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Effect of Ba-Ions on The Structural Properties of The $[(Pb_xba_{1-X})_{0.81}La_{0.125}]Tio_3$ Ceramic

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Abstract. Eight samples were prepared according to the concentration of Ba-content (0, 10, 20, 30, 40, 55, 60 and 70 %). In the present research, full structural Investigations for of the $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$ ceramic compounds were accomplished using x-ray diffraction technique. The results extracted includes: the lattice parameters, the grain size and the percentage of crystallinity % of the compound. The investigation of the structural properties of this compound is useful for studying the dielectric and related properties such as the piezoelectric applications. Among the unique results found in the present investigation, we found that above 40 % of Ba, the compound is no longer tetragonal but it is converted into the cubic system (structural transformation).

***Keywords*:** $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$, Ceramic, X-ray Diffraction, Lattice Parameters, Grain Size, and Crystallinity % **.**

1. Introduction

In recent years, lead titanate ($PbTiO_3$) ceramics have attracted a great deal of attention due to its high Curie temperature (490^oC) 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 titanite 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 (107 – 108 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 denser. Mn doped $PbTiO_3$ produces a material with high mechanical strength, low dielectric losses and low dielectric constant reliable for piezoelectric resonator applications [4].

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 our Lab., we have attempted several experiments to improve the properties of the lead titanite. Influence of some preparation conditions on Debye's relaxation time and related properties of (Pb, La)TiO_3 ceramics was also reported earlier [5] . Dielectric properties, Debye′s relaxation time and activation energy of $[(Pb_{1-x}\ Sr_x)_{\ 1-1.5z}La_z]\ TiO_3$ ceramics have been studied earlier [6]. Effect of sintering time on the particle size and dielectric properties of La-doped $PbTiO_3$ ceramic nanoparticles was previously reported [7]. An attempt was done by studying the effect of grain size on the dielectric properties of lanthanum- doped $PbTiO_3$ perovskite ceramic [8]. The present study is a new attempt by checking the effect of the variation Ba-content (0, 10, 20,30, 40, 55, 60 and 70 %). The goal of this study is to find out the influence of Ba content on the structural properties of the system $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$. In this respect, x-ray diffraction is useful. For diffraction applications, only short wavelength X-rays (hard X-rays) in the range of a few angstroms to 0.1 Å (1 keV - 120 keV) are used. Because the wavelength of X-rays is comparable to the separation of the atoms in the unit cell,

Therefore, it is ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic X-rays can penetrate deep into the materials and provide information about the bulk structure. Also this is important because it is an introductory part prior to the research of the ferroelectric behavior of the compound.

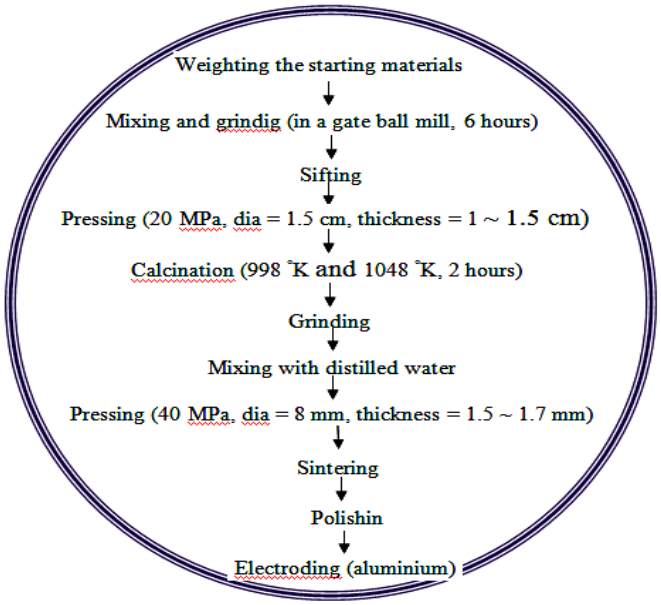

Fig. (1). Sum up Diagram for the Preparation Procedures

2. Experimental Procedure

2.1. Preparation technique of the samples:

Specimens of the general formula $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$ were prepared according to the procedures of the usual firing technique [9] . The starting materials (99.9% purity PbO, $BaCO_3$, TiO_2 and La_2O_3) in corresponding stoichiometric ratios were homogenized and pressed into discs. The discs were then calcined in the temperature range between 998 and 1048 °K. 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 $BaTiO_3$ – ceramics, for two hours.

