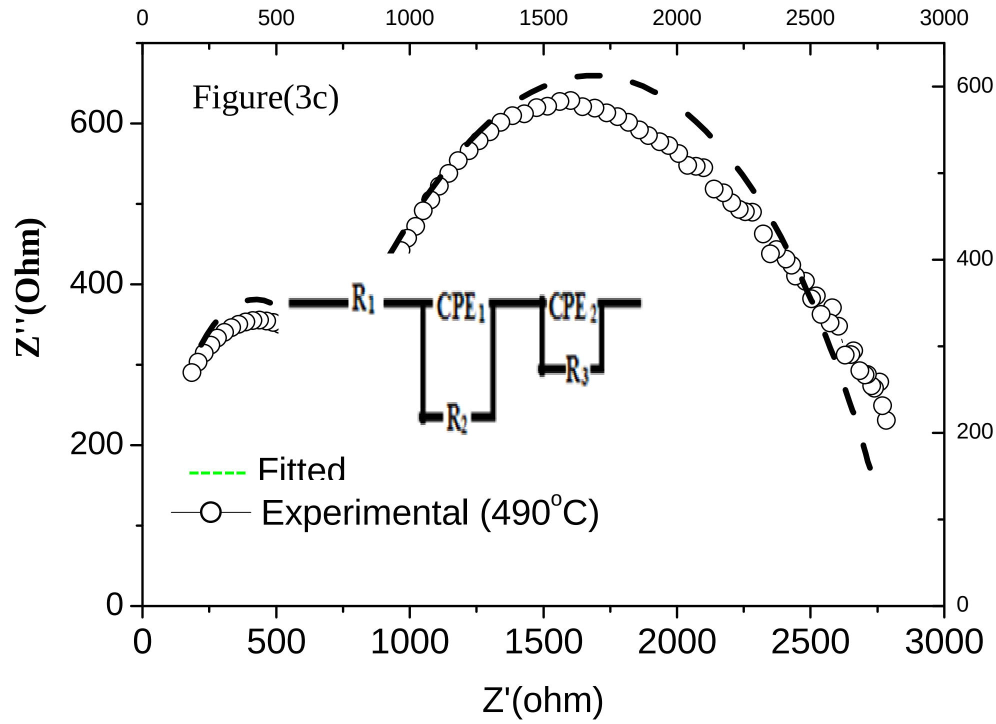

Fig 3c Z' vs. Z' at 490°C (Inset fig: equivalent circuit)

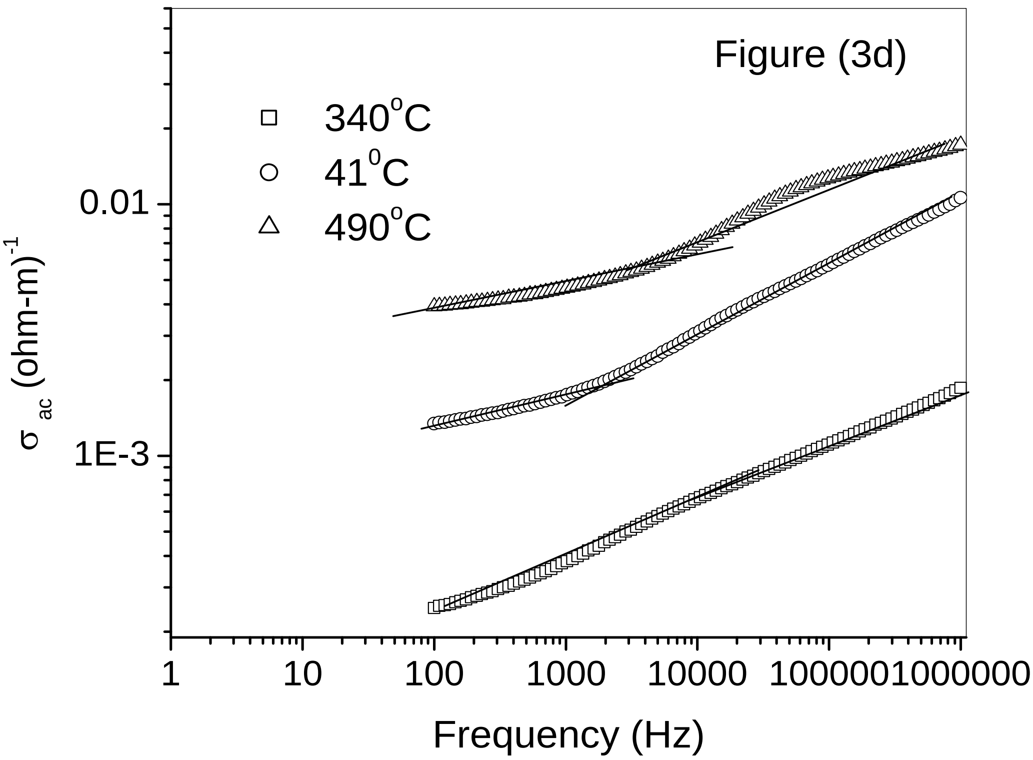

Fig 3d □ ac vs. Frequency

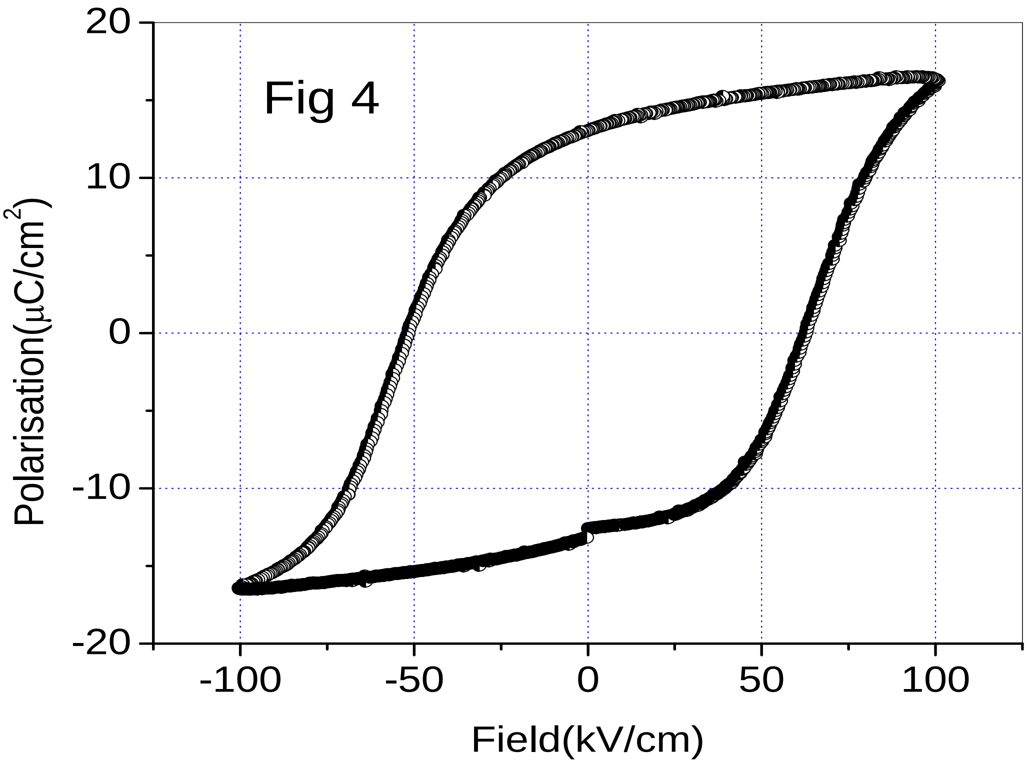

Fig 4 P vs. E for BLT

4. CONCLUSION

In summary promising FRAM ceramic namely BLT was prepared by conventional solid state route. Impedance resistivity analysis seems to be powerful tool to understand the defect role. The complex impedance analysis is used to separate out the grain and grain –electrode effects. The interfaces which act as trap sites for oxygen vacancies or defects. A noteworthy aspect is that the BLT showed higher Pr value on account of minimizing the defects, by forming complex dipoles. The results are consistent with our earlier work [7].

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