Effect of sintering time on the particle size and dielectric properties of La-doped PbTiO₃ ceramic nanoparticles

A. A. Abd El-razek[*1], E. M. Saed[1], M. K. Gergs[1]

[1]Ferroelectric Lap, Physics Department, Faculty of science, South Valley University,
Qena-83523, Egypt

ABSTRACT

Nanoparticles of $[Pb_{0.7} La_{0.2}]$ TiO_3 ceramics were prepared by conventional combust technique from the oxides of PbO, La_2O_3 and TiO_2 with different sintering time (t_s) (2, 6, 10, 12, 16 a 20h) while keeping the calcination temperature at 1200 °C. Particle size of the samples was estima between 25 to 65 nm through Scherrer formula and was found to increase with increasing sintering ti (t_s). Microstructural analysis of the samples was carried out using scanning electron microscope wh showed that grain boundary increased with increasing sintering time (t_s) while dislocations were reduc The dielectric constant and Curie temperature of the samples was increased with increasing sintering ti (t_s), but the activation energy in both of ferroelectric and paraelectric (E_a) decreased with increasing The diffusion coefficient (γ) decreased with increasing t_s. In other words the optimum sintering ti conditions was found.

KEYWORDS: - A. Ceramics, B. Crystal growth, C. X-ray diffraction, D. Dielectric properties

I.   INTRODUCTION

In recent years, lead titanate (PbTiO₃) ceramics have attracted lot of attention due to its high Curie temperature (490 °C) and low dielectric constant (200), which makes it suitable for high-temperature and high-frequency transducer applications than that of PZT ceramic system [1,2]. However, pure lead titanate ceramics are very difficult to be sintered because of its large lattice anisotropy (c/a = 1.064). On cooling through Curie temperature, the large anisotropy of ceramic material becomes fragile. In addition, it's difficult to pole the ceramics with low resistivity ($10^7 – 10^8$ Ω cm).

By substitution of isovalent (Ca^{2+}, Ba^{2+}, Cd^{2+}, ……etc) or off-valent (Sm^{3+}, Gd^{3+}, La^{3+}, Y^{3+}, ……etc) ions into the Pb sites, the lattice anisotropy is reduced [3], and the samples become more dense. Mn doped PbTiO₃ produces a material with high mechanical strength, low dielectric losses and low dielectric constant reliable for piezoelectric resonator applications [4].

M.K. Gerges and et al. studied effect of preparation conditions (pressure, sintering time and temperature) on the ferroelectric properties of $(Pb_{0.1825}La_{0.125})TiO_3$ ceramics, where the optimum pressure was 40 MPa and they summarized that the sintering time and sintering temperature are considered to be the essential factor for improving quality of ceramics [5].

La- and Zr-doped lead titanate (PLT, PLZT) powder ceramics and thin films are known to have interesting dielectric, pyroelectric, electro-optic and piezoelectric properties [6-9], and so have a wide range of applications such as infrared sensors [10], capacitors [11], ferroelectric memories (dynamic random access memory (DRAM) and non-volatile random access memory (NVRAM)) [12], shutters [7], optical modulators [13], etc.

PLT and PLZT belong to the family of ferroelectric relaxors, and so show anomalies in their properties in a relatively extended interval around a temperature, T_m at which the permittivity, ε_r, reaches a maximum. The corresponding phase transition is called diffuse phase transition.

Piezoelectric ceramics are commonly used as sensors. These materials have good detection and output characteristic, and can operate over a wide range of frequencies. However, pure piezoelectric ceramics are often too stiff and brittle to be used as embedded sensors in polymeric composites.

In the present work, ferroelectric and piezoelectric properties have been investigated for nanoparticles of PLT ceramics synthesized through conventional ceramic preparation technique.

