

Influence of Some Preparation Conditions on Debye's Relaxation Time and Related Properties of (Pb, La)TiO₃ Ceramics

M. K. Gergs

Physics Department, Faculty of Science (Qena),
South Valley University, Egypt

The chemical formula of the samples in this paper is $(\text{Pb}_{0.8125}\text{La}_{0.125}\text{Ti}_{0.0625})\text{TiO}_3$ and they are classified into two groups according to the condition of their preparation. The first group of samples was prepared under different sintering times. The other group was prepared under different sintering temperatures. Both groups of ceramics were used to study the influence of the previous conditions on the ferroelectric properties, Debye's relaxation time and the activation energy. The dielectric measurements have been carried out under electric field of frequencies equal to 1 KHz and 100 KHz. The result of first group showed that the peak value of the dielectric constant ϵ_{\max} increases and shifts slightly to higher temperatures on increasing the value of sintering time t_s . The value of ϵ_{\max} tends to saturation at $t_s \geq 18$ h. The critical relaxation times τ_c has a similar behavior as the dielectric peak ϵ_{\max} . In the result of second type of sample, the increasing in the value of dielectric peak ϵ_{\max} was faster at low sintering temperatures ($1433 \leq T_s < 1493$ K) and tends to saturation at ($T_s \geq 1523$ K). The critical relaxation time has a similar behavior as the same as ϵ_{\max} . The interpretation of the dielectric constant behavior is dependent strongly on the grain size and consequently the volume of the domain. Also, the values of Curie Weiss constant (C) and the activation energy as a function of t_s and T_s have been studied.

1. Introduction:

The effect of sintering time and temperature on the ferroelectric properties of any ferroelectric ceramics are closely related to crystallite size and therefore to the grain size [1]. The sintering time and temperature are considered as the essential factors for improving the quality of ceramics [2]. Many literatures [1-8] were published about the influence of increasing the

sintering time and temperature on the value of dielectric constant peak ϵ_{\max} and the grain size. McNeal *et al.* [4] described a theoretical model according to which the relaxation time increases as the domain width increases and vice versa. The investigation of Infrared spectroscopy which was studied by Dongol *et al.* [9] confirmed that the stretching frequency for $(\text{Pb}_{1-1.5x}\text{La}_x\text{TiO}_3)$ ceramics is dependent on the La content (x) and its maximum value at x equals to 0.125. The sample with the that concentration of La-ions is characterized by the highest value of force constant, binding energy and, hence, possess the more crystallization properties than the samples with other x-values. This is the reason for choosing such samples of the present paper. The present work aims to study the influence of sintering time and temperature on the dielectric properties and related features, such as the phase transition temperature T_c , Curie-Weiss constant C, Debye's relaxation time and, as consequence, the activation energy in the ferroelectric and paraelectric phases for ceramics. In this respect, we tried also to find the sintering time t_s and temperature T_s which provides the former samples with maximum value of the dielectric peak.

2. Experimental Procedures:

2.1. Sample preparation:

Specimens of ceramics with formula $(\text{Pb}_{0.8125}\text{La}_{0.125}\text{TiO}_3)$ were prepared according to the firing technique. The starting materials (99.9% purity PbO , TiO_2 and La_2O_3) in the proper stoichiometric ratios were homogenized by grinding in an agate ball mill and then pressed into discs at 20 MPa. The discs were then calcined at 750 °C for 2 hours and the calcined materials were thoroughly reground. The average particle size of the powder, in this way, was $\leq 2 \mu\text{m}$. The calcined powder was mixed with very small amount of distilled water and then pressed into disks at 40 MPa. The discs for the samples of first group were thereafter sintered at 1503 K in an oxygen atmosphere for 2, 4, 6, 8, 10, 12, 14, 16 and 18 h. The discs for the samples of second group were sintered at $T_s = 1433, 1463, 1493$ and 1523 K in an oxygen atmosphere for 4 h. Finally, the discs were mechanically treated.

2.2. Preparation of samples for dielectric measurements:

The relative dielectric constant ϵ_r of the samples can be calculated from the measured capacitance by using the formula:

$$\epsilon_r = d \cdot C / (A \cdot \epsilon_0)$$

where d , A , C and ϵ_0 are the sample thickness in m, the sample surface area in m^2 , the capacitance of the sample in farad and permittivity of free space, respectively. Note that $\epsilon_0 = 8.854 \times 10^{-12}$ F/m. Polishing process was performed for producing the samples of dielectric measurements with perfect circular and smooth faces. The two opposite faces of the samples were coated with a thin film of aluminum.

2.3. Measuring instruments:

A cell for the dielectric measurements in the high temperature range (25 - 750 °C) was used. The sample was fixed in a position between two copper electrodes which were connected to an automatic capacitance meter (RLC-meter model SRS) for measuring the capacitance of the sample at two values of frequency (10^3 and 10^5 Hz). The temperature was measured with an accuracy of $\pm 1\%$ by means of a calibrated thermocouple connected to a digital meter. The system was working as a part of computer programs for processing the output form RLC-meter and the used digital meter for measuring the temperature.

3. Results and discussion:

3.1. Samples with different sintering time:

3.1.1. Dielectric constant and phase transition temperature:

Figure (1) shows the temperature dependence of the dielectric constant of $(Pb_{0.8125}La_{0.1250}\square_{0.0625})TiO_3$ ceramics as a function of different values of sintering time ($t_s = 2, 8, 12$ and 18 h) at electric field frequency equals to 1KHz. The peak value of the dielectric constant ϵ_{max} increases and shifts to the higher temperatures with increasing the value of t_s . The value of ϵ_{max} was changed from 6500 to 11500 when t_s was increased from 2 to 18 h. A similar behaviour can be observed in Fig. (2), where, the frequency of electric field equals to 100KHz. The values of ϵ_{max} accordingly, are 6150 and 10587 at $t_s = 2$ and 18 hours, respectively. It is noticed that the peak of dielectric constant ϵ_{max} in case of $t_s = 18$ h is sharper than that of the peak ϵ_{max} at $t_s = 2$ h. Fig. (3) represents a plot of the phase transition temperature T_c versus the sintering time t_s . The values of T_c increase slightly with increasing the values of t_s .

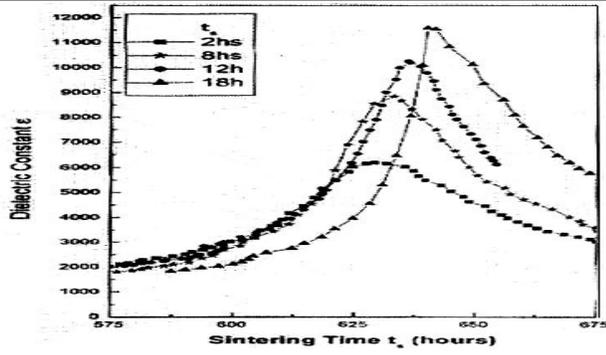


Fig.(1): The temperature dependence of the dielectric constant ϵ for $(\text{Pb}_{0.8125} \text{La}_{0.125} \square_{0.0625})\text{TiO}_3$ ceramics at different values of the sintering time ($t = 2, 8, 12, 18$ h). The frequency is equal to 1 kHz.

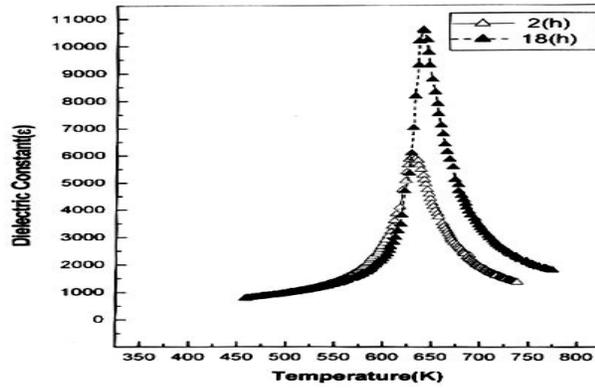


Fig.(2): The temperature dependence of the dielectric constant ϵ for $(\text{Pb}_{0.8125} \text{La}_{0.125} \square_{0.0625})\text{TiO}_3$ ceramics at two values of the sintering time ($t_s = 2$ and 18 h). The frequency of electric field is equal to 100 kHz.

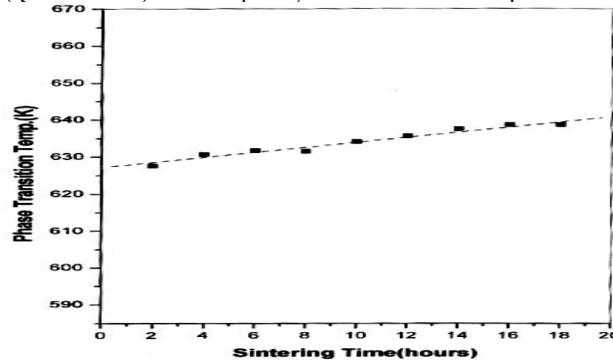


Fig. (3): A plot the phase transition temperature T_c versus the sintering time t_s for samples with formula $(\text{Pb}_{0.8125} \text{La}_{0.125} \square_{0.0625})\text{TiO}_3$.

3.1.2. Debye's relaxation time:

Figure (4) shows the temperature dependence of Debye's relaxation time for $(\text{Pb}_{0.8125}\text{La}_{0.125}\square_{0.0625})\text{TiO}_3$ ceramics as a function of sintering time ($t_s = 2$ and 18 h) at frequency of electric field equals to 100 kHz. The behavior of the relaxation time, as seen in this figure, is in contrary to the behavior of the dielectric constant, ϵ . The results revealed that the phase transition temperature for these materials is characterized with minimum value of relaxation time. This result is in a good agreement with those known from literature which was reported by Kang *et al.* [10]. The relaxation time at the Curie temperature τ_c shifts towards higher temperatures with increasing the value of t_s . The higher value of τ_c is observed at $t_s = 18$ h.

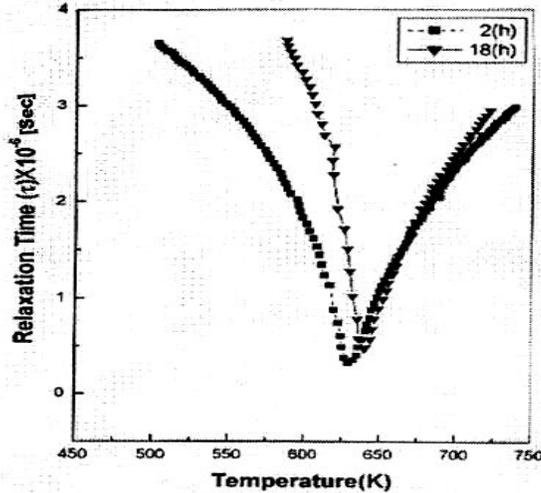


Fig. (4): The temperature dependence of Debye's relaxation time τ for $(\text{Pb}_{0.8125}\text{La}_{0.125}\square_{0.0625})\text{TiO}_3$ ceramics at two values of the sintering of time ($t_s = 2$ and 18 h). The frequency of electric field is equal to 100 KHz.

Figure (5) represents a plot of both relaxation time at the Curie temperature τ_c and dielectric peak ϵ_{max} at frequencies equal to 1 and 100 kHz versus the sintering time t_s for $(\text{Pb}_{0.8125}\text{La}_{0.125})\text{TiO}_3$ -ceramics. The rate of increasing of both values of τ_c and ϵ_{max} are rapid at low sintering time t_s but it becomes slow at its higher values. Both values of τ_c and ϵ_{max} tend to saturation at $t_s \geq 18$ h. The results in this figure show a remarkable difference between the values of ϵ_{max} which corresponds to the two frequencies (1 and 100 kHz) at relatively highest sintering time ($t_s = 18$ h). The highest value of τ_c at $t_s = 18$ h

corresponds the highest value of ϵ_{\max} . Hence, from the above result and the literatures [1, 3, 4 & 8], one can conclude that increasing of sintering time t_s produces an increase in the volume of the domain and, therefore, an increase in the critical relaxation time τ_c , i.e., the critical relaxation time τ_c is proportional to the volume of the domain. This result is in good agreement with the theoretical model which was reported before [4].

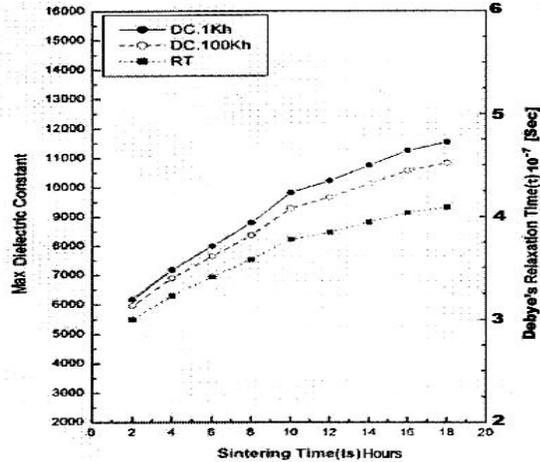


Fig. (5): A plot of ϵ_{\max} and Debye's relaxation time τ versus the sintering time t_s for samples with formula $(\text{Pb}_{0.8125}\text{La}_{0.125}\square_{0.0625})\text{TiO}_3$, since DC(1K), DC(100K) and Rt represent, respectively, the values of ϵ_{\max} at frequencies equal to 1, 100 kHz and τ .

3.1.3. Curie- Weiss Constants and Activation Energy:

Figure (6) shows the temperature dependence of the inverse dielectric constant ϵ^{-1} for $(\text{Pb}_{0.8125}\text{La}_{0.125}\square_{0.0625})\text{TiO}_3$ ceramics as a function of sintering time ($t_s=2$ and 18 h) at frequency of electric field equals to 1KHz. This figure is necessary for determination the Curie Weiss constant (C') from the linear relationship between ϵ^{-1} and temperature near the Curie temperature T_c . It is remarkable that the region of the inverse dielectric constant around T_c at t_s equals to 2 hours is broader than that of the same corresponding region of the inverse dielectric at t_s equals to 18 hours. This result means that the value of Curie Weiss constant (C') at the highest sintering time ($t_s = 18$ h) is smaller than its value at t_s equals to 2 h. Then, the quality of investigated samples for the ferroelectric properties is improved by increasing the time of sintering temperature.

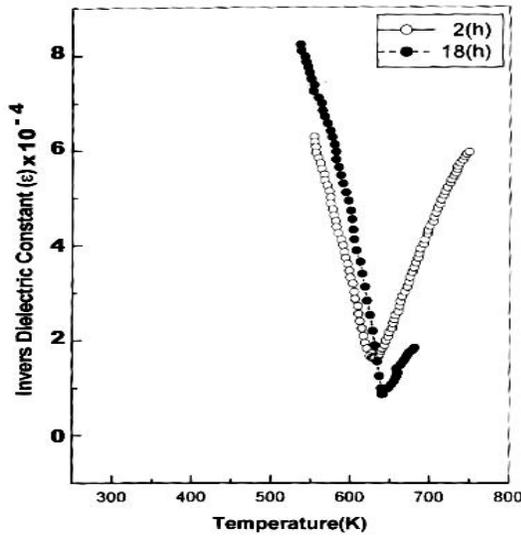


Fig. (6): The temperature dependence of the inverse dielectric constant ϵ^{-1} for $(\text{Pb}_{0.8125}\text{La}_{0.125}\square_{0.0625})\text{TiO}_3$ ceramics at two values of the sintering time ($t_s = 2$ and 18 h).

Figure (7) represents a plot of both the Curie Weiss constant (C^{\cdot}) and activation energy (E_{af} , E_{ap}) versus the sintering time t_s , where E_{af} and E_{ap} are the activation energy in ferroelectric and paraelectric phases. In whole range of t_s the value of E_{ap} is higher than the value of E_{af} . The interpretation of this behavior is related with crystal structure which is tetragonal before the Curie temperature T_C and cubic after that. The rate of decreasing for both values of C and E_a is rapid at low sintering time t_s while it slows down at higher values. The both values of E_a and C^{\cdot} were reached a minimum values at $t_s \geq 18$ h. It is evident from this figure that the variations of the values of E_a are not only dependant upon the crystal structure of ceramics but also it depends on the Curie Weiss constant (C^{\cdot}) and consequently the quality of ceramics.

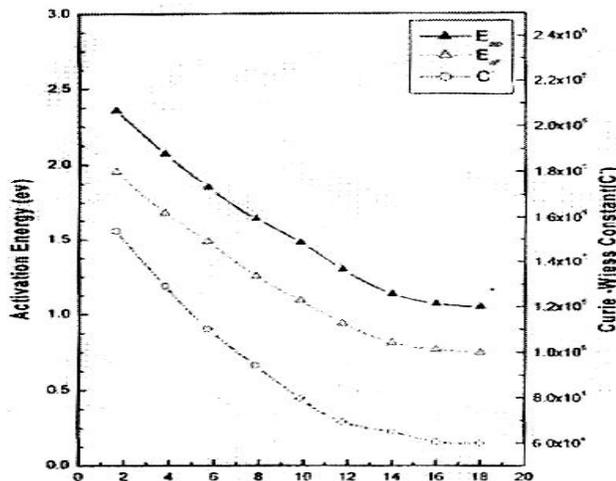


Fig. (7): A plot of activation energy at the ferroelectric (E_{af}) and paraelectric phases (E_{ap}) and Curie Weiss constant C^{\cdot} versus the sintering time t_s for samples with formula $(\text{Pb}_{0.8125}\text{La}_{0.125}\square_{0.0625})\text{TiO}_3$.

3.2. Samples with different sintering temperature:

3.2.1. Dielectric Constant and Phase Transition Temperature:

Figure (8) shows the temperature dependence of the dielectric constant of $(\text{Pb}_{0.8125}\text{La}_{0.125}\text{□}_{0.0625})\text{TiO}_3$ ceramics as a function of sintering temperature ($T_s = 1433$ and 1523 K) at frequencies of electric field equal to 1KHz and 100KHz. The peak value of the dielectric constant ϵ_{max} increases and shifts slightly to higher temperatures on increasing the value of T_s . At frequency of electric field equal to 1 kHz the value of ϵ_{max} is changed from 2700 to 8000 when T_s increased from 1433 to 1523 K. A similar behavior can be seen at an electric field frequency of 100 kHz but the value of ϵ_{max} is changed from 2400 to 7000 at the same variation of T_s . It is noticed that the peak of dielectric constant ϵ_{max} at T_s equals to 1523 K is sharper than the peak ϵ_{max} at $T_s = 1433$ K. The previous results can be summarized in Fig. (9), which represents a plot of both ϵ_{max} and T_c versus the values of T_s . At frequency of electric field equal to 1 kHz, the increasing of the value of dielectric peak ϵ_{max} was faster at low sintering temperatures ($1433 \leq T_s < 1493$ K) and tends to the saturation at ($T_s \geq 1523$ K). The phase transition temperature, T_c , increases slightly with increasing the values of T_s . The interpretation of increasing ϵ_{max} with increasing the values of T_s is related with the grain size and the domain volume which is expected to be increased with increasing of values of T_s as already reported [5-8].

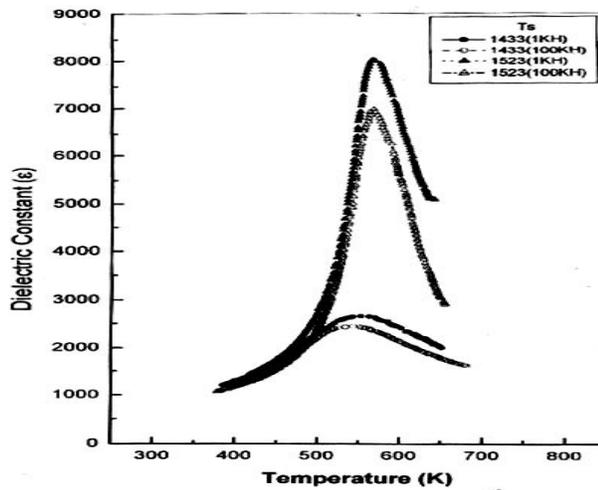


Fig. (8): The temperature dependence of the dielectric constant ϵ for $(\text{Pb}_{0.8125}\text{La}_{0.125}\text{□}_{0.0625})\text{TiO}_3$ ceramics at two values of the sintering temperature T_s , The lowest and the highest value of T_s are 1433 and 1523 K. The frequencies of electric field are equal to 1 and 100 kHz.

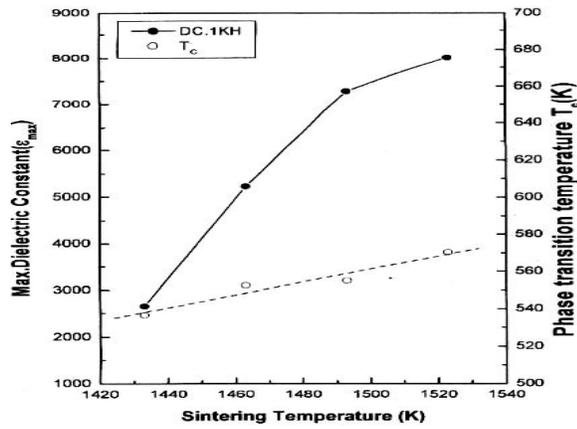


Fig. (9): A plot of ϵ_{\max} and the phase transition temperature T_c versus the sintering temperature T_s for samples with formula $(\text{Pb}_{0.8125} \text{La}_{0.125} \square_{0.0625})\text{TiO}_3$, since DC(1K) and T_c represent, respectively, values of ϵ_{\max} and T_c at frequency equal to 1 KHz and T_c .

3.1.2. Curie - Weiss Constants:

Figure (10) shows the temperature dependence of the inverse dielectric constant for $(\text{Pb}_{0.8125} \text{La}_{0.125} \square_{0.0625})\text{TiO}_3$ ceramics as a function of sintering temperature ($T_s = 1433$ and 1523K) at frequency of electric field equal to 1KHz. It is clearly remarkable that the region of the inverse dielectric constant around the Curie temperature at T_s equal to 1433 K is broader than the same corresponding region of the inverse dielectric at $T_s = 1523$ K.

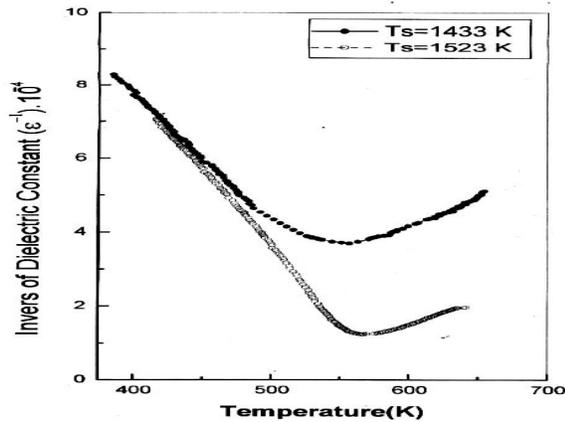


Fig.(10): The temperature dependence of the inverse dielectric constant ϵ^{-1} for $(\text{Pb}_{0.8125} \text{La}_{0.125} \square_{0.0625})\text{TiO}_3$ ceramics. The frequency of electric field = 1 kHz.

versus the values of T_s . It is noticed that the rate of decreasing of the values of Curie-Weiss constant (C^- and C^+) is, relatively, rapid for the lower values of T_s and becomes slowly at $1493 \leq T_s \leq 1523$ K. Since the quality of ferroelectric material for the dielectric behavior is inversely proportional to the value of Curie-Weiss constant C . So, the results reflect the role of sintering temperature on improving the quality of ceramics for the dielectric properties, and as consequence, the ferroelectric properties, especially, at $T_s = 1523$ K.

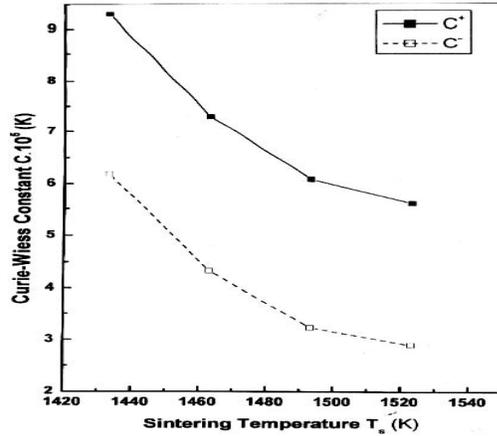


Fig. (11): A plot of Curie Weiss constant C^- and C^+ vs sintering temperature T_s for samples with formula $(\text{Pb}_{0.8125}\text{La}_{0.125}\square_{0.0625})\text{TiO}_3$. The frequency of electric field = 1 kHz.

3.2.3. Debye's Relaxation Time and Activation Energy:

Figure (12) shows the temperature dependence of Debye's relaxation time in $(\text{Pb}_{0.8125}\text{La}_{0.125}\square_{0.0625})\text{TiO}_3$ ceramics as a function of sintering temperature ($T_s=1433$ and 1523 K) at frequency of electric field equal to 100 kHz. The behavior of the relaxation time, as seen in this figure, is in opposite direction with the dielectric constant, ϵ . The relaxation time at the Curie temperature, τ_c , shifts to higher temperatures with increasing T_s and the highest value at $T_s = 1523$ K.

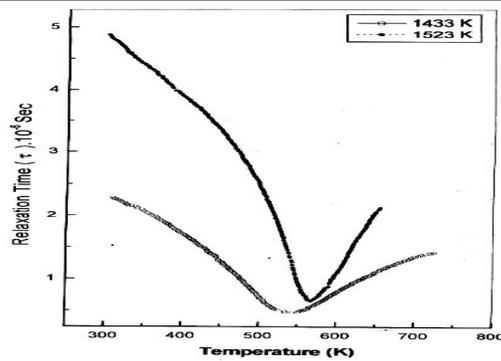


Fig. (12): The temperature dependence of Debye's relaxation time τ for $(\text{Pb}_{0.8125} \text{La}_{0.125} \square_{0.0625})\text{TiO}_3$ ceramics at two sintering temperature. The lowest and the highest value of T_s are 1433 and 1523 K. The frequency of electric field = 100 kHz.

Figure (13) represents a plot of both τ_c and ϵ_{\max} versus sintering temperature T_s . In this figure the variation of the critical Debye's relaxation time τ_c is similar to the variation of the value of ϵ_{\max} . The highest value of τ_c at $T_s = 1523$ K is corresponded to the highest value of ϵ_{\max} . Hence, the critical Debye's relaxation time τ_c is proportional with sintering temperature T_s , since both ϵ_{\max} and the grain size are also proportional with sintering temperature T_s as mentioned in literatures [5-7]. Then, the critical Debye's relaxation time τ_c is proportional with the grain size and consequently the volume of the domain. This conclusion copes with those known from literature which was reported by Mcneal *et al.* [4].

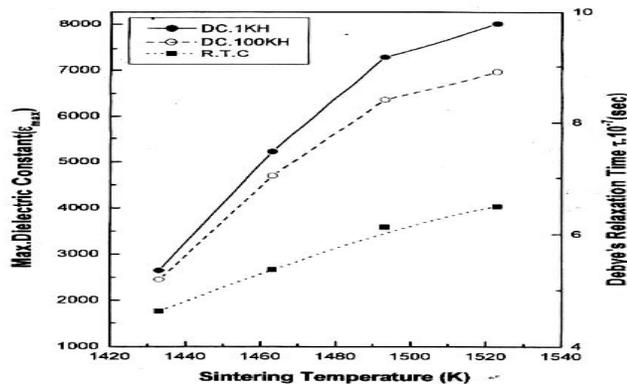


Fig. (13): A plot of ϵ_{\max} and Debye's relaxation time τ vs sintering temperature T_s for samples of formula $(\text{Pb}_{0.8125} \text{La}_{0.125} \square_{0.0625})\text{TiO}_3$. DC (1K), DC (100K) and Rt represent, respectively, the values of ϵ_{\max} at frequencies equal to 1 and 100 kHz and τ .

Figure (14) represents the relationship between the activation energy in ferroelectric and paraelectric phase (E_{af} , E_{ap}) and the variation in sintering temperature T_s for $(\text{Pb}_{0.8125}\text{La}_{0.125}\square_{0.0625})\text{TiO}_3$ ceramics. It is noticed that the rate of decreasing of the values of E_{af} and E_{ap} is, relatively, rapid for the lower values of T_s and becomes slowly at $1493 \leq T_s \leq 1523$ K. It is also clear from this figure that the value of E_{ap} is higher than the value of E_{af} . This conclusion means that the activation energy is dependant upon the type of the phase transition in ferroelectric materials, i.e., it depends on crystal structure of ceramics.

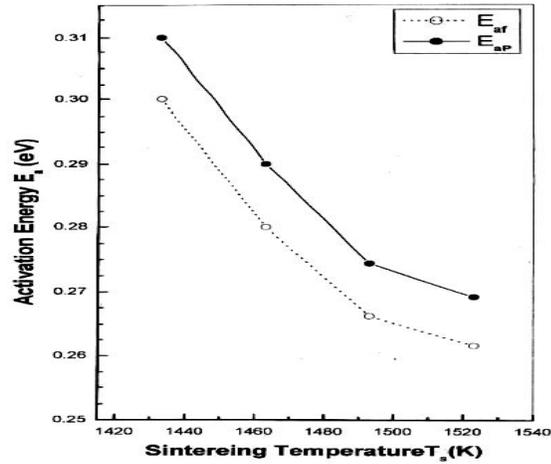


Fig. (14): A plot of activation energy E_{af} and E_{ap} versus the sintering temperature T_s for samples with formula $(\text{Pb}_{0.8125}\text{La}_{0.125}\square_{0.0625})\text{TiO}_3$.

Figure (15) represents a plot of both E_{af} and the Curie Weiss constant (C) versus sintering temperature T_s . Both E_{af} and C are decreased with increasing of T_s . It is obvious from this figure that the variation of the values of E_a is not only dependant upon the phase transition temperature but it also depends on the Curie Weiss constant (C) and as a consequence, the quality of ceramics. The equations which were used for the calculation the value of the Debye's relaxation time τ and its critical values τ_c can be seen in reference [11].

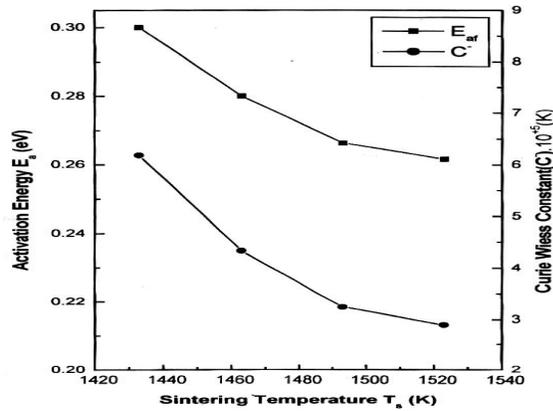


Fig. (15): A plot of activation energy at the ferroelectric phase E_{af} and Curie Weiss constant C^- versus the sintering temperature T_s for samples with formula $(Pb_{0.8125}La_{0.125}□_{0.0625})TiO_3$.

4. Conclusions:

In the samples with the formula $(Pb_{0.8125}La_{0.125}□_{0.0625})TiO_3$, the value of ϵ_{max} at 1 kHz is higher than at 100kHz for the same sintering time t_s . The sample with $t_s = 18$ h is characterized, relatively, by the highest value of dielectric constant peak, which is related strongly with increasing the grain size and consequently the volume of the domain. This sample has also the lowest value of Curie-Weiss constant and, hence, it is characterized with the best quality for the ferroelectric properties and its applications. The variation of the activation energy values are not only dependant upon the crystal structure of ceramics but also depends on the Curie-Weiss constant (C^- and C^+). The increasing of the value of dielectric peak ϵ_{max} was faster for low sintering temperatures ($1433 \leq T_s < 1493$ K) and tended to saturation at ($T_s \geq 1523$ K). The critical relaxation times show a similar behavior as that of ϵ_{max} . The phase transition temperature T_c increased slightly while the Curie-Weiss constants (C^- and C^+) decreased with increase of sintering temperature T_s . The activation energy is a function of Curie temperature and Curie-Weiss constant which is considered as an indicator to the quality of ceramics for ferroelectric properties.

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