The calcined powder was pressed into discs. The discs were thereafter sintered at the temperature range between 1473 and 1653 °K, according to the pre-mentioned technique but for two sintered temperatures, for 4 hours in an oxygen atmosphere. The pellets were of 7.4 mm diameter and about 1.5 mm thickness. The samples were polished and coated with aluminum thin film to form electrodes .The above diagram is a good sum up for the preparation procedures.

2.2. X-ray diffraction:

The crystal structure of $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$ ceramic was examined by XRD using X- ray diffractometer with CuKα line (λ=1.5418 Å) as the radiation source. The crystallographic orientation was determined by XRD rotation over (0-

2θ). The scanning range was 0-80° with a scan step size of 0.06° (2θ)/step and the counting time of 1 sec/step. The X-ray diffraction was employed for calculation the lattice constants (*a*,*b*,*c*), the grain size and finally the ratio of crystallinity %.

2.2.1. Lattice parameters:

We calculated the lattice parameter constants (*a*,*b* and *c*) from the equations [10]:

(1) For tetragonal $a = b \neq c, \alpha = \beta = \gamma = 90$

(2) $$1/d_{hkl}^2 = (h^2 + k^2)/a^2 + (l^2/c^2)$$

Where h, k and l are the usual Miller indices

2.2.2. Grain size and crystallinity %:

Scherrer's method was applied for the calculation of the grain size of the grown samples. From the following equations, we calculated the grain size [11]:

$$\Gamma = \frac{0.9\lambda}{L_{vol}\cos\theta} \quad (3)$$

Where L_{vol} is the column lengths.

Substituting the value of (the full width at half maximum) and the value of the main peak we can obtain the value (the column lengths). The primarily obtained column lengths of an ensemble of particles can be transformed into average grain sizes if all the crystallites in the sample have roughly the same shape. The standard assumption is a spherical shape, then:

$$D_{vol} = {}^4/_3 L_{vol} \quad (4)$$

Where D_{vol} is the crystal size

The crystallinity % was calculated directly with the help of X-ray diffraction pattern of the samples by using the following equation [12]:

$$\%\ \text{Crystallinity} = \frac{100\ A_c}{A_c + A_a} \quad (5)$$

Here, A_c and A_a represent the respective area contributions from the crystalline and amorphous phases of the sample to the diffractograms. It must be mentioned that the x- ray instrument is equipped with a copper anode generating Ni filtered CuKα radiation (λ = 1.5406 Å, 40 kV, 30 mA, back monochromator). The equipment was used in a θ - 2θ geometry in the range between 10 and 80o with a divergence slit of 1°. This was done in (CMRDI - Cairo) - Egypt.

3. Results and Discussion

3.1. X–ray diffraction for $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$ ceramics

As mentioned the x-ray diffraction was employed for calculation the lattice constants (*a*,*b*,*c*), the grain size and finally the ratio of crystallinity % for the ceramic structure of the form $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$ (Fig. 2).