*Corresponding author*1: Tel: +20966904409; Fax: +20965211273*
E-mail address: abdelrazek.mahmoud@sci.svu.edu.eg; abdophy2010@yahoo.com

II.   EXPERIMENTAL PROCEDURE

Nanoparticles of the PLT were prepared with conventional ceramic method where stoichiometric ratios of oxide powders of PbO, La_2O_3 and TiO_2 were mixed together, and pressed into disc shaped pellets of 2 cm diameter and about 1 cm thickness by applying a pressure of 20 MPa. These discs were calcined for 2 h at a temperature of 700 °C. These discs were further sintered at different sintering times (t_s) 2, 6, 10, 12, 16 and 20 h at 1200 °C. Finally, the disks were rushed and grinded mechanically to produce samples with 7.5 mm diameter and about 1.5mm thickness and were coated with on opposite face with aluminum thin films to study the electrical properties. Compositional analysis and lattice parameters of the samples were carried out through X-ray diffraction (XRD) and microstructure analysis was done using scanning electron microscope (SEM) (JEOL, JSM-5500LV). The dielectric properties were measured using LCR meter (TH2826) The Curie temperature was calculated by measuring the dielectric behavior as a function of temperature.

III.   RESULTS AND DISCUSSIONS

a. *Structural properties*

The X-ray diffraction patterns of ceramic nanoparticles of [$Pb_{0.7}$ $La_{0.2}$] TiO_3 sintered under different times (2, 12 and 20h) at sintering temperature 1200 °C are shown in Fig. 1. The X-ray analysis indicated that the La-doped $PbTiO_3$ ceramic nanoparticles have major peaks at (101), and all of them are tetragonal in phase. The average grain size (D) of the samples was calculated using Debye-Scherrer method from the broadening of the diffraction line using the expression [14]:

$$D = 0.94\lambda/\beta\cos(\theta) \qquad (1)$$

Where λ is the wave length of the CuKα radiation, β is the full width at half maximum (FWHM) of the diffraction peak and θ is the Bragg diffraction angle. Fig. 2 shows the variation of grain size as a function of sintering time (t_s), and it was found that with increasing t_s, grain size increases. The behavior can be explained according to the phenomenological kinetic grain growth equation expressed as [15]:

$$\log G = (1/n) \log t + (1/n) [\log K_o – 0.434 (Q/RT)] \qquad (2)$$

Where G is the average grain size at the time sintering, n is the kinetic grain growth exponent, K_o a constant, Q the apparent activation energy, R the gas constant, and T is the absolute temperature. The average grain size of all the studied samples has been found increased with increasing of sintering time (t), where the average grain size increased from 25 nm to 65 nm, if the sintering time increased from 2h to 20 h are respectivelly between 25 to 65 nm. The growth in grain size as a function of sintering time can be observed in [16].

Fig. 3(a) and (b) shows the lattice constant and lattice anisotropy of La-doped $PbTiO_3$ ceramic nanoparticles as a function of sintering time (t_s) at sintered temperature 1200 °C, respectively. It is seen that the lattice constant c-axis decreases correspondingly with increasing the sintering time, while the a-axis changes little, so that the lattice anisotropy (c/a) decreases with increasing sintering time. This results indicate that the system is approaching towards cubic structure. The increasing of sintering time it will assist the modified Lead titanate ceramics in sintering process and improve the crystal structure of the samples. This behavior can be observed in [17,18]. According to Arlt's model [19], the lattice anisotropy (c/a) is inverse proportional to the partical size.

The microstructural analysis of La doped $PbTiO_3$ ceramic nanoparticles were carried out using scanning electron microscope (SEM). Fig.4 (a-c) presents the SEM micrographs of 20% doped $PbTiO_3$ sample sintered at 1200 °C and at different sintering time (2, 10, 16 and 20h). It can be seen that the diameter of grain boundary increased with increasing sintering time of the sample.

b. **Dielectric properties**

Figs. 5(a) presents the variation of dielectric constant with sintering temperature 1200 °C for three sintering times 2, 12 and 20h under an applied field of 100 kHz. While Fi.5 (b) presents the variation of dielectric constant with respect to the sintering time at two fixed frequencies, 10 KHz and 100 KHz, respectively., Fig. 5(a) shows that for each sample, the general mode of (ε) variation against (T) yields a bell curve, where the dielectric constant increases with increasing temperature and reaches to a maximum value (ε_{max}) at Curie temperature (T_c), then it decreases with further increase of sintering temperature. Further, it is also seen that ε_{max} increases with increasing sintering time, where if the sintering time is increased from 2h to 20h, the ε_{max} increases from 5367 to 8217. This increase in dielectric constant is due to increasing grain size corresponding to the increase in sintering time. Similar behavior has been reported by M. Dongle et al. where they report that the dielectric constant increases with increasing sintering time [5]. From Fig.5(b) it can be seen that the Curied temperature (T_c) for all the studied samples is independent of frequency and the ε_{max} decreases with increasing frequency of the applied field, where in low-frequency region, the dielectric constant has high value, which can be attributed to various polarization effects. At higher frequencies, electronic polarization contribution dominates over ionic and orientation polarization and hence the dielectric values are less [20-22].

Fig.6 shows the variation of Curie temperature with respect to the sintering time. It is seen that the Curie temperature increases with increasing sintering time, where if the sintering time is increased from 2 to 20h, the T_c increases from 423 to 453 ^{o}K. This increase in T_c can be related to the configuration of new dipole moments.

Fig. 7 presents plot of activation energy (Ea_f, Ea_p) versus the sintering time (t_s), where Ea_f and Ea_p are the activation energy in ferroelectric and paraelectric phases, which can be calculated from the equation [23].

$$\mathbf{Ln\ (\tau^{-1}) = Ln\ (\tau_o^{-1}) - (E_a/k)(1/\ T)} \qquad (3)$$

Where, τ and τ_o represents the relaxation and critical relaxation times at T_c, respectively. E_a is the activation energy and k is the Boltzmann constant. The slope of $\ln(\tau^{-1})$ versus (1/T) gives the value of E_a. From Fig.7, it is seen that in whole range of sintering time the value of Ea_p is higher than that of Ea_f. The behavior can be related with crystal structure which is tetragonal before the Curie temperature T_c and cubic after it. The rate of decrease for both values of Ea is rapid at low sintering time t_s while it is slowed down at higher values and both the values of Ea reach to a minimum at $t_s \geq 20$ h. These results can indicate the behavior of maximum value for dielectric constant according to the following equation [24]

$$\mathbf{\mu = \mu_o\ exp\ (-E/KT)} \qquad (4)$$

Where μ the mobility of dipole moment, E is the activation energy, K is the Boltzmann constant and T is the temperature. The last equation show that the mobility of dipole moment and consequently the maximum value of dielectric constant is inverse proportional to the activation energy, and as the sample was sintered at $t_s = 20$h posses minimum value for activation energy, so that it posses maximum value for dielectric constant.

c. Sintering time effect-induced diffused phase transition

The broadening of the dielectric peak of nanocrystalline PLT suggests a typical non-relaxor behavior with diffuse phase transition. A quantitative estimate of the diffuseness parameter (γ) of the ferroelectric-paraelectric phase transition can be obtained using the equation [25]:

$$\mathbf{(1/\varepsilon - 1/\varepsilon_{max}) = 1/C(T - T_c)^{\gamma}, (T > T_c),} \qquad (5)$$

Where γ and C are modified constants with $1 < \gamma < 2$. The value of γ determines the degree of diffuseness of the phase transition. The value of γ is equal to 1 for a system with a completely ordered transition. On the basis of a local compositional fluctuation model, the value of γ is equal to 2 for a completely diffuse system. The value $\gamma > 1$ suggests diffused transition [26]

The plots of $\ln(1/\varepsilon - 1/\varepsilon_{max})$ versus $\ln(T - T_c)$ corresponding to the samples for sintering time = 2, 12 and 20h, respectively, are shown in Fig. 8 at an applied field of 10 kHz.

According to Eq (4) the slope of $\ln(1/\varepsilon - 1/\varepsilon_{max})$ versus $\ln(T - T_c)$ gives the value of γ. From the plot, it can noted that value of γ decrease from 1.3 to 1.11 when the sintering time is increased from 2 to 20h, indicating that the ferroelectric transition becomes less diffuse and the quality of the samples is more. These results are in agreement with the results reported by S.K.S. Parashar et al [27,28]. The values of γ calculated from the fitting of curve in Fig.8 are listed in Table 1.

IV.   CONCLUSIONS

We have successfully grown the nanoparticles of $(Pb_{0.7}La_{0.2})TiO_3$ ceramic and studied the effect of sintering time on the samples sintered at 1200 ^{o}C which show that the sintering time cannot only reduce the lattice anisotropy (c/a), but also keep good dielectric properties, where the value of ε_{max} increased from 6010 to 18200 if the sintering time is increased from 2 to 20h at a frequency 10 kHz of the applied field. For all the ceramics samples, the values of ε_{max} at 10 kHz were more than that at 100 kHz at the same sintering time. Also the phase transition increased with increasing sintering time and it is independent of the frequency of applied electric field. The grain sizes of the samples were increased with increasing sintering time which means that the dislocations were reduced and the samples became harder. The γ coefficient decreased with increasing sintering time which means that the sample quality was further improved and the bell curve was sharper with increasing sintering time. We can conclude that the sintering time is considered to be the essential factor for improving the quality of the ceramics samples.

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Table Caption

Table.1. Comparison of lattice parameter (nm), dielectric data, grain size (nm), diffusivity and activation energy (eV) for the sample (Pb$_{0.7}$ La $_{0.2}$□$_{0.1}$)TiO$_3$ ceramics, with different sintering time.

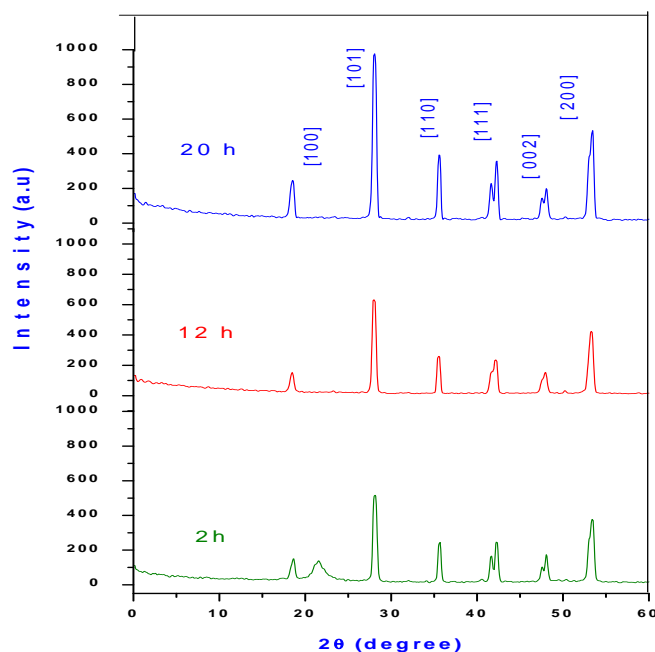| Parameter	2	6	10	12	16	20h
c (A^o)	4.1	4.09	4.075	4.065	4.05	4.045
a (A^o)	3.9	3.901	3.9015	3.9018	3.902	3.9022
c/a	1.05	1.048	1.044	1.041	1.037	1.035
ε$_{max}$ (10 kHz)	6010	9153	13308	15427	17500	18200
ε$_{max}$ (100 kHz)	5367	7149	7305	7650	7966	8217
T$_c$ (K)	423	427	433	440	447	453
partical size (nm)	25	38	50	57	61	65
γ	1.3	1.24	1.19	1.16	1.13	1.11
E$_{af}$ (eV)	1.6	1.18	1.07	0.983	0.903	0.853

Figure caption

Fig. 1. Shows XRD patterns of variation sintering time for the sample [(Pb$_{0.7}$ La$_{0.2}$ □$_{0.1}$)] TiO$_3$ ceramics sintered at 1200 ^{o}C.
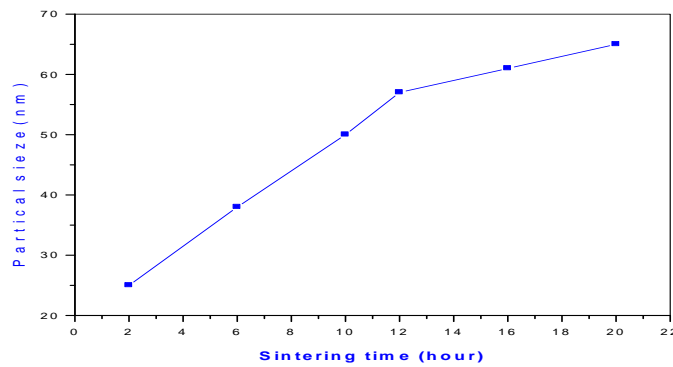
Fig. 2. Shows variation of average grain size for the sample [(Pb$_{0.7}$La$_{0.2}\square_{0.1}$)] TiO$_3$ ceramics with sintering time sintered at 1200 ^{o}C.

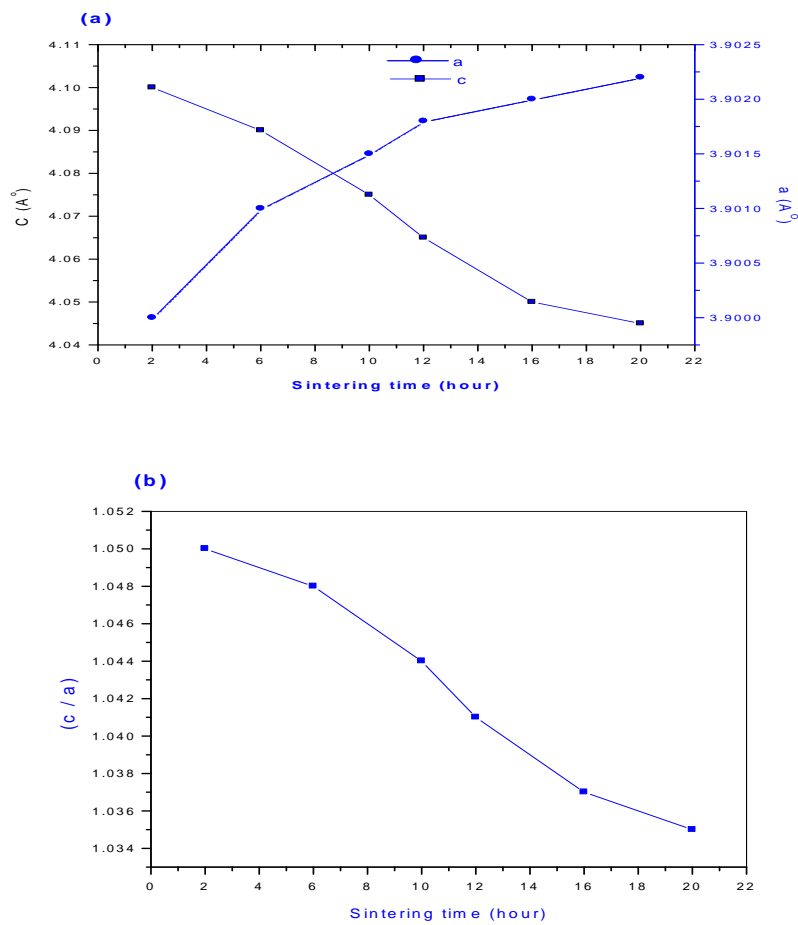**Fig.3.** Dependence of the (a) lattice constant and (b) lattice anisotropy (c/a) of   [(Pb$_{0.7}$La$_{0.2}\square_{0.1}$)] TiO$_3$ ceramics on the sintering time.

