

## Effect of La-ions on Debye's Relaxation Time and Activation Energy of $(\text{Pb}_{1-1.5x}\text{La}_x)\text{TiO}_3$ Ceramics

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*The present paper is essentially a study of the influence La -ions on Debye's relaxation time and consequently the activation energy in  $(\text{Pb}_{1-1.5x}\text{La}_x)\text{TiO}_3$  ceramics. The dielectric measurements have been carried out under electric field of frequencies equal to 1 and 100 KHz. The results which were calculated by Debye's equation for the ferroelectric materials revealed that the sample with  $x= 20$  mole % La characterizes with highest value of the critical relaxation time. The interpretation of the anomaly peak of dielectric constant of the sample with  $x= 20$  mole % La was attributed to the increasing the volume of the domain. Curie-Weiss constant (C) and activation energy as a function of La- content have been determined. The calculated activation energy for the samples was found to be dependent on three parameters: La-ions, phase transition temperature and quality of ceramics which, in turn, is a function of Curie-Weiss constants.*

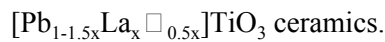
### 1.Introduction:

Lanthanum is one of the essential elements for producing dense  $\text{PbTiO}_3$  ceramics with good piezoelectric properties where  $\text{La}^{3+}$ -ions occupy  $\text{Pb}^{2+}$ -sites and generate cation vacancies. X-ray investigation for  $(\text{Pb}_{1-1.5x}\text{La}_x)\text{TiO}_3$  ceramics reveals a decrease of tetragonality (c/a) with increasing La content. At room temperature it decreases from 1.06 for  $x = 0$  to 1 for  $x = 0.25$  [1-3]. Salzer et al [4] reported a work about the FTIR spectroscopy for the bending vibration in  $(\text{Pb}_{1-1.5x}\text{La}_x)\text{TiO}_3$  ceramics. The components of FTIR spectra for the bending vibration are changed by varying the concentration of La content between 0 and 100 mol %. The vibration bands seem to be attributed to:  $\text{PbTiO}_3$ ,  $(\text{Pb}_{0.625}\text{La}_{0.25})\text{TiO}_3$ ,  $(\text{Pb}_{0.25}\text{La}_{0.5})\text{TiO}_3$  and  $\text{LaTiO}_3$  – octahedral. The results support the model of incorporation of La – ions in the crystal at Pb -sites and a binomial distribution of the four stoichiometric species. The present author [5] has already published the experimental and theoretical studies on some ferroelectric properties of  $(\text{Pb}_{1-$

$_{1.5x} \text{La}_x \square_{0.5x} \text{TiO}_3$  ceramics. In these studies it was observed that the behavior of dielectric peak  $\epsilon_{\text{max}}$  was similar to the behavior of single vacancies at the same La-content. The highest value of  $\epsilon_{\text{max}}$  at  $x=0.2$  had the maximum number of single vacancies. Wu *et al.* [6] reported for the perovskite structure with general formula  $\text{ABO}_3$  that, the A-site vacancies reduce the local stress in the domains which undergo domain switching. Besides was reported in many literatures

[7-12] about, the increasing of dielectric peak  $\epsilon_{\text{max}}$  with increasing the value of grain size. McNeal *et al.* [13] in a theoretical model concluded that as the domain width increases the relaxation time increases and vice versa. Also, the domain width, as reported by King *et al.* [14], is proportional with the grain size.

The aim of our investigation is to study the influence of La -ions on Debye's relaxation time and, consequently, the activation energy for the samples of general formula:



## 2. Debye's Relaxation Time Model:

In the ferroelectric materials, the dielectric constant changes with temperature according to the relation,

$$\epsilon_r'(\omega) = B + C/(T - T_c) \quad (1)$$

where B and C are constants independent on temperature. This relation is known as the Curie-Weiss law. The parameter C and  $T_c$  are called the Curie-Weiss constant and Curie Temperature, respectively. The second term in Eqn.(1) is usually much larger than the first one. Therefore, one can ignore B and rewrite the previous equation in the following form:

$$\epsilon_r'(\omega) \approx C/(T - T_c) \quad (2)$$

From Debye's equation, the frequency dependent dielectric constant is given by:

$$\epsilon_r'(\omega) = \epsilon_r(\infty) + \{[\epsilon_r(0) - \epsilon_r(\infty)]/(1 + \omega^2 \tau^2)\} \quad (3)$$