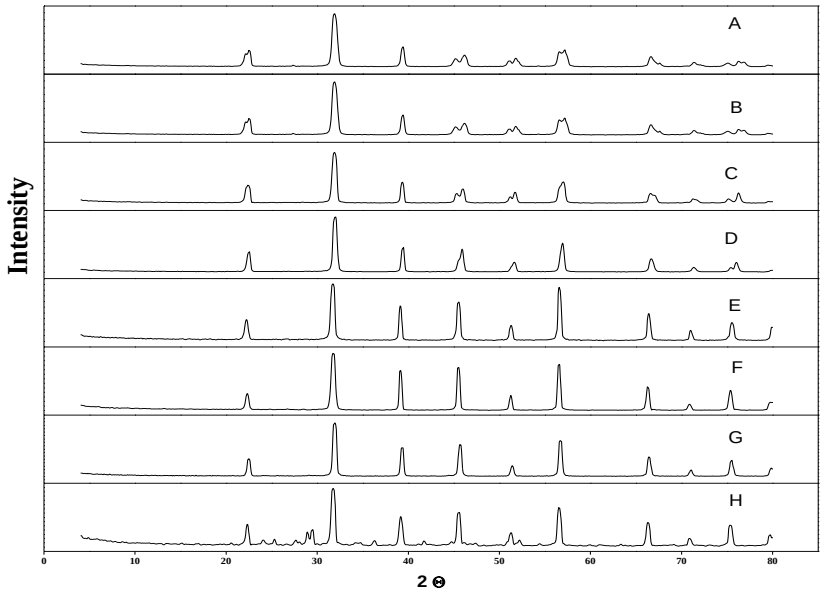

Fig. (2). X-ray diffraction of $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$ ceramics under different concentration of Ba content. Where A, B, C, D, E, F, G and H are corresponding to Ba content equal to 0, 10, 20, 30, 40, 55, 60 and 70 %, respectively.

From the position of the strong peaks d-space has been calculated according to Bragg equation; $n\lambda = 2 d \sin\theta$. The calculated values of d - space for different reflection planes were useful to verify the main phase of our compound. The lattice parameters have been also calculated. It must be mentioned that the obtained X-ray diffraction pattern was compared with the Powder Diffraction File No. 06-0452 [13]. This proved that the prepared compound is highly pure without any secondary phases.

3.2.1. Calculation of lattice parameters

Figure (1) shows the X-ray diffraction pattern of the sample[$(Pb_xBa_{1-}$

$_x)_{0.81}La_{0.125}]TiO_3$ ceramics with different concentrations of Ba-ions at sintering time equals to 4 hours and at several values of sintering temperatures (according the concentration of Ba-ions).

From this figure, we conclude the followings:-

1- Changing the concentrations of Ba-ions causes peaks shift. Since the peak height depends on the crystal quality, so it is easy to conclude that Ba-ions variation changes the crystallinity and hence the crystal quality.

2- In spite of the observable broadening, the peak positions are the same for the different Ba-ions.

Figures (3) and (4) are useful to understand the relation between the crystal lattice *c* versus the Ba content. From these two, figures, we also conclude the followings:-

1- The values of the lattice constants (*a,b,c*) at the concentrations 20 % and 55 % which are (3.9834, 3.9834, 3.9938 Å) and (3.9839 , 3.9839, 3.9839 Å) ,respectively. Consequently, the numbers of unit cells per unit volume are 1.578 x 10^{24} and 1.5815 x 10^{24} u.c/cm^3.

2- The variation of the unit cell volume is attributed to the fluctuation in the lattice parameters under the different Ba content.

3- The figures also tell us that there is a change in crystal structure associated to the Ba content variation.

4- Bearing in mind the above remarks; we conclude that such change may be responsible for any abnormal behavior in the ferroelectrics properties.

Figure (5) represents the relation between (*c/a*) and Ba content, where *c/a* represents the tetragonility of the sample $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$. This figure shows that the tetragonality (*c/a*) decreases with increasing Ba content. However, when the Ba content lies between 40 – 70 %, the ratio are stabilized at value equals to one. The reason of this stabilization is the appearance of the cubic structure of the sample in this region of Ba content.

