# XRD and Electric properties of lead barium titanate ferroelectric ceramic

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**Abstract:** Lead-barium-titanate (LBT) ferroelectric ceramic have been synthesized using appropriate amount of PbO, BaO and $0.25TiO_3$. X-ray diffraction pattern was used to identify phases present in the crystalline ceramic and indicate the formation of ferroelectric Pb-Ba-TiO$_3$ with tetragonal perovskite structure ceramic. The temperature dependence of ac and dc conductivities was studied. Curie temperature was investigated and equals to 310 $^o$C. It was found that the resistance abnormally increased with increasing temperature from room temperature up to 70 $^o$C showing positive temperature coefficient (PTC). While below the Curie temperature, the LBT ceramic possess semiconductor behavior which give rise to negative temperature coefficient (NTC).

**Kew words:** XRD, Electric properties, lead barium titanate.

## INTRODUCTION

Barium titatnate, BaTiO$_3$, and lead titanate, PbTiO$_3$, ceramic have a great interest for many applications referring to their ferroelectric properties such as piezoelectric sonar and ultrasonic transducers and ferroelectric thin film memories (Kin, *et al.,* 2007). The high dielectric constant of barium titanate based electronics is responsible for selecting these materials for capacitors (fabrication Bera, *et al*., 2007). On the other hand the main advantage of glass over ceramic materials is the relatively simple methods which can form complex shapes, such as casting and lost wax techniques. They are pore-free and usually have fine-grained microstructures (Chiang Mai, 2008). Many researches were carried out to investigate and develop fine grained, pore –free glass ceramics containing BaTiO$_3$, PbTiO$_3$ and NaNbO$_3$ ferroelectric phases (Lee, *et al*., 1999). Such materials with variable dielectric properties and shapes could be used also to regulate and homogenize fields in microwave furnaces. These materials poses wide ranges of dielectric permittivity with low dielectric loss which are suitable for operating these furnaces.

Glass ceramic nanocrystals are important class of materials (Garbarczyk, *et al*., 2007). because of their physical properties which are not exist in other classes of materials. These ceramics could be formed with a wide verity of crystals types and shapes (nano, micro, etc…). Crystal and grain sizes are the most significant structural parameters in ferroelectric crystalline glassy phases. These phases are with very high dielectric permittivity. This is attributed to the presence of BaTiO$_3$ on nanocrystalline size form (Sadhukhan, *et al*., 1999). Glass ceramic are composites prepared by the controlled crystallization of glass (Al-Assiri, *et al*., 2009). (Kokubot *et al*., 1974); have controlled crystallization of $SiO_2 – Al_2O_3 –TiO_2 – PbO$ glasses. These glasses were crystallized in a subsequent heat treatment in the temperature range 620-750 $^o$C. Several studies on to the crystallization of glass ceramics containing ferroelectric PbTiO$_3$ phase have demonstrated the close relationship existing between microstructure and dielectric properties of these glass ceramics (Chiang Mai, 2008; Kokubot, *et al*., 1974; wange, *et al*., 2002). Substitution as lead for barium results in the increase in tetragonal to cubic phase transition temperature and decrease in room temperature dielectric constant. The temperature dependence of dielectric of lead substituted materials was studied and it was found that it is better than pure barium titanate (Juneja *et al*., 2010). Barium titanate poses a series of structural phase transition with changing temperatures from ideal paraelectric cubic perovskite structure to the ferroelectrics of tetragonal to (120 C) and rombohedral (-90 C) structure (Lines, *et al*., 1977). The glass ceramic materials exhibit one or more crystalline phases in the glass matrix. Therefore the dielectric properties can be extended according to the content, particle size, composition and the way of distribution of its constituent phases. Each of them has its contribution to the polarization processes occurring in the glass ceramic material (Golezardi, *et al*., 2010).

*Experimental procedure:*
Stoichiometric amounts of oxides PbO-BaO-TiO$_2$ with the ratio 0.5:0.25:0.25. The mixture was melted in porcelain crucible in air at 1100 $^o$C for about 30 min. The excess PbO is intended to acts as a fluxing agent. The melt was stirred to ensure complete mixing. The melt was then poured on copper plates and left to crystallize independently. A yellowish sheet of ceramic was formed and polished. X-ray diffraction pattern for the resulting perovskite glass-ceramic sample was measured and recorded using X'Pert PRO MPD, Philips, Eindhoven, Netherlands, with Cuk$_{a1}$ radiation (λ=1.5406 A$^o$). The pattern was measured in the 2θ range from 10 to 85 degree. Conducting silver paste was applied on the both flat surfaces for carrying out the electrical measurements.

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## RESULTS AND DISCUSSION

*XRD Results:*
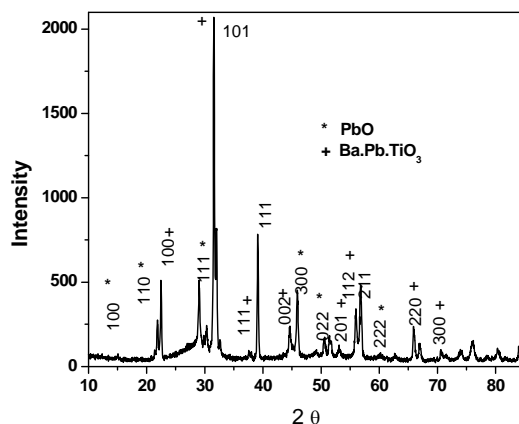The different phases in the crystallized ceramic are shown and identified in the XRD pattern fig.1.



**Fig. 1:** XRD patterns of 2x PbO – x BaO – xTiO   ( x = 0.25 mol % ) Crystal.

The primary peak at $2\theta = 31.5^o$ is attributed to $Pb_{0.5}Ba_{0.5}TiO_3$ phase indicating the formation of ferroelectric phase with tetragonal perovskite structure. It is noticed that the highest peak (101) corresponds to $Pb_{0.5}Ba_{0.5}TiO_3$. There is no evidence for the presence of separate phase of $BaTiO_3$, which is possibly due to the substitution of Ba ion in the $PbTiO_3$ crystalline phase. Structure and formation of $Pb_{0.5}Ba_{0.5}TiO_3$ solid solutions have a tetragonal structure in which the degree of tetragonality (c/a) increases in going from $BaTiO_3$ to $PbTiO_3$ (Venevtsev, *et al.*, 1985). In perovskite titanate the increase of c/a ratio is desirable because the higher c/a ratio normally increases the polarizability and improves the ferroelectric properties (Moulson, *et al.*, 2003). The other largest peaks at angles $2\theta = 22.1^o$, $29.07^o$ and $46.156^o$ are corresponding to PbO phase at planes of hkl: (110-111- 300). The harping of the peaks indicates that the sample was fully crystallized  (Xiuli Chen, *et al.*, 2005).This means that the powder with excesses PbO gives rise to nucleation behavior.
The structural stability of LBT ceramic ( lattice strain η)  and the average grain size can be calculated according to the following equation Ohsato:

$$\beta \cos \theta = \lambda/D + 2\eta \sin \theta \tag{1}$$

where $\beta$ is the full width at half maximum of XRD peak in radians, $\lambda$ is the x-ray wavelength, *D* is the grain size, and $\theta$ is the Bragg angle. The lattice strain $\eta$ could be measured from the slope of the plot of $\beta \cos \theta$ versus $\sin \theta$. The results are listed in table (1).

**Table 1:** Structural Parameters of the perovskite structure ceramic

| Cell parameters | BaPbTiO$_3$ | PbO |
|---|---|---|
| a (A$^o$) | 3.977 | 4.7544 |
| c (A$^o$) | 4.042 | 5.8952 |
| c/a | 1.016 | 0.806 |
| Cell volume (A$^{o3}$) | 63.93 | 153.96 |
| η (strain) % | 0.228 | 0.132 |
| Grain size (A$^o$) | 140.9 | 189.2 |

As mentioned before, substitution of lead for barium results in the increase in tetragonal to cubic phase, as recorded in table 1,where going from PbO to BaPbTiO$_3$ accompanied by a cell volume (grain size) decreases and as a result a strain increases. Makoto kuwabara *et al.*, (1985). stated that for (Ba,Pb)TiO$_3$  ceramic the atom structure of grain boundary was more relaxing than grain, which leads to ions diffusion, therefore the acceptor defect will first formed on the grain boundary during preparation process and then diffused to the inside of grains by, sintering, oxidation, cooling or heating, an acceptor defect diffusion layer of Ba vacancy was formed on the grain surface.
It was reported that the resistance-temperature properties of (Ba,Pb)TiO$_3$ ceramics were affected by semiconducting of grain, grain boundary potential barrier, grain size and ferroelectric-paraelectric phase transition (Tian Yuming, *et al.*, 2005).

***Electrical measurements:***

Fig. 2 represents the temperature dependence of the dc resistivity. The resistance of LBT ceramic increases
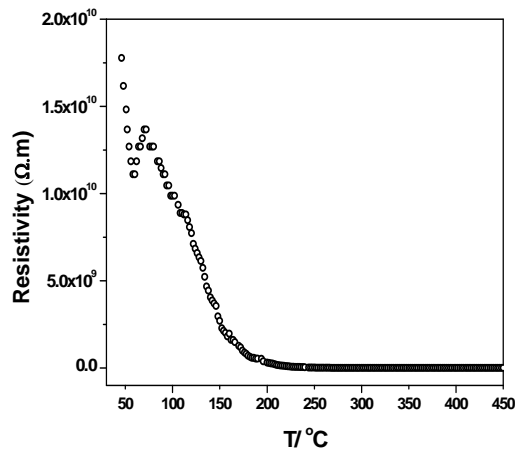


**Fig. 2**: Temperature dependence of resistance of LBT ceramic.

as the temperature increases from room temperature up to 70 $^oC$, showing PTC behavior. Several researches showed that this abnormal behavior was identified by (Tian Yuming, *et al.*, 2005). The decrease in resistance with increasing temperature is a normal behavior for the semiconductor materials. This decrease in resistance may be referred to compensation of surface charges by polarization and the disappears of potential barrier. The activation energy of the presented ceramic sample at high temperatures was calculated from the slope of dc curve Fig. 3 according to (Mott, 1987) formula:
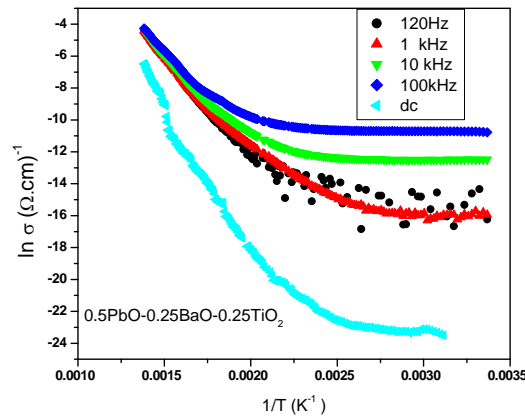


**Fig. 3:** Temperature dependence of ac conductivity at different frequencies from 0.012 to 100 kHz for LBT ceramic.

$$\sigma = \sigma_o \exp(-W_H / k\,T) \qquad\qquad (2)$$

where $\sigma_o$ is a pre-exponent factor, $W_H$ is the activation energy and k is Boltzmann constant. The present sample show linear temperature dependence up to a critical temperature $\theta_D/2$ and then the slope changes with deviation from linearity, this behavior suggested the small polaron hopping SPH mechanism. The measured $W_H$ and $\theta_D$ in the present study was 1.2 eV and 888 K respectively. It is known that $T_C$ of $BaTiO_3$ (120 $^oC$) rises to (490 $^oC$) for $PbTiO_3$ (Venevtsev *et al.*, 1985). perovskite ceramic. In this work $T_c$ of $BaPbTiO_3$ was indentified at 310 $^oC$ as seen from the dielectric permittivity measurements shown in Figs. 4 and 5 and satisfy a relation of the form:
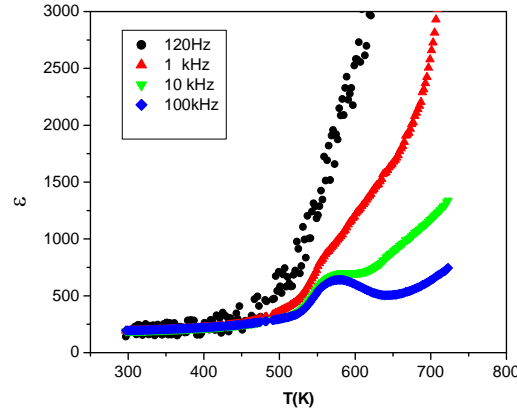
**Fig. 4:** The dielectric permittivity as a function of temperature for LBT Glass ceramic.

$$T_C (Ba_xPb_{1-x}TiO_3) = T_C (BaTiO_3)_x + T_C (PbTiO_3)_{1-x} \qquad (3)$$

Where from the present results, x, was found to be 0.49 in good agreement with previous study (Tian Yuming, *et al.*, 2005).

On the other hand, the temperature dependence of the dielectric constant on the AC conductivity of the present sample is shown in Fig.5 at five frequencies $0.12$-$10^2$ kHz. As it is noticed that the ferroelectric properties is established for the present sample which show high dielectric constant compared to pure crystalline $BaTiO_3$, this was attributed to the presence of nanocrystalline $BaTiO_3$ (Sadhukhan, *et al.*, 1999). In most ferroelectrics, the effect of ferroelectric properties can be expressed according to the Curie–Weiss law:
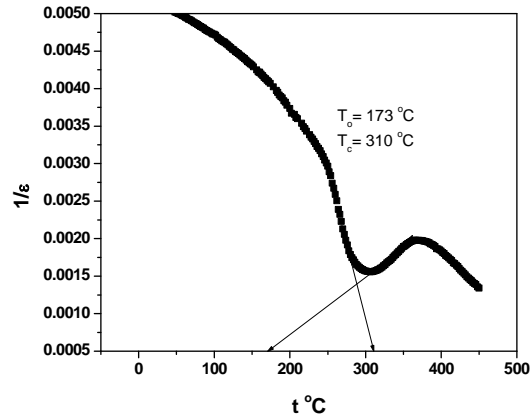


**Fig. 5:** The variation of reciprocal of dielectric constant with temperature for LBT ceramic at a frequency 100 kHz .

$$\varepsilon = \varepsilon_o + C/ (T - T_o) \qquad (4)$$

Where $\varepsilon$ is the real part of the dielectric permittivity, $\varepsilon_o$ is free space permittivity, C is the Curie – Weiss constant, $T_c$ is Curie temperature and $T_o$ is the Curie-Weiss temperature. The Curie temperature for the present sample of the composition $0.5PbO+0.25BaO+0.25TiO_3$, $T_c = 310$ $^oC$ , this result is with agreement with semiconductor ceramics $(Ba,Pb)TiO_3$ Tian Yuming *et al.*, (2005). The asymptotic temperature $T_o = 173$ $^oC$. When $T_o < T_c$, this is the case of first–order phase transition.

However, as shown in Fig. 6 sample exhibits a frequency dependent conductivity of the type (Mott, 1987):

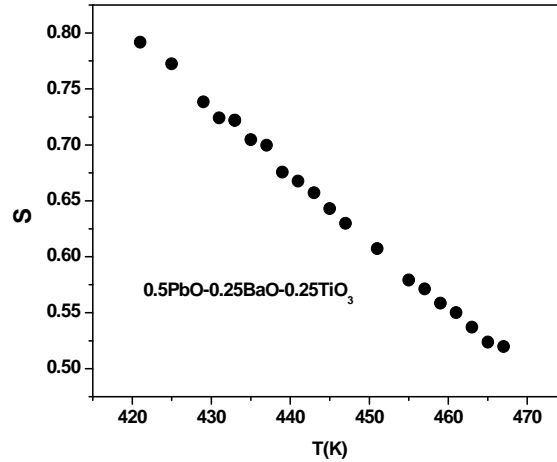$$\sigma_{ac} (\omega) = A \omega^S \qquad (5)$$

**Fig. 6:** The temperature dependent of the frequency exponent(s) for the Glass ceramic sample.

where A is the constant of temperature dependence and s is the frequency exponent which is less than or equal one. Fig.6 illustrates the dependent of frequency exponent, s, on temperature, it is clear that s is inversely proportional to the temperature which indicates that the mechanism of conductivity is by hopping process.
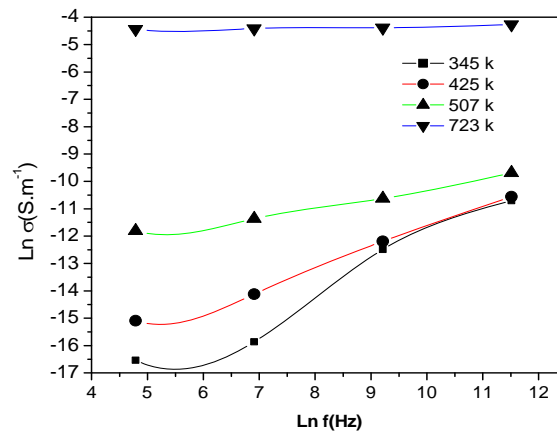


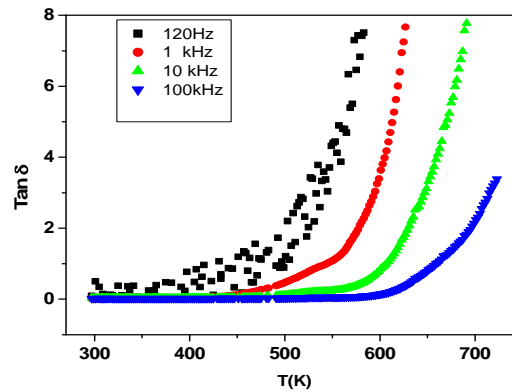**Fig. 7:** The conductivity dependent on frequency of BLT ceramic at different temperatures.



**Fig. 8:** Loss factor as a function of temperature for $0.5PbO+0.25BaO+0.25TiO_3$ glass ceramic.

Fig.7 nonetheless, illustrates the conductivity dependent on frequency of LBT ceramic at different temperatures. It is shown that the conductivity increases as both of the temperature and frequency are increases. The temperature dependence of loss factor tan$\delta$ is shown in Fig.8 representing the semiconductor behavior. The importance of tan$\delta$ quantity is that it measures the phase difference due to the loss of energy within the glass ceramic matrix. The observed dielectric loss factor may be due to two main contributions, the first one is the thermally activated relaxation where the thermal energy is the only type of excitation (h$\omega\ll$kT) where h$\omega$ = photon energy. The second one occurs at high temperatures and is due to electrical conduction (Saisha *et al*., 2006).

*Conclusion:*

The LBT ceramic can be fabricated under control to produce a perovskite tetragonal ferroelectric ceramic and improve properties. The resistance increases with increasing temperature from room temperature to 70 $^{o}$C enhanced a PCTR then it decreases with increasing temperature which enhanced the NCTR and identified semiconductor behavior in the present sample. The multi phases were exhibited in the X- ray diffraction pattern indicating the fully crystallization of the present sample. The Curie temperature as measured indicates that the final ceramic product is $Pb_{0.51}Ba_{0.49}TiO_3$ and it has a Curie's temperature 310 $^{o}$C.

## ACKNOWLEDGMENT

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