$\epsilon_r(\infty)$  is the dielectric constant at high frequency and equals to  $n^2$ , where n is optical index of refraction. So, Eqn. (3) can be re-written in another form by

putting  $\epsilon_r(\infty) = n^2$ , then

$$\epsilon_r'(\omega) - n^2 = [\epsilon_r(0) - n^2] / (1 + \omega^2 \tau^2) \tag{4}$$

For the ferroelectric materials  $n^2$  is negligible with respect to  $\epsilon_r'$  and  $\epsilon_r(0)$ , then

$$\epsilon_r'(\omega) = \epsilon_r(0) / (1 + \omega^2 \tau^2) \tag{5}$$

From Debye's equation, the frequency dependent dielectric loss is given by:

$$\begin{aligned} \epsilon_r''(\omega) &= [\epsilon_r(0) - \epsilon_r(\infty)] \cdot \omega \tau / (1 + \omega^2 \tau^2) \\ &\approx \epsilon_r(0) \cdot \omega \tau / (1 + \omega^2 \tau^2) \end{aligned} \tag{6}$$

By substituting from Eqn. (5) in Eqn.(6), we obtain

$$\epsilon_r''(\omega) \approx \epsilon_r'(\omega) \cdot \omega \tau \tag{7}$$

and by substituting from Eqn. (2) in Eqn. (7), we obtain

$$\epsilon_r''(\omega) \approx C \cdot \omega \tau / (T - T_c) \tag{8}$$

Then,

$$\tau \approx \epsilon_r''(\omega) \cdot (T - T_c) / \omega C \tag{9}$$

So, when  $T \rightarrow T_c$  then  $\tau \rightarrow 0$  and from Eqn. (5)

$$\epsilon_{r \max}' = \epsilon_r(0),$$

This conclusion means that the dielectric peak at the phase transition temperature in ferroelectric materials can be considered as  $\epsilon_r'(0)$  in Debye's equation for the dielectric materials. But  $\epsilon_{r \max}'$  is a function of the frequency, i.e.,

$$\epsilon_r'(0) \geq \epsilon_{r \max}'(\text{low frequency}) > \epsilon_{r \max}'(\text{high frequency})$$

So, Eqn. (9) can not be used for the calculation of the relaxation time, especially, at phase transition temperature  $T_c$ . Then the previous model which was described by Eqn. (9) can be modulated into another simplified model and taken into consideration that, with the variation of temperature, when  $T \rightarrow T_c$  then  $\tau \rightarrow \tau_c$ , where  $\tau_c$  is relatively the smallest value for the relaxation time in the ferroelectric material and corresponding the highest value of dielectric constant. So, according to the value of  $\tau_c$  and Eqn.(5),  $\epsilon_{r \max}'$  for the low and

high frequency can be described by Eqns.(10 and 11)

$$\epsilon'_{\max}(L) = \epsilon_{\max}(0) / (1 + \omega^2 \tau_c^2) \quad (10)$$

$$\epsilon'_{\max}(H) = \epsilon_{\max}(0) / (1 + \omega^2 \tau_c^2) \quad (11)$$

From both last equations one can find an equation to describe the value of  $\tau_c$  as in the Eqn. (12)

$$\tau_c = \{ [R(\epsilon_{\max}) - 1] / [\omega_H^2 - \omega_L^2 R(\epsilon_{\max})] \}^{1/2} \quad (12)$$

where  $R(\epsilon_{\max}) = \epsilon'_{\max}(L) / \epsilon'_{\max}(H)$ .

By substituting with the value of  $\tau_c$ , which can be determined from Eqn. (12) in Eqn. (11), the value of  $\epsilon_{\max}(0)$  can be obtained. By substituting the value of  $\epsilon_{\max}(0)$  instead of  $\epsilon_r(0)$  in Eqn. (5), one can obtain the value of  $\tau$  (Debye's relaxation time) as a function of temperature. Hence, the equation which gives the value of  $\tau$  for all the ranges of temperature, except at phase transition temperature, can be re-written as in Eqn. (13)

$$\tau = \omega^{-1} \{ [ \epsilon_{\max}(0) / \epsilon_r(T) ] - 1 \}^{1/2} \quad (13)$$

The values of  $\tau$  from the previous equation are corrected for the whole range of temperature both for ferroelectric phase and for paraelectric phase except at  $T = T_c$ ,  $\tau = \tau_c$ .

The relation between the relaxation time  $\tau$  and the activation energy  $E_a$  is well known and described by this formula:

$$\tau = \tau_0 \exp E_a / k T \quad (14)$$

where  $\tau$  is considered as Debye's relaxation time,  $k$  is the Boltzmann's constant. The activation energy  $E_a$  (eV) can be obtained from the slope of the straight line between  $[\ln(\tau^{-1})]$  and  $(1000/T)$  in the case of plotting the former equation, then,

$$\ln(\tau^{-1}) = \ln(\tau_0^{-1}) - (E_a/c)(1000/T) \quad (15)$$

where  $c = 1000/k = 0.08616$ .

### 3. Experimental Procedures:

#### 3.1. Sample Preparation:

Specimens of general formula  $(\text{Pb}_{1-1.5x} \text{La}_x \square_{0.5x})\text{TiO}_3$  were prepared according to the firing technique. The starting materials (99.9% purity  $\text{PbO}$ ,  $\text{TiO}_2$  and  $\text{La}_2\text{O}_3$ ) in the corresponding 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 1023K for 2 hours and then they were reground thoroughly. The average practical 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 were thereafter sintered at 1503 K in an oxygen atmosphere for 6 hours, and finally the discs were mechanically treated.

#### 3.2. Measuring Cell and Circuit:

The cell employed in the present work for the dielectric measurements can be used for temperature range (25 – 750 °C) as shown in Fig. (1). The sample is situated between two copper electrodes which were connected to an automatic capacitance meter (RLC-meter model SRS) for the purpose of measuring the capacitance of the sample at two corresponding frequencies (103 and 105 Hz). The temperature was measured with accuracy of  $\pm 1\%$  by means of thermocouple connected to a digital meter. The system was matched to a computer programs for treating the output results obtained form RLC-meter and temperatures digital meter.

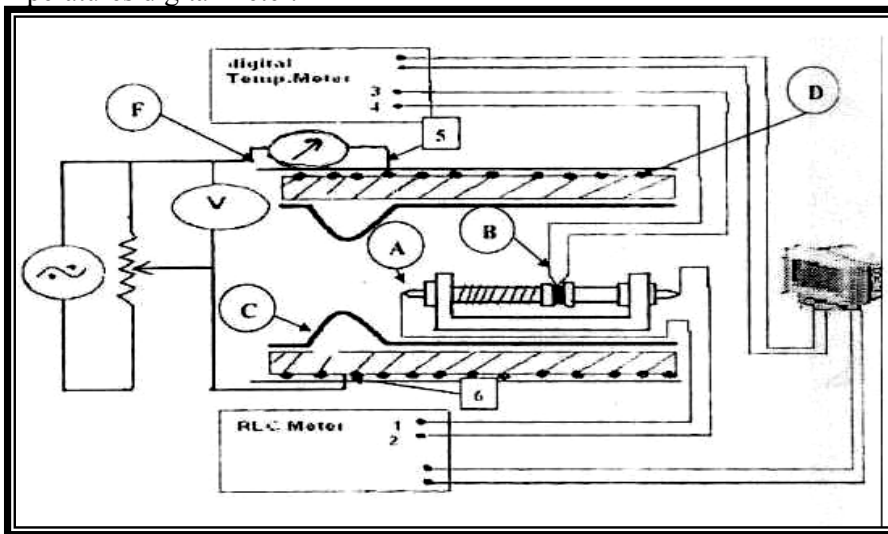
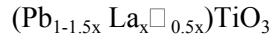


Fig. (1): Block diagram of the measuring system of the dielectric constant (A , B , C , D, and F are sample holder, thermocouple, cell holder, heater and isolating tube, respectively).