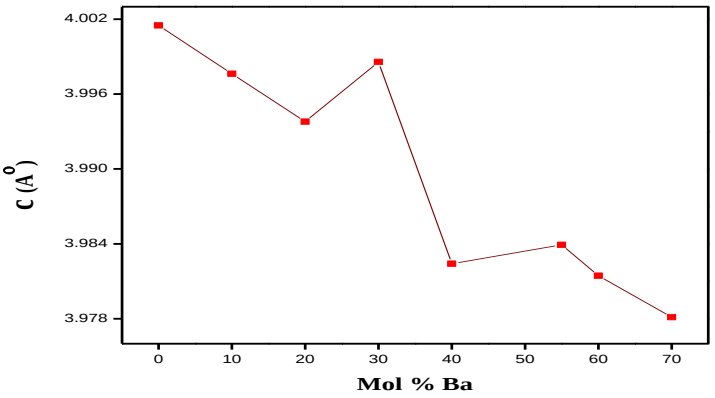

Fig. (3). A plot of crystal lattice c versus the Ba content for samples of ceramics with formula $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$

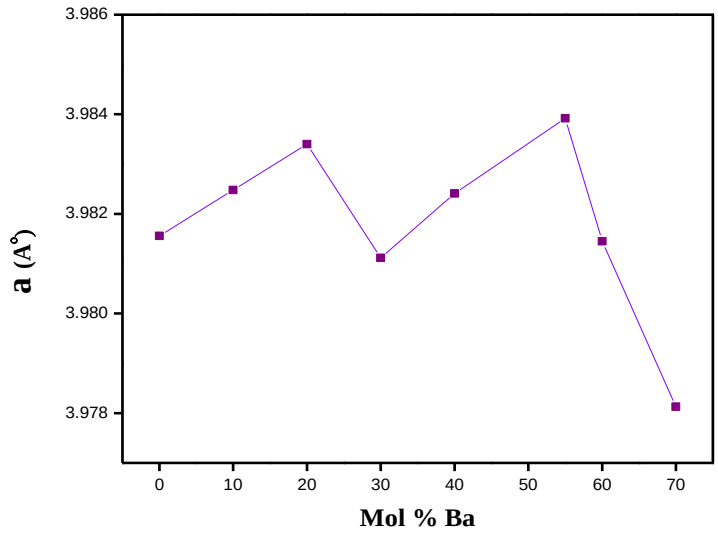

Fig. (4). A plot of crystal lattice a versus the Ba content for samples of ceramics with formula $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$.

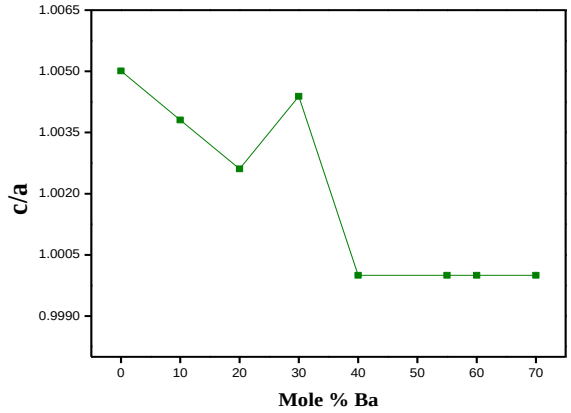

Fig. (5). A plot of (c/a) versus the Ba content for samples of ceramics with formula $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$

3.2.2. Calculation of grain size:

Figure (5) represents the relationship between Ba content and the values of grain size for $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$ceramics. Scherrer's method which was mentioned previously is used for calculation the grain size. Generally, the grain size is increased with increasing of Ba content except for the two abnormal values (24.81 and 29.69 nm) corresponding 20 and 55 mole % Ba, respectively.

