Dielectric Properties, Debye′s Relaxation Time and Activation Energy of [(Pb$_{1-x}$ Sr$_x$) $_{1-1.5z}$La$_z$] TiO$_3$ Ceramics

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The samples were classified into three types according to the concentration of La-content. The dielectric measurements have been carried out under electric field (1 KHz and 100 KHz). The samples of the first type (z=3 mole % La) exhibited two unusual peaks for dielectric constant. The first peak lies at x= 20 and the second one lies at x=40 mole %Sr. The samples of the second type (z= 6 mole % La) showed a similar behaviour but the first peak shifts to x= 25 and the second shifts to 35 mole %Sr. The samples of the third type (z=9 mole %La) are characterized with only one anomaly peak for dielectric constant at x= 30 mole %Sr. In comparison, it is evident that both contents of Sr- and Pb–ions for the abnormal peak in the third type of samples existed in the other types of samples for the first and second peak, respectively. The Sr content of 26 % and Pb content of 60.5% are responsible for the first and second peaks. respectively. The behaviour of critical Debye′s relaxation time for all samples of this investigated is similar to the behaviour of dielectric constant peak. The interpretation of anomalous peaks for dielectric constant is discussed on the basis of the critical Debye′s relaxation time and consequentially the volume of the domain. Finally, the activation energy for the samples of third type (z=9 mole %La) is found to be dependant on Sr content and the phase transition temperature which is in turn a function of crystal structure .

1. Introduction:

Strontium titanate $SrTiO_3$ is one of the most popular materials since the discovery of its dielectric properties [1]. It was been widely used to fabricate some electronic ceramic components, such as grain boundary layer capacitors (GBLC), sensors, and so on. Like most compounds with general formula ABO_3, $SrTiO_3$, it has a simple cubic perovskite structure at room temperature. The Curie temperature (T_c) of pure $SrTiO_3$ is about 44 K, which can shift to the higher temperature by Ba^{2+} or Pb^{2+} substituting for Sr^{2+}. The composite

perovskite structure materials, such as $(Sr,Ba)TiO_3$, $(Sr,Pb)TiO_3$ have been developed to fabricate some devices. Strontium titanate $SrTiO_3$ [2], is known to be an incipient ferroelectric and a quantum paraelectric. At low temperature, the dielectric constant in $SrTiO_3$ attains very high values. Various impurities substituted in $SrTiO_3$ at A-and B-positions have been studied. It is shown that divalent impurities substituting for Sr^{2+} such as Ba, Pb and Cd induce a ferroelectric phase transition with the transition temperature T_c.

In lanthanum containing lead titanate [3], La^{3+} ions occupy Pb^{2+} sites and generate vacancies in the cation lattice $(Pb_{1-1.5x}La_x\square_{0.5x})$ TiO_3. With increasing La^{3+} content [4] the transition temperature T_c decreases linearly. At x = 0.25 the value of T_c approaches room temperature. The present author [5] has already published the experimental and theoretical studies on some ferroelectric properties of $(Pb_{1-1.5x} La_x\square_{0.5x})TiO_3$ ceramics. In these studies it was observed that the behavior of dielectric peak ε_{max} was similar to the behavior of single vacancies at the same La – content. The highest value of ε_{max} at x = 0.2 had the maximum number of single vacancies. Wu *et al.* [5] reported about the perovskite structure with general formula ABO_3 where the A-site vacancies reduce the local stress in the domains which undergo domain switching. Tura *et al.* [7] showed in their studies that the grain size is increased with decreasing the internal stress. Also, the domain width, as reported by G. King *et al.* [8], is proportional to the grain size. It has been reported [9-14] about increasing dielectric peak ε_{max} with increasing of grain size. McNeal *et al.* [15] have reported about a theoretical model which concluded that as the domain width increases the relaxation time increases and vise versa.

Preparation of the samples of present work was based on previous introduction. According to the concentration of Sr- and La- ions, the samples of present work can be classified into three of types with the following general formula: $[(Pb_{1-x}Sr_x)_{0.955}La_{0.03}\square_{0.015}]TiO_3$, $[(Pb_{1-x}Sr_x)_{0.91}La_{0.06}\square_{0.03}]TiO_3$ and $[(Pb_{1-x} Sr_x)_{0.865}La_{0.09}\square_{0.045}] TiO_3$.

The aim of this investigation is to study the dielectric properties and their related features, such as the phase transition temperature T_c, Debye's relaxation time, and as, a consequence, the activation energy of the ferroelectric and paraelectric phases for mentioned before ceramics bearing in mind to find the suitable concentration of Sr- and La- ions which provides the former samples with optimum ferroelectric properties.

2. Experimental Procedures:

2.1. Preparation technique of the samples:

Specimens of the general formula $(Pb_{1-x} Sr_x)_{1-1.5z} La_z \square_{0.5z})TiO_3$ were prepared according to the procedures of the usual firing technique. The starting materials (99.9% purity PbO, $SrCO_3$, TiO_2 and La_2O_3) in corresponding stoichiometric ratios were homogenized and pressed into discs. The discs were then calcined at the range of temperature between 700 and 850 °C. This was done on the basis of the calibration line between the two calcined temperatures where one of them for $PbTiO_3$ - and the other for $SrTiO_3$ – ceramics, for two hours. The calcined powder was pressed into discs. The discs were thereafter sintered at the temperature ranging between 1210 and 1250 °C, according to the prementioned technique but for two sintered temperatures, for 4 hours in an oxygen atmosphere. The samples are classified into three types according to the concentrations of La-contents. The values of z for the three types equal to 0.03, 0.06 and 0.09, respectively.

2.2. Measuring instruments:

The cell employed in the present work for the dielectric measurements is described before [17]. The sample is positioned 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 (10^3 and 10^5 Hz). The temperature was measured with an 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 digital meter for measuring the temperature.