## 4. Results and Discussions:

### 4.1. Dielectric Constant and Phase Transition Temperature:

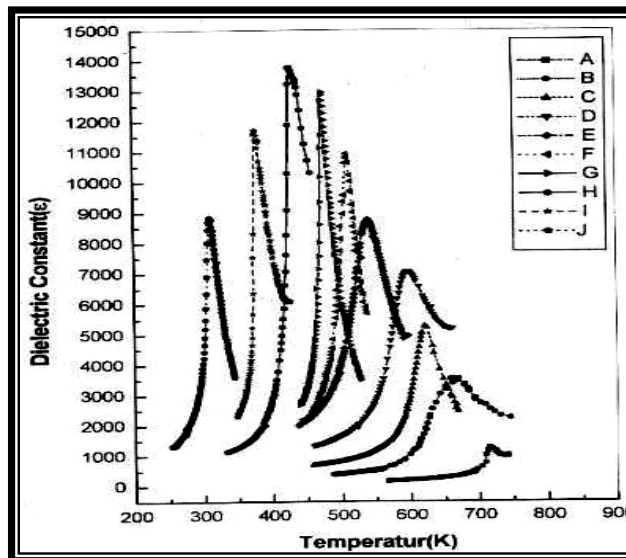
The general formula for the prepared samples which were considered in this experiment is:



where  $x = 0.05, 0.075, 0.10, 0.15, 0.175, 0.20, 0.225, 0.25$ . For simplicity, the general formula of the above samples can be written in this form:



Figure (2) shows the temperature dependence of the dielectric constant of  $(\text{Pb}_{1-1.5x} \text{La}_x)\text{TiO}_3$  -ceramics as a function of the La- content at frequency equal to 1KHz. The peak of the dielectric constant,  $\epsilon_{\text{max}}$  shifts to lower temperatures on increasing the La content. The higher value for  $\epsilon_{\text{max}}$ , equals to 13767 at  $x = 0.20$ . On increasing the La content above  $x = 0.20$ , the dielectric peak decreases and has lower value of  $\epsilon_{\text{max}}$ . The similar behavior for the temperature dependence of the dielectric constant of  $(\text{Pb}_{1-1.5x} \text{La}_x)\text{TiO}_3$  -ceramics as a function of the La- content at frequency equals to 100KHz is observed in Fig. (3). The higher value of  $\epsilon_{\text{max}}$  in this case equals to 12065 at  $x = 0.20$ . In Fig. (4), one can see that the values of the phase transition temperature ( $T_c$ ) decreases linearly as the La content increases, this result is in good agreement with the work published by Windsch *et al.* [1].



**Fig. (2):** The temperature dependence of the dielectric constant  $\epsilon$ , where A, B, C, D, E, F, G, H, I, J represent La content  $x = 0.025, 0.05, 0.075, 0.1, 0.125, 0.15, 0.175, 0.2, 0.225$  and  $0.25$ , respectively. The frequency of electric field = 1 kHz.

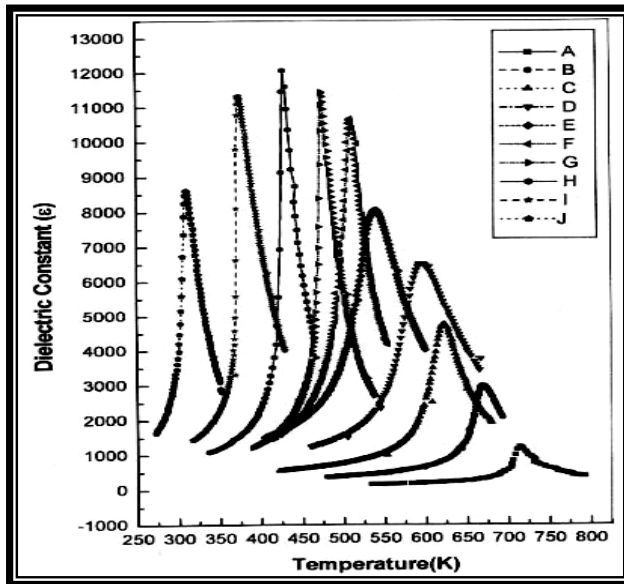


Fig. (3): The temperature dependence of the dielectric constant  $\epsilon$  where B, C, D, E, F, G, H, I, J represent La content (x) with values equal to 0.05, 0.075, 0.1, 0.125, 0.15, 0.175, 0.2, 0.225 and 0.25, respectively. The frequency of electric field = 100 kHz.