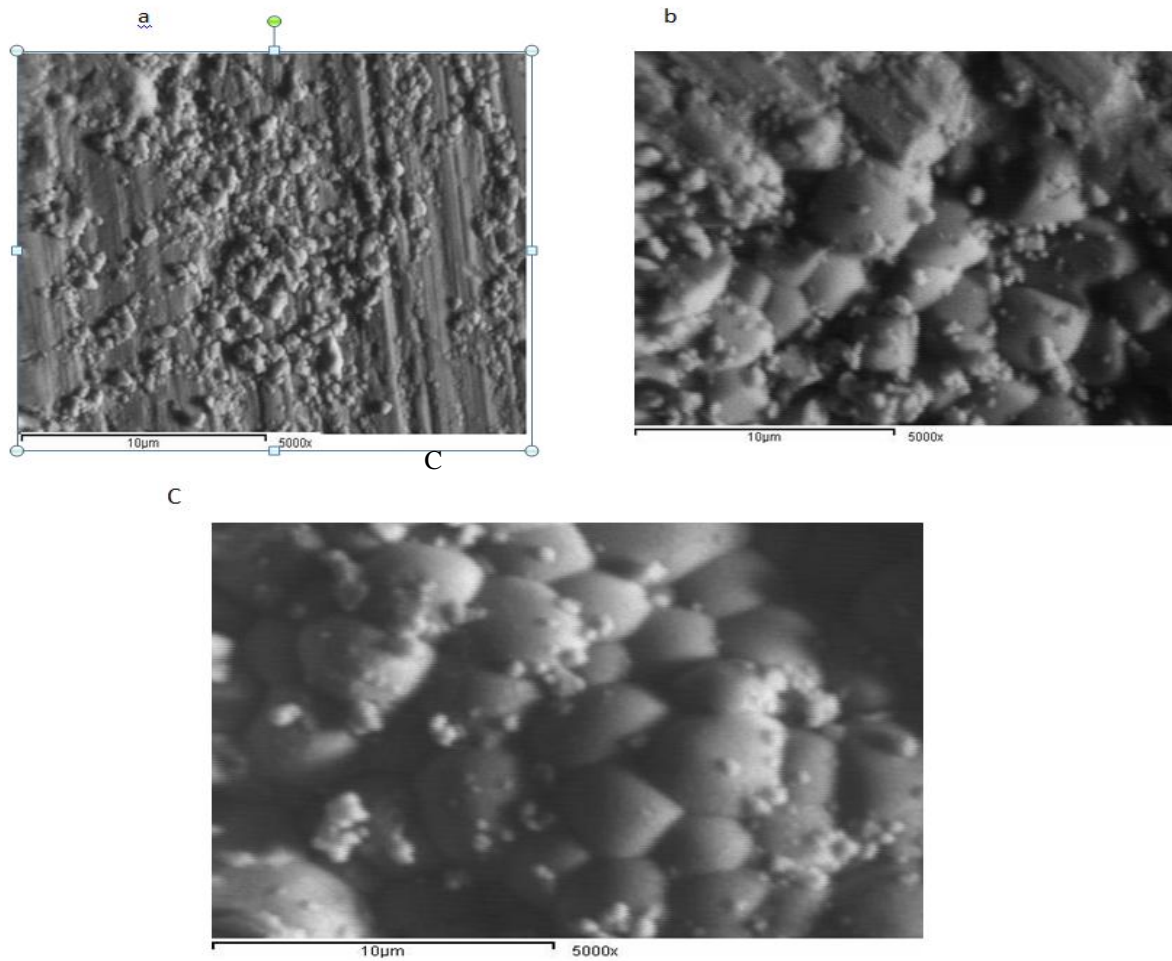**Fig. 4.** SEM photographs of (a), (b) and (c) represented the sample [(Pb$_{0.7}$La$_{0.2}$ $\square_{0.1}$)] TiO$_3$ ceramics   sintered at 1200 ^{0}C on the sintering time 2, 12 and 20h are respectively.

(a)

(b)
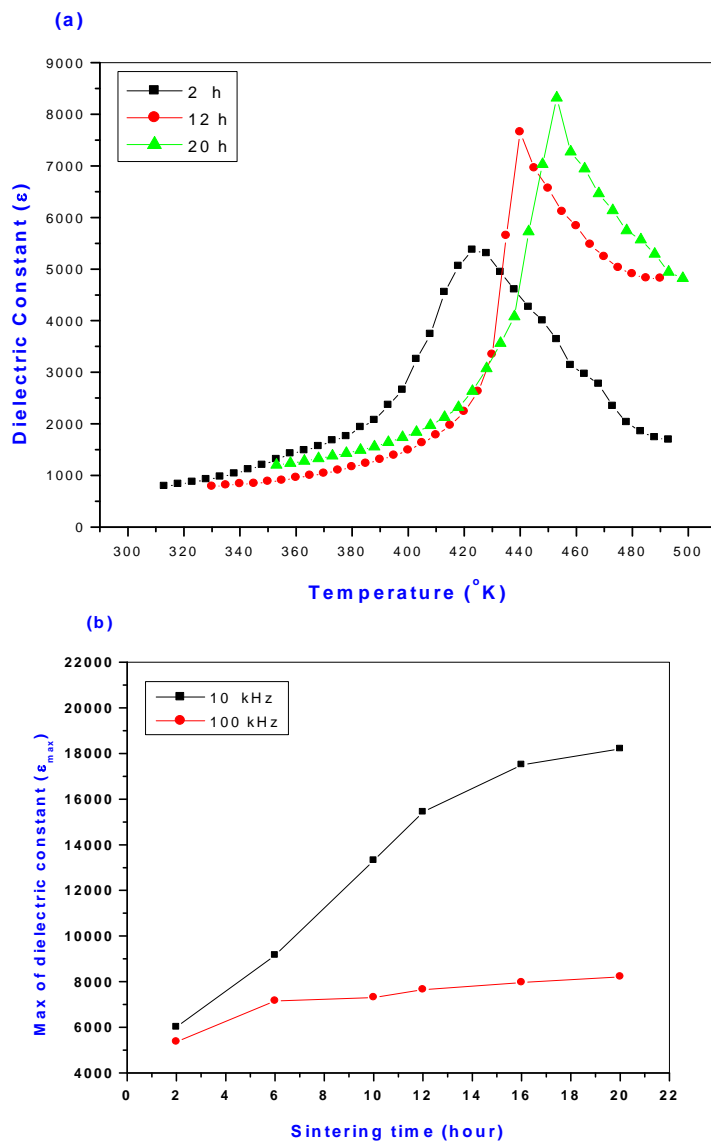
Fig. 5. (a) Variation of dielectric constant with temperature for the sample PLT ceramics sintered at 2, 12 and 20h. (b) Depending (ε_{max}) with two various frequencies (10 and 100 kHz) for all studied the samples
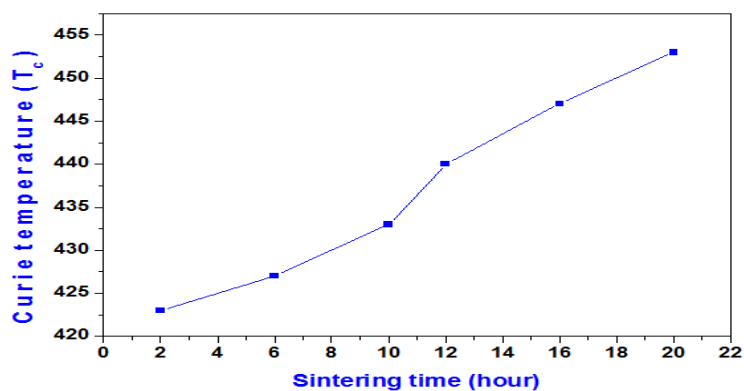

Fig.6. Depending Curie temperature for the sample $[(Pb_{0.7}La_{0.2}\square_{0.1})]$ TiO_3 ceramics sintered at 1200 ^{0}C as a function of the sintering time.
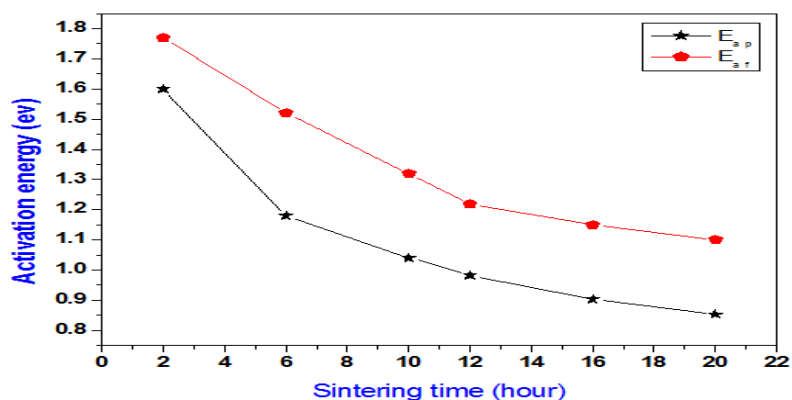
Fig. 7. A plot of activation energy at the ferroelectric (E_{af}) and paraelectric phases (E_{ap}) for the sample $(Pb_{0.7}La_{0.2}\square_{0.1})TiO_3$ ceramics versus with the sintering time.
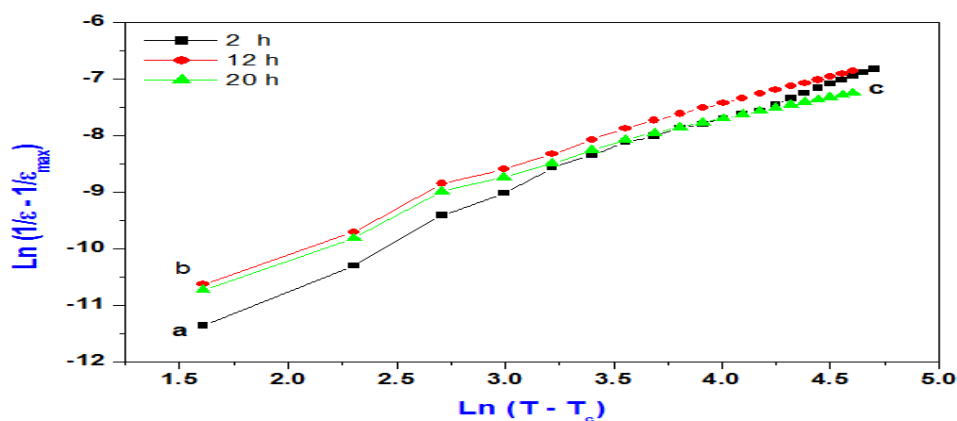

Fig. 8. A plot of ε_{max} versus the $\ln(1/\varepsilon - 1/\varepsilon_{max})$ versus $\ln(T - T_c)$ for $(Pb_{0.7}La0_{.2}\square_{0.1})TiO_3$ ceramics, with sintering time (a) = 2h, (b) = 12h, and (c) = 20h.