3. Results and Discussion:

3.1. Dielectric constant and phase transition temperature:

3.1.1. $(Pb_{1-x}Sr_x)_{0.955}La_{0.03}TiO_3$ Ceramics:

Figure (1) represents the temperature dependence of the dielectric constant ε for $(Pb_{1-x}Sr_x)_{0.955}La_{0.03}TiO_3$- ceramics at different Sr–contents under electric field of frequency equals to 1 KHz. This figure contains a set of curves corresponding to seven Sr contents (x = 0 , 10 , 20 , 30 , 40 , 50 and 60 mole%). The general behavior of each curve is the same where ε grows with temperature reaching a maximum value and then decreases. The value of ε_{max} appears at the phase transition temperature (from ferroelectric to paraelectric phase). From this figure we may conclude the following:-

- The peak value of the dielectric constant ε_{max} shifts towards lower temperatures with increasing the Sr content.
- Two peaks for ε_{max} are observed. They are at x= 20 and 40 mol% Sr with value of ε_{max} equal to 4933 and 5668, respectively.
- A similar behavior can be seen in Fig. (2) where the same work was repeated but under an electric field of frequency equals to 100 KHz for the same type of ceramic. The same abnormal peaks was also observed at the same Sr content. The values of ε_{max} are equal to 4729 and 5382, respectively. The same observation as in case of 1KHz was found where T_c values decreases with increasing Sr content.
- In all ranges of variations of Sr-contents as shown in Fig.(3), the values of ε_{max} at frequency equal to 1 kHz is higher than its value at frequency equal to 100 KHz for the same corresponding Sr-content .
- Value of ε_{max} for the second peak (x = 0.4 mol Sr) is higher than that of the first peak.
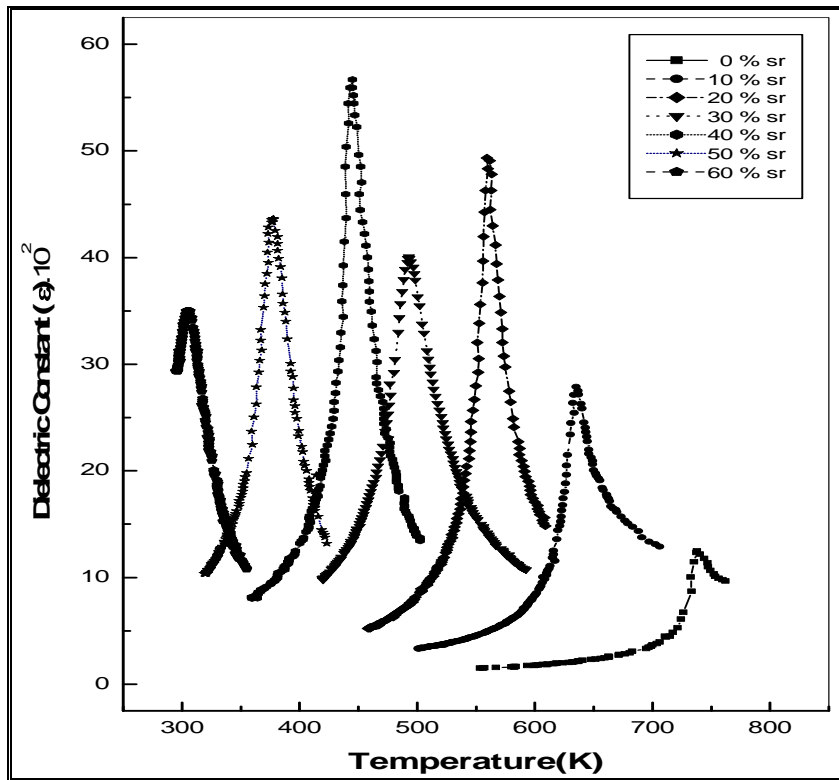

Fig.(1): The temperature dependence of the dielectric constant ε for samples with structure formula $(Pb_{1-x}Sr_x)_{0.955}La_{0.03}TiO_3$ (the frequency of electric field equal to 1KHz).
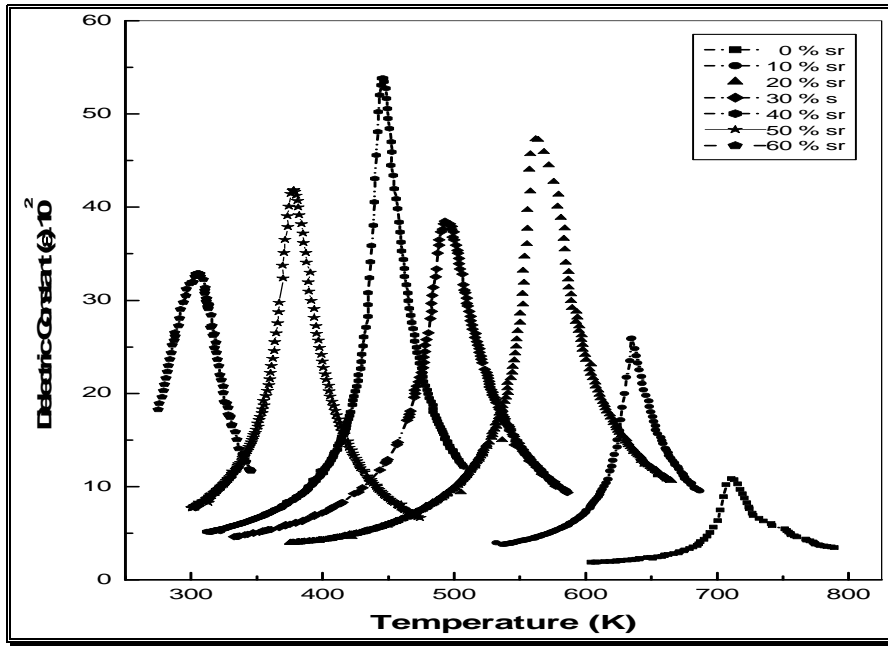
Fig. (2): The temperature dependence of the dielectric constant ε for samples with structure formula $(Pb_{1-x}Sr_x)_{0.955}La_{0.03}TiO_3$ (the frequency of electric field equal to 100 kHz).

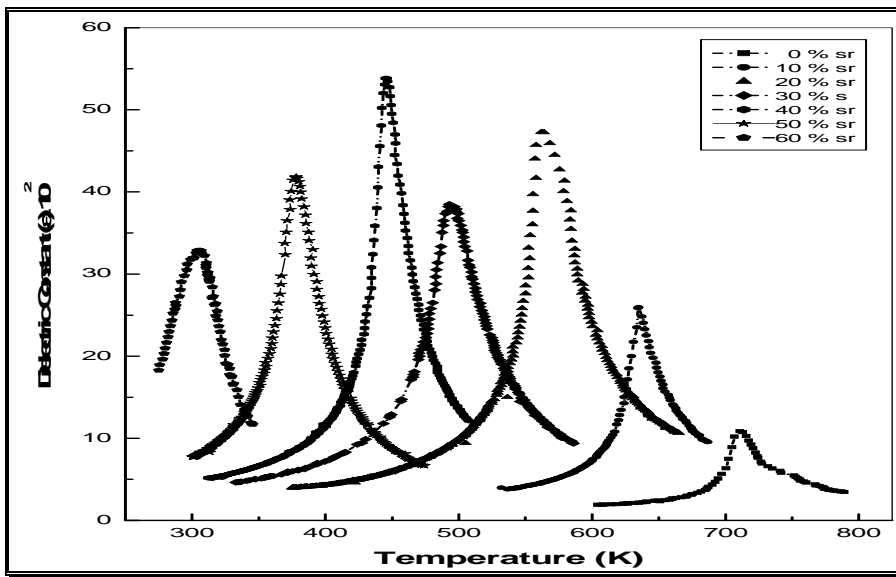**Fig. (3):** A plot of ε_{max} and the phase transition temperature (T_c) verses the Sr content for samples with formula $(Pb_{1-x}Sr_x)_{0.955}La_{0.03}TiO_3$.

3.1.2. $(Pb_{1-x}Sr_x)_{0.91}La_{0.06}TiO_3$ Ceramics:

Generally the previous behavior which was obtained before, can be seen for $(Pb_{1-x}Sr_x)_{0.91}La_{0.06}$ TiO_3- ceramics . However the two peaks are obsereved at x equals to 25 and 35 mol% Sr, where as the values of ε_{max} equal to 7700 and 8070 respectively. This is done under the influence of 1KHz electric field. A similar behavior was observed under another higher electric field with frequency equals to 100 KHz for the same type of ceramic. In this case the two peaks are also appeared at x equals to 0.25 and 0.35 mol % Sr with the values of ε_{max} equals to 7336 and 7560, respectively. For this purpose Figure (4) is depicted. It is clear that the behavior of ε_{max} in both the solid   line (1 KHz) and the dashed one (100 kHz) is the same. Also, it can be seen from the same curve, i.e Fig. (4) that the phase transition temperature T_c decrease linearly with increasing of Sr-content. This result is logic, since, the phase transition temperature T_c of $SrTiO_3$ equals to 44 K as reported in reference [1].
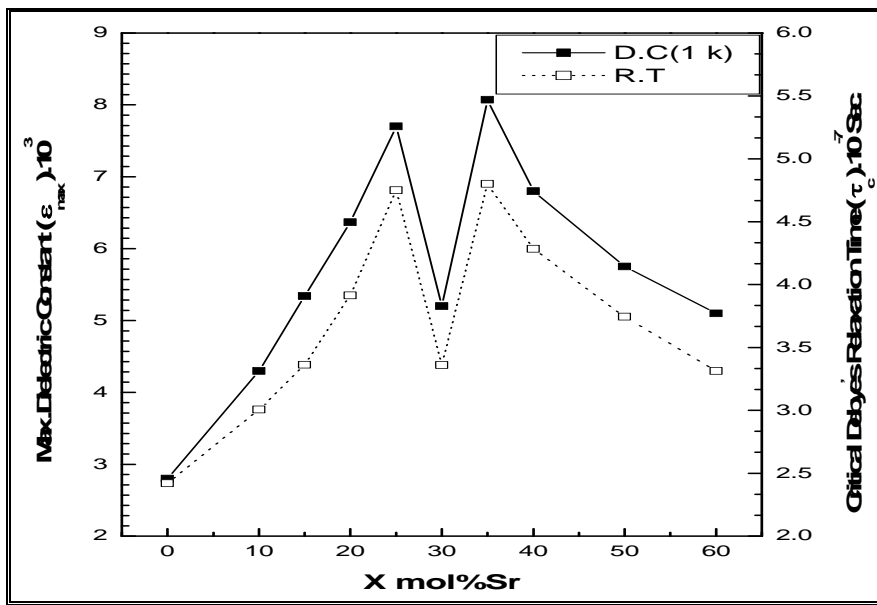

Fig. (4): A plot of ε_{max} and the phase transition temperature (T_c) verses the Sr content for samples with formula $(Pb_{1-x}Sr_x)_{0.91}La_{0.06}TiO_3$**.**

3.1.3. $(Pb_{1-x}Sr_x)_{0.865}La_{0.09}TiO_3$ Ceramics:

Figure (5) represents the temperature dependence of the dielectric constant for $(Pb_{1-x}Sr_x)_{0.865}La_{0.09}$ TiO_3 - ceramics as a function of Sr content under electric field frequency equals to 1KHz. Variation of ε against T has usual style where ε increase monotonically with increasing T till the transition

temperature. After which it decreases again. This is natural as a result of sample transition from ferroelectric to paraelectric mode. We sum up the results as follows:-

- The peak value of dielectric constant ε_{max} shifts to lower temperatures on increasing the Sr content.
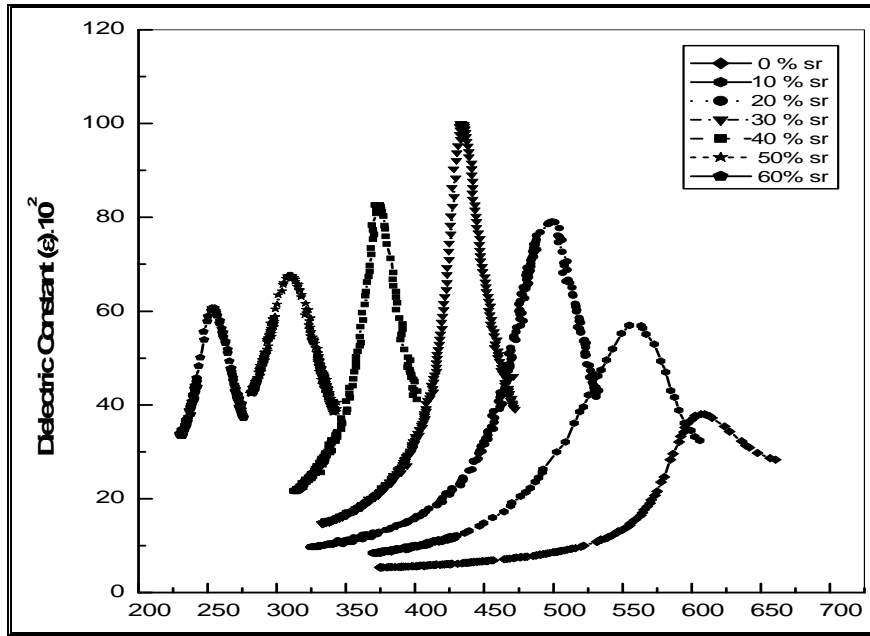- There is only one anomaly peak at x equals to 30 mol % Sr corresponding to $\varepsilon_{max} = 10000$.

Fig. (5): The temperature dependence of the dielectric constant ε for samples with structure formula $(Pb_{1-x}Sr_x)_{0.87}La_{0.09}TiO_3$ (the frequency of electric field equal to 1 kHz).

Figure (6) was depicted in the same way except for the electric field with frequency equals to 100 kHz for the same type of ceramic. The values of ε_{max}, is equal to 9034 at x=0.3 mol% Sr. For all ranges of variations for Sr-contents ,the value of ε_{max} at frequency equals to 1KHz is higher than its value at frequency equals to 100KHz for the same concentration of Sr content. For spotting some light on this point Fig. (7) is presented . One can see the quite similarity between the dashed and solid line. The phase transition temperature T_c decrease linearly with increasing of Sr-contents.
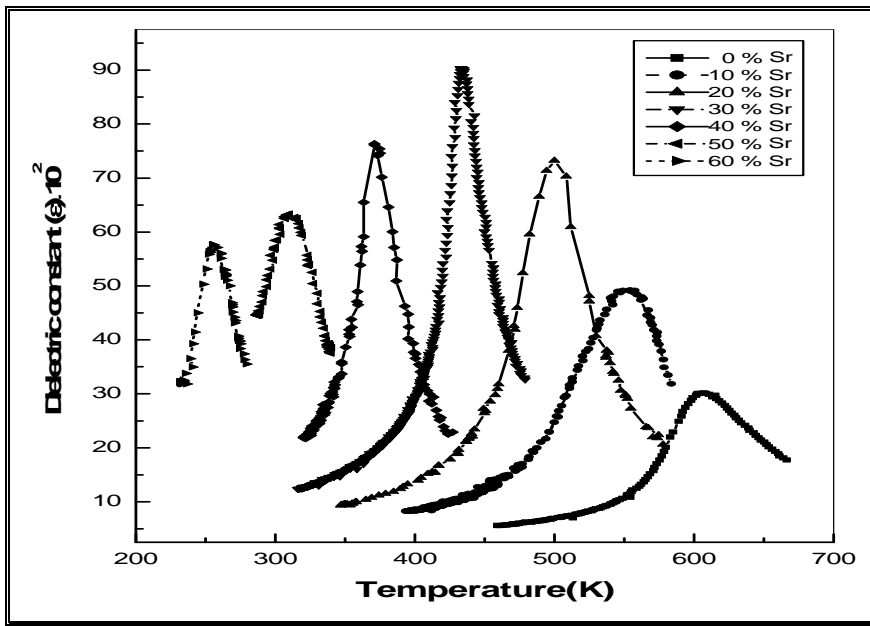
Fig. (6): The temperature dependence of the dielectric constant ε for samples with structure formula $(Pb_{1-x}Sr_x)_{0.87}La_{0.09}TiO_3$ (the frequency of electric field equal to 100 kHz).

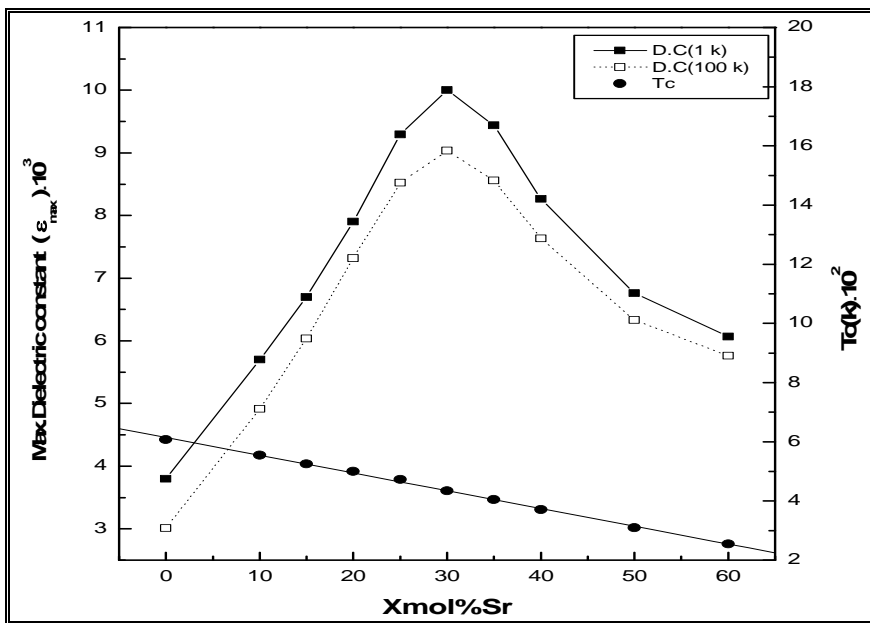**Fig. (7):** A plot of ε_{max} and the phase transition temperature (T_c) verses the Sr content for samples with formula $(Pb_{1-x}Sr_x)_{0.87}La_{0.09}TiO_3$.

All the values of dielectric peaks by the three types of samples are represented as a function of Sr content (see Fig.8) or as a function of Pb content (see Fig.9). From these figures one can conclude that the both contents of Sr- and Pb-ion for the anomaly peak in the third type of samples are existed in other types of samples for the first and second peak, respectively. Hence, the Sr content equals to 26 % and Pb content equals to 60.5 %are responsible for the first and second anomaly dielectric peak, respectively. So, the present investigation revealed the existence of five distinguished samples for the dielectric constant peak ε_{max}, the formula of these samples are $(Pb_{0.70}Sr_{0.26}La_{0.03}\square_{0.02})TiO_3, Pb_{0.61}Sr_{0.35}La_{0.03}\square_{0.02})TiO_3, Pb_{0.65}Sr_{0.26}La_{0.06}\square_{0.03})TiO_3$, $(Pb_{0.61}Sr_{0.31}La_{0.06}\square_{0.03})TiO_3$ and $(Pb_{0.61}Sr_{0.26}La_{0.09}\square_{0.05})TiO_3$.

The gradual increases in the value of dielectric constant peak ε_{max} is function of the single vacancies which , according to the reference (5) increased with increasing of La-ions, since the La content in present investigation is ($0 \leq z \leq 0.09$) i.e. less than 20 mol %.
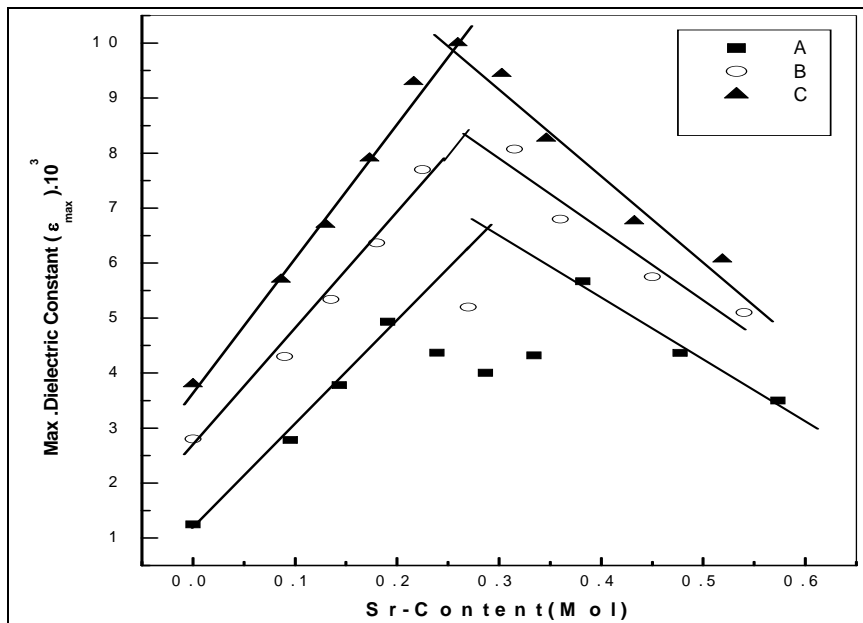

Fig. (8): A plot of ε_{max} verses the Sr content (Y) for samples with formula $(Pb_{1-x}Sr_x)_{1-1.5z}La_zTiO_3$, where A, B and C for z = 0.03 , 0.06 and 0.09, respectively, N.B: Y= x . (1-1.5z).
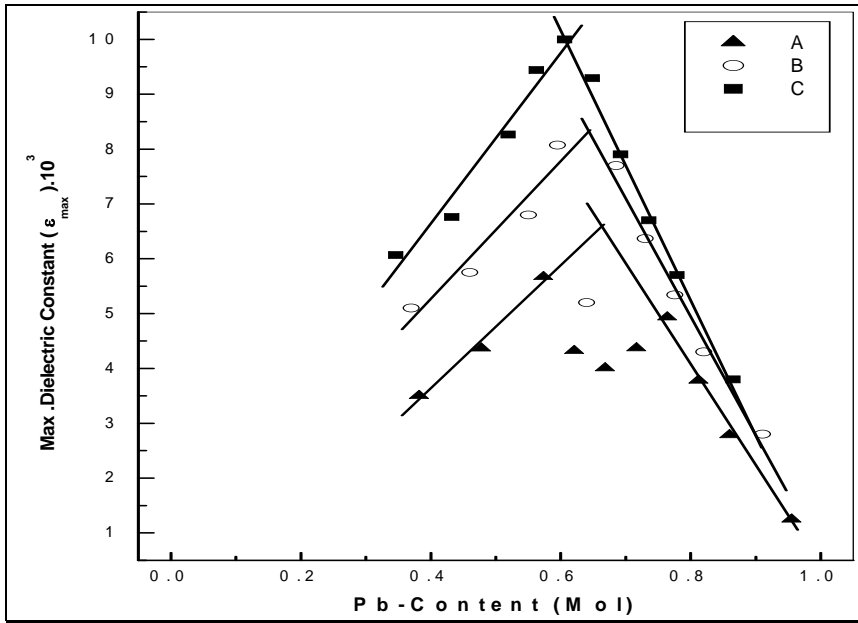
Fig. (9): A plot of ε_{max} verses the Pb content (1-Y) for samples with formula $(Pb_{1-x}Sr_x)_{1-1.5z}La_zTiO_3$, where A, Band C for z = 0.03, 0.06 and 0.09, respectively, N.B: Y= x . (1-1.5z).

3.2. Debye's Relaxation Time(τ):-

3.2.1. $(Pb_{1-x}Sr_x)_{0.955}La_{0.03}TiO_3$ Ceramics:

Figure (10) shows the temperature dependence of Debye's relaxation time for $(Pb_{1-x}Sr_x)_{0.955}La_{0.03}TiO_3$ ceramic as a function of Sr-content (x) at frequency equals to 100 KHz. The behavior of the relaxation time, in this figure, is in good agreement with the inverse values of the dielectric constant ε. The samples which characterizes with anomalous values of ε_{max} possess the high value of relaxation time at the phase transition temperature (x = 0.2 mol % Sr, x=0.4 mol % Sr). Fig. (11), represents a plot of both τ_c and ε_{max} at frequency equal to 1KHz versus the Sr–content (x) for $(Pb_{1-x}Sr_x)_{0.955}La_{0.03}TiO_3$ ceramics. In this figure, the variation and behavior of ε_{max} value as a function of Sr–content (x) are the same that of values of τ_c. At the two observed peaks the value of τ_c at concentration of Sr corresponding to x = 20 and 40 mol %Sr are 3.832×10^{-7} and 4.086×10^{-7} sec, respectively.
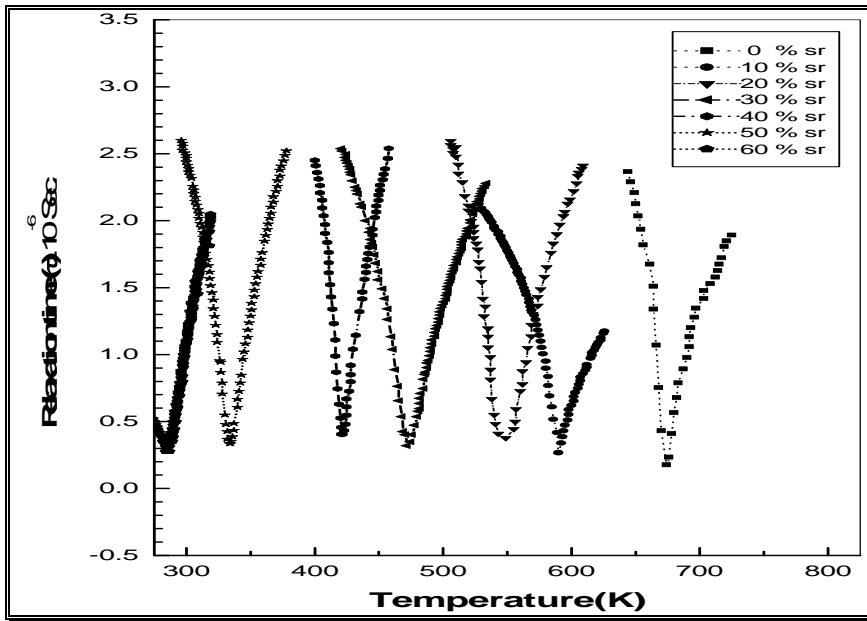
Fig. (10): The temperature dependence of Debye´s relaxation time τ for $(Pb_{1-x}Sr_x)_{0.95}La_{0.03}TiO_3$ (frequency of electric field equal to 100 kHz).
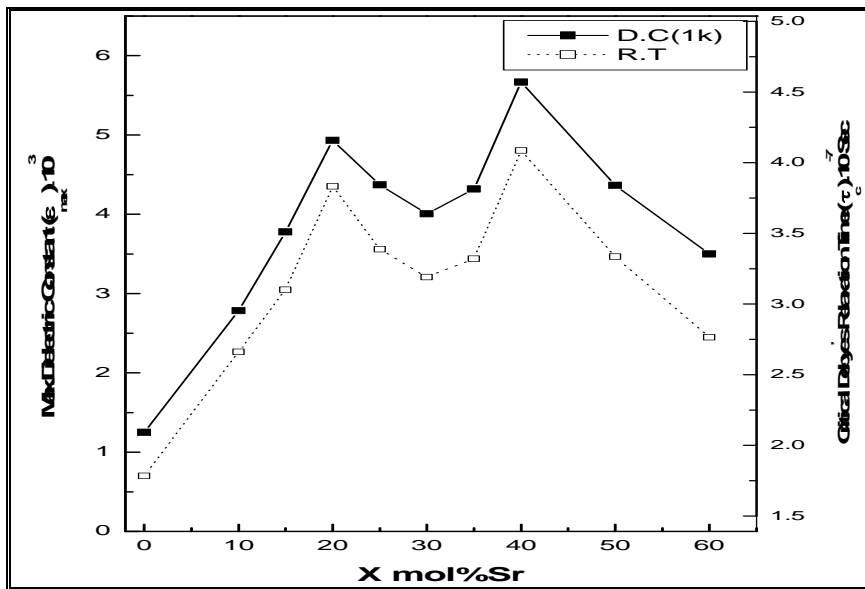

Fig. (11): A plot of ε_{max} and critical Debye´s relaxation time verses the Sr content for samples with formula $(Pb_{1-x}Sr_x)_{0.95}La_{0.03}TiO_3$, since D.C and R.T represent ε_{max} and τ_c, respectively.

3.2.1. (Pb1-xSrx)0.91La0.06TiO3 Ceramics:

The earlier behaviour which was obtained before can also be seen for $(Pb_{1-x}Sr_x)_{0.91}La_{0.06}TiO_3$- ceramics, but the samples which are characterized with anomalous values of ε_{max} possess the high value of relaxation time at the phase transition temperature are at x equals to 25 and 35 mol% Sr, where the value of τ_c are 4.749×10^{-7} and 4.80×10^{-7} sec, respectively.

3.2.1. (Pb1-xSrx)0.865La0.09TiO3 Ceramics:

Figure (12) shows the temperature dependence Debye's relaxation time τ in $(Pb_{1-x}Sr_x)_{0.865}La_{0.09}TiO_3$ - ceramic as a function of Sr-content (x). The behavior of relaxation time for any sample, in this figure, is in a good agreement with inverse value of the dielectric constant ε with temperature for the same sample. It must be mentioned that the samples which characterizes with highest values of ε_{max} possesses also the highest value of Debye's relaxation time.
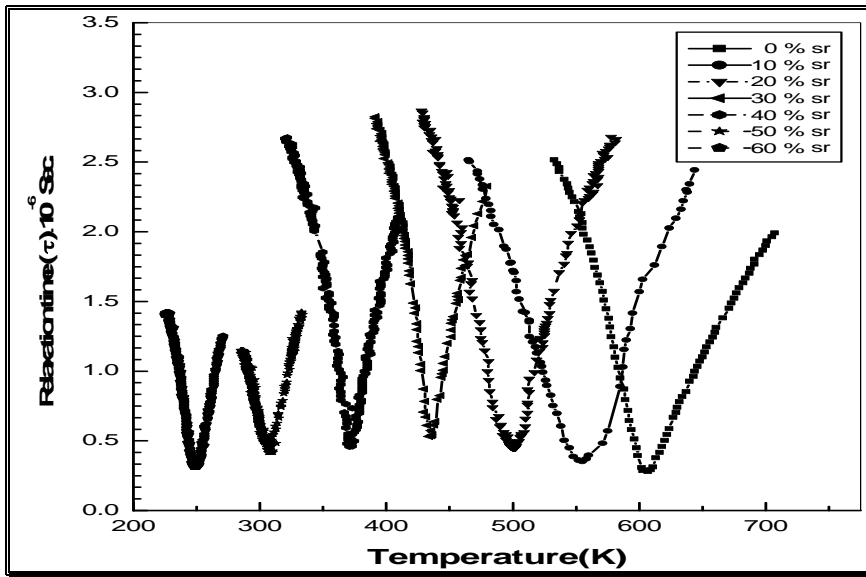

Fig. (12): The temperature dependence of Debye´s relaxation time for $(Pb_{1-x}Sr_x)_{0.87}La_{0.09}TiO_3$ (the frequency of electric field equal to 100 kHz).

Figure (13) represents a plot of ε_{max} and τ_c versus the Sr–content (x) for $(Pb_{1-x}Sr_x)_{0.865}La_{0.09}TiO_3$ ceramics. The variations of ε_{max} at a frequency equal to 1KHz as a function of Sr–content (x) is the same as that of relation between critical Debye's relaxation time τ_c and Sr content (x). The value of τ_c at concentration of Sr equals to x =30 mol % Sr is equal to 5.232×10^{-7} s.
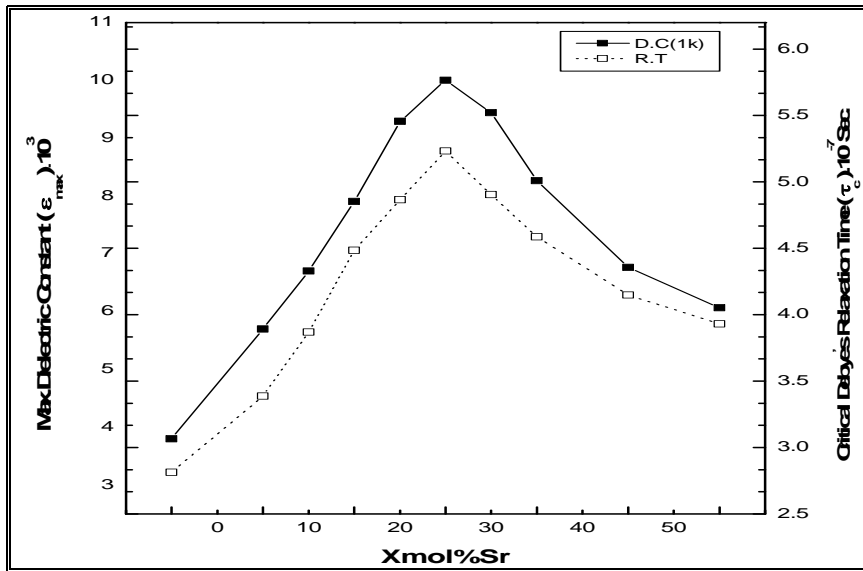
Fig. (13): A plot of ε_{max} and critical Debye´s relaxation time verses the Sr content for samples with formula $(Pb_{1-x}Sr_x)_{0.87}La_{0.09}TiO_3$, since D.C and R.T represent ε_{max} and τ_c, respectively.

It is evident from the literature which was reported by McNeal *et al*. [15] and from previous results which show the similarity behavior for both ε_{max} and critical Debye's relaxation time τ_c one can conclude that the anomalies dielectric peaks is related strongly with increasing the volume of the domain. The Sr content equals to 26 % and Pb content equals to 60.5 % are responsible for the anomalies behavior of the domain.

The equations which are used for calculation of Debye's relaxation time τ and activation energy E_a where mentioned in appendix. The equations which can be seen in the appendix were discussed and used for calculation the results in reference [16].

3.3. Activation Energy:

Figure (14) represents the relationship between both the activation energy (Ea_f, Ea_p) for $(Pb_{1-x}Sr_x)_{0.87}La_{0.09}TiO_3$ –ceramics and the variation of Sr content (x). The variation of both Ea_f and Ea_p against Sr content (x) are decreased with increasing x reaching a minimum value at x=0.3. However, when x is increased more than this value they increase slightly and then another decrease is observed. From this figure it is evident that the value of Ea_p is higher than the value of Ea_f. This means that the activation energy is not Sr content dependant but dependant also on the crystal structure which is function of the phase transition temperature.
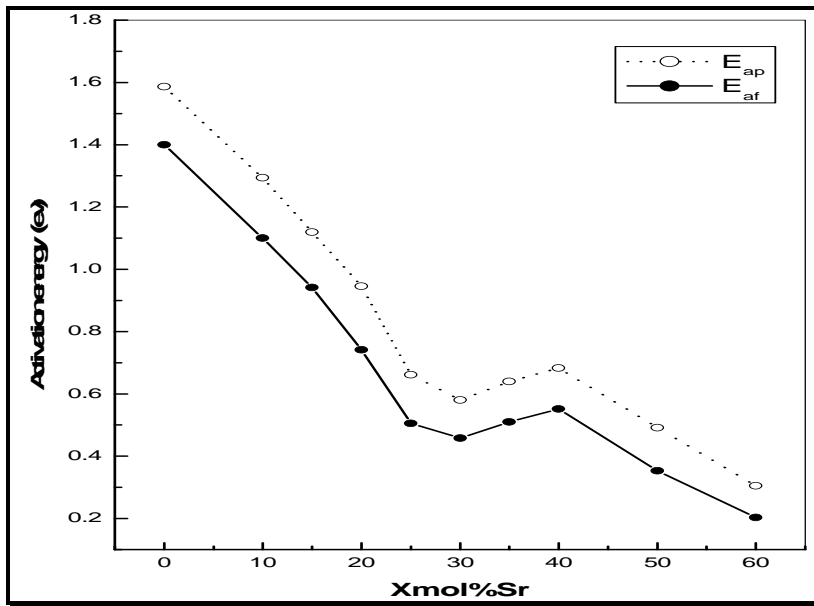
Fig. (14): A plot of activation energy E_a verses the Sr content (x) for samples with formula $(Pb_{1-x}Sr_x)_{0.87}La_{0.09}TiO_3$, since E_{af} and E_{ap} represent the values of E_a at the ferroelectric and paraelectric phase, respectively.

Appendix
Debye s relaxation time for ferroelectric materials

Dielectric constant $_r(\ )$ from Debye's equation for dielectric materials is given by:

$$_r(\ ) - _r(\infty) = [\ _r(o) - \ _r(\infty)]/(1+ \ ^2 \ ^2) \qquad (1)$$

where   is the relaxation time,   is the frequency of electric field and $_r(\infty)$ is the dielectric constant at ∞ which equals to n^2, where n is optical index. For the ferroelectric materials n^2 is negligible with respect to $_r$ and $_r(o)$, then

$$_r(\ ) = \ _r(o)/(1+ \ ^2 \ ^2) \qquad (2)$$

Hence, the value of   for all the ranges of temperature, except at $T = T_c$ (Curie temperature), can be written by:

$$\ = \ ^{-1} \cdot \{[\ _r(o)/\ _r(T)] -1\}^{1/2} \qquad (3)$$

when T T_c, then $_c$, where $_c$ in the ferroelectric material is the

relaxation time which corresponded the peak of dielectric constant $\varepsilon_{r\,max}$. So, for the low and high frequency $\varepsilon_{r\,max}$ can be described as follows:

$$\varepsilon_{r\,max}(L) = \varepsilon_{r\,max}(o)/(1+ \omega^2_L \tau^2_c) \tag{4}$$

$$\varepsilon_{r\,max}(H) = \varepsilon_{r\,max}(o)/(1+ \omega^2_H \tau^2_c) \tag{5}$$

then

$$\tau_c = \{[R-1]/[\omega^2_H - \omega^2_L R\}^{1/2} \tag{6}$$

where R= $\varepsilon_{r\,max}(L) / \varepsilon_{r\,max}(H)$. From equs (5) and (6) the value of $\varepsilon_{r\,max}(o)$ can be obtained. By substituting the value of $\varepsilon_{r\,max}(o)$ instead of $\varepsilon_r(o)$ in eq.(3), one can obtain the value of τ (Debye's relaxation time) for any value of temperature $\neq T_c$. Hence, The value of E_a (activation energy) can be determine as function of τ Debye's relaxation time) and temperature T by this formula:

$$\tau = \tau_o \exp E_a / k T \tag{14}$$

where k is the Boltzman's constant. The activation energy E_a (eV) can be obtained from the slope of the straight line between [Ln (τ^{-1})] and (1000 / T) in the case of plotting the former equation.

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