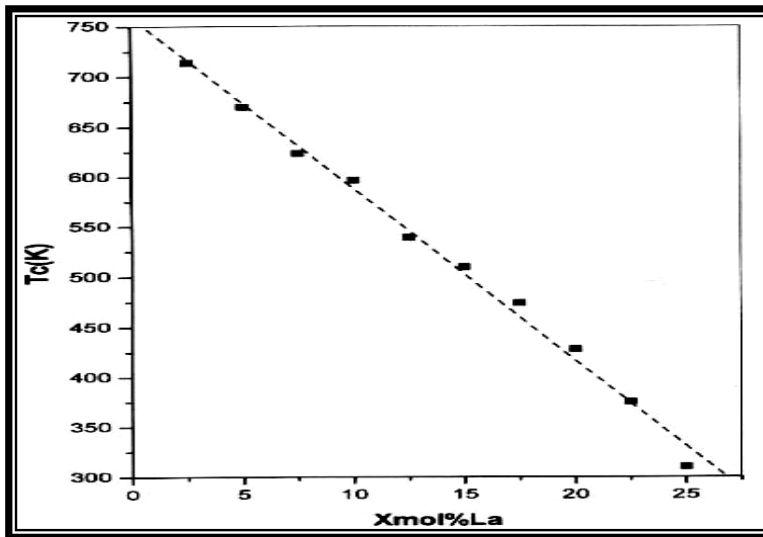
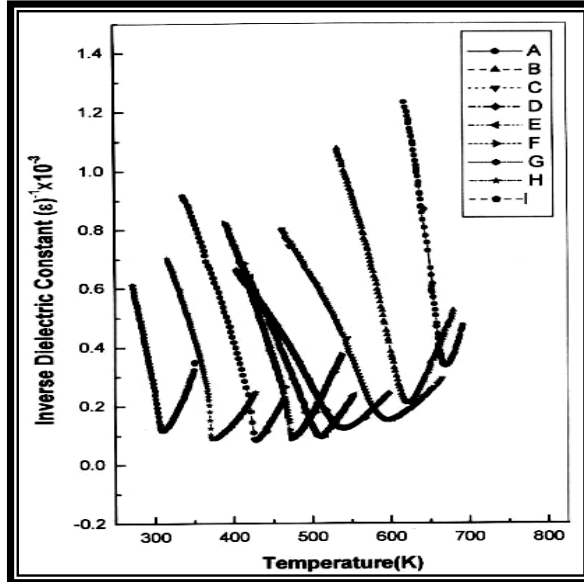


Fig. (4): The phase transition temperature  $T_c$  versus the La content for ceramic samples.

#### 4.2. Curie- Weiss Constants:

Figure (5) illustrates the temperature dependence of the inverse dielectric constant  $\epsilon^{-1}$  for  $(\text{Pb}_{1-1.5x} \text{La}_x) \text{TiO}_3$  -ceramics as a function of the La-content at frequency equals to 100 kHz. The minima were shifted toward the lower temperatures on increasing the La content. The lower value of  $\epsilon^{-1}_{\text{max}}$  exists at  $x = 0.20$ . This result is needed for the calculation of the Curie-Weiss constants which is, in turn, important for studying the quality of ceramics.



**Fig. (5):** The temperature dependence of the inverse dielectric constant  $\epsilon^{-1}$  where B, C, D, E, F, G, H, I, J represent La content (x) with values equal to 0.05, 0.075, 0.1, 0.125, 0.15, 0.175, 0.2, 0.225 and 0.25, respectively. The frequency of electric field = 100 kHz.

Figure (6) represents the relationship between the Curie-Weiss constant (C) and the variation of La content for  $(\text{Pb}_{1-1.5x} \text{La}_x) \text{TiO}_3$  ceramics at frequency equal to 100 kHz. As one can see the Curie-Weiss constant decreases with increasing of La content. However, when the La content increases more than the value equals to 20%, the Curie-Weiss constant increases. Hence, the sample with  $x = 0.20$  represents the best one among the other values of La-content. Accordingly this sample is of optimum quality for ferroelectric properties.



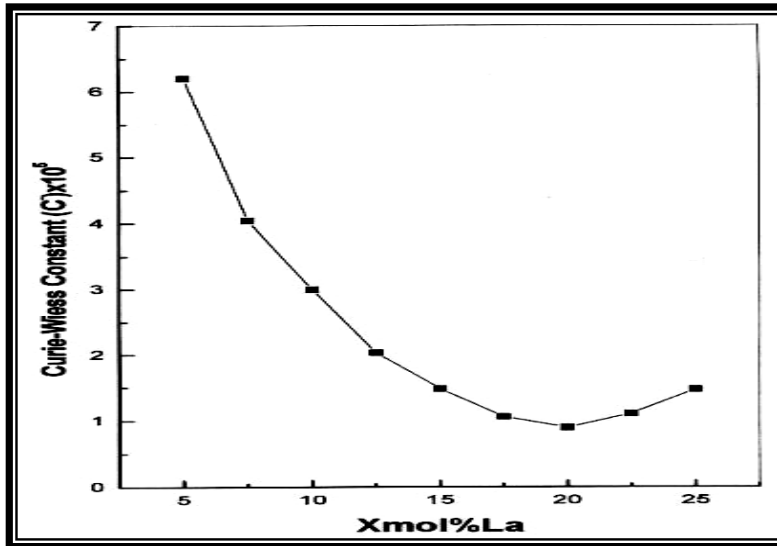


Fig. (6): A plot of Curie Weiss constant C versus La content.

#### 4.3. Debye's Relaxation Time and Activation Energy :

Figure (7) shows the temperature dependence of Debye's relaxation time in  $(\text{Pb}_{1-1.5x}\text{La}_x)\text{TiO}_3$ -ceramics as a function of the La-content at frequency equal to 100 kHz. The behavior of the relaxation time, in contrary to the behavior of dielectric constant  $\epsilon$  with temperature. The relaxation time at the peak of dielectric constant ( $\tau_c$ ) shifts towards lower temperatures on increasing the La-content. Again the highest value for  $\tau_c$  is at  $x = 0.20$ . Fig. (8) represents a plot of both  $\tau_c$  and  $\epsilon_{\text{max}}$  at frequencies equals to 1 kHz and 100 kHz versus the La content for  $(\text{Pb}_{1-1.5x}\text{La}_x)\text{TiO}_3$ -ceramics. This figure shows clearly that, in all the range of the variation of La content, the value of  $\epsilon_{\text{max}}$  at a frequency equal to 1 kHz is higher than its value at frequency equal to 100 kHz for the same La content. The maximum difference between them at  $x = 0.20$ . So, the results denote that the sample with  $x = 20$  mol %La is characterized by the highest value of dielectric constant. This result reflects the relationship between the peak of dielectric constant and highest number of single vacancies which is accompanied the former sample. Hence, the volume of the domain in this case is expected to be expanded through the vacancies in ceramics. In this figure, the variation in  $\epsilon_{\text{max}}$  at the two values of frequency (1 kHz and 100 kHz) is also similar to the change which has occurred in the critical Debye's relaxation time  $\tau_c$ . It is evident that the highest value of  $\tau_c$  at  $x = 0.20$  corresponds to the highest value of  $\epsilon_{\text{max}}$ . This result proves the correctness of our suggestion about the

influence of increasing the number of single vacancies in unit cells on increasing the volume of domain.

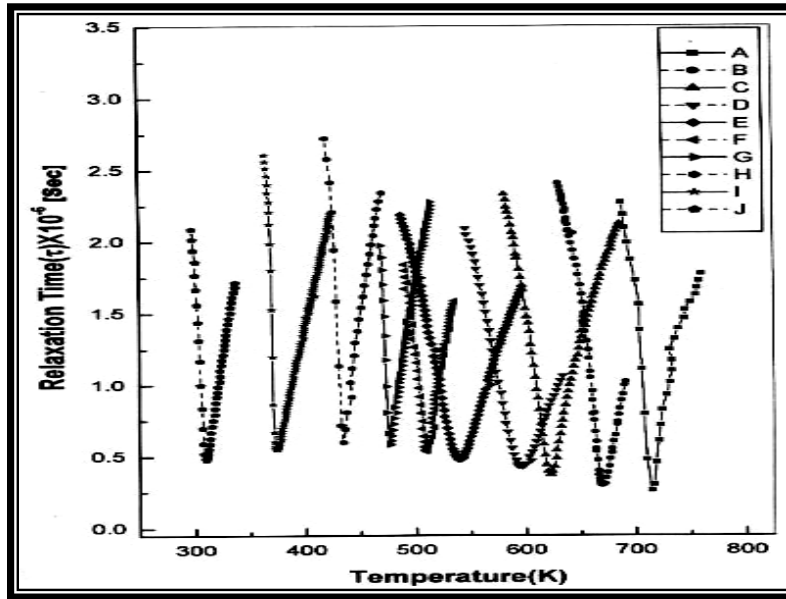


Fig. (7): The temperature dependence of Debye's relaxation time  $\tau$  (A, B, C, D, E, F, G, H, I, J represent La content (x) with values equal to 0.025, 0.05, 0.075, 0.1, 0.125, 0.15, 0.175, 0.2, 0.225 and 0.25, respectively). The frequency of electric field = 100 kHz.

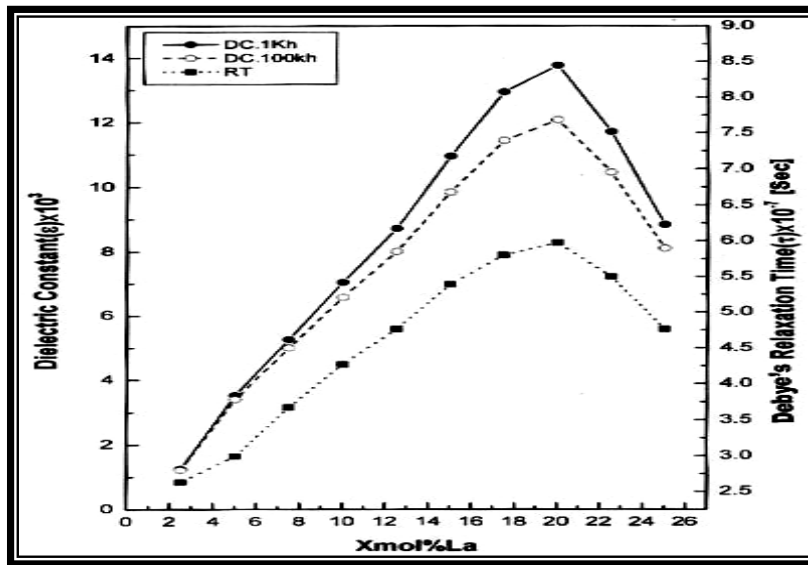


Fig. (8): A plot of  $\epsilon_{max}$  and Debye's relaxation time  $\tau$  versus the La content (x) at frequencies equal to 1 and 100 KHz, where DC is  $\epsilon_{max}$

Figure (9) represents a plot of both  $E_a$  and the Curie-Weiss constant ( $C$ ) versus La content for  $(\text{Pb}_{1-1.5x} \text{La}_x)\text{T iO}_3$  ceramics. It is clear from this figure that the value of  $E_{a_p}$  is higher than the value of  $E_{a_f}$ . Both  $E_{a_f}$ ,  $E_{a_p}$  and  $C$  are decreasing rapidly with increasing the La content and reaches its minimum value at  $x = 18\%$ . Even though when La content increased more than  $x = 18\%$  mol %, the behaviour of  $E_a$  is not similar to the Curie-Weiss constant ( $C$ ). It is clear from this figure that the variation of the values of  $E_a$  is not only dependant on the phase transition temperature and the structure of the ferroelectric materials but also it is dependant on the Curie-Weiss constant ( $C$ ) and as a consequence, the quality of ceramics.

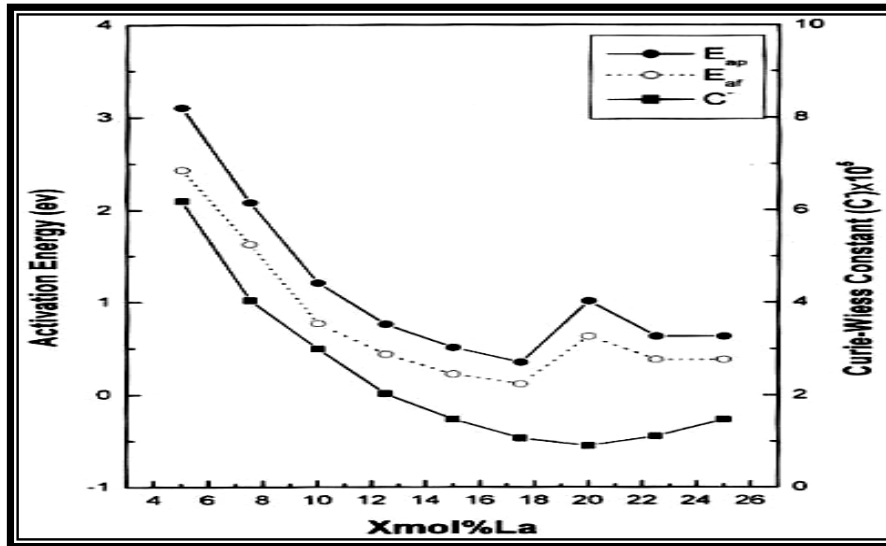


Fig. (9): A plot of activation energy  $E_a$  and Curie-Weiss constant  $C$  versus the La content ( $x$ ).

## 5. Conclusions:

The experimental values of the phase transition temperature ( $T_c$ ), decreases linearly on increasing the La content.. For all samples, the behaviour of the critical relaxation time  $\tau_c$  is similar to that of dielectric peak  $\epsilon_{\max}$ . This result was important for understanding the relationship between the critical relaxation time  $\tau_c$  and the volume of domain. The phase transition temperature, the structure and the quality of ceramics which in turn is a function of the Curie-Weiss constant were responsible for the variation, which was observed in the values of  $E_{a_f}$  and  $E_{a_p}$ .

**References**

1. W. Windsch, M.K.Gergs , D. Michel , H. Schlembach , A . Salzer and P. Reich, *Ferroelectric* **109** ,119 (1990).
2. M.K.Gergs, *Egypt .J. Sol.* **19** (1) 129 (1996).
3. D. Hennings and G . Rosentein, *Mat. Res.Bull.***7**, 1505 (1972).
4. R. Salzer, J. Dressler, M.K.Gergs, D. Michel, H. Schlembach, W. Windsch, and P. Reich, *J. Molecular Structure* **219**,177 (1990).
5. M. K. Gergs, *Egypt. J. Sol.* **19**, (2), 305 (1996).
6. L. Wu, C. C. Wei, T.S. Wu and C.C.Teng, *J. Phys. C: Solid State Phys.* **16**, 2803 (1983).
7. C.Chan, Y. Hsieh, C. Yang and P. Cheng, *Ceramics International* **29**, 495 (2003).
8. S. L. Swartz , T. R. Shrout , W. A.Schulze and L. E. Cross, *J. American Ceramics Society* **67** (5), 311(1984).
9. M.Chen, X.Yao and L. Zhang, *Ceramics International* **28**, 201 (2002).
10. B.S. Kang and S. K.Choi, *Solid State Communications* **121** ,441 (2002).
11. S. Garcia, J. Portelles, F. Martinez, R. Fount, J. R .Quinones, *Revista Mexicana De Fisica* **49** (1), 15 (2003).
12. L . Szymczak, Z. Ujma, J. Handerek, J. Kapusta, *Ceramics International* **30**, 1003 (2004).
13. M.P.Mcheal, S.J.Jang and R.E.Newnham, *J. Applied Physics* **83** (6), 3288 (1998).
14. G.King and E.K. Goo, *J. American Ceramics Society* **73** (6), 1534 (1990).