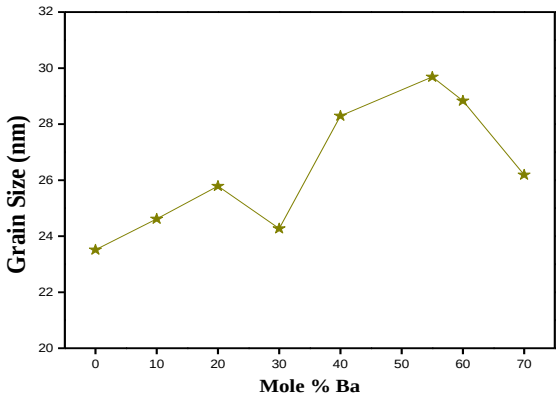

Fig. (6). A plot the grain size versus the Ba content for samples of ceramics with formula $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$

3.2.3. Crystallinity:

The histogram shown in figure (7) represents the relationship between the crystallinity % and the Ba content for $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$ ceramics. The maximum crystallinity % value which is 86.74 % at 20 is corresponding to the concentration 55 mole % Ba content. It is worth mentioning that the crystallinity % at 20% equals to 83.76. The general behavior of the above results is similar to the results of grain size observed in figure (6).

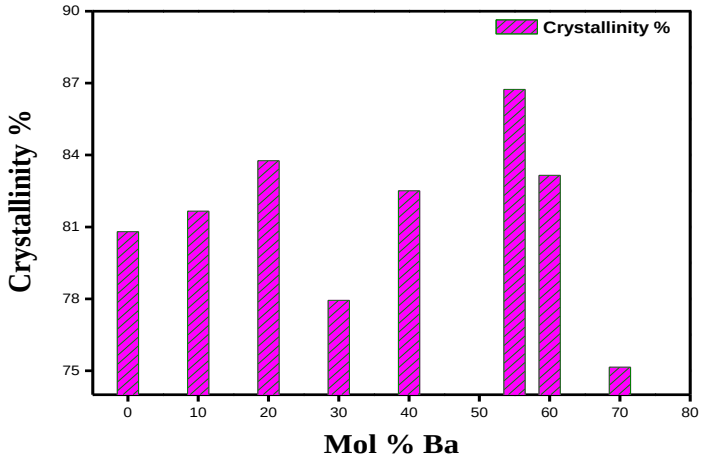

Fig. (7). A plot the crystallinity % versus the Ba content for samples of ceramics with formula $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$.

4. Conclusions

In this work a detailed study is presented in order to check the effect of the Ba-content variation (0, 10, 20,30, 40, 55, 60 and 70 %) on the structural properties of the system $[(Pb_xBa_{1-x})_{0.81}\ La_{0.125}]\ TiO_3$. The structural properties (such as; the lattice parameters, the grain size and the crystallinity %) of $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$ compound with different Ba content were examined by the of x-ray diffraction data. Among the obtained striking results that changing the concentrations of Ba-ions causes the followings:-

- The crystallinity and hence the crystal quality of the samples are changed as concluded from the XRD work.

- The values of the lattice constants (*a*,*b*,*c*) at the concentrations 20 % and 55 % which are (3.9834, 3.9834, 3.9938 Å) and (3.9839, 3.9839, 3.9839 Å) ,respectively. Consequently, the numbers of unit cells per unit volume are 1.578 x 10^{24} and 1.5815 x 10^{24} u.c/cm^3.

- The variation of the unit cell volume was attributed to the fluctuation in the lattice parameters under the different Ba content.

- Generally, the grain size is increased with increasing of Ba content except for the two abnormal values (24.81 and 29.69 nm) corresponding 20 and 55 mole % Ba, respectively.

- When the Ba content lies between 40 –70 %, the tetragonality ratio (*c/a*) equals to one. The reason of this is the appearance of the cubic structure of the sample.

The results of the structural properties are useful for studying the dielectric and related properties such as the piezoelectric applications.

5. References

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تأثير تغيير نسبة أيونات الباريوم على الخواص التركيبية لمركب $[(Pb_xBa_{1-x})_{0.81}La_{0.125}]TiO_3$ السيراميكي

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مخلص البحث. تعتبر تيتانيات الرصاص من المواد الشائعة الإستخدام وتنتمى الى المواد الفروكهربية. تيتانيات الرصاص فى حالتها النقية أى الخالية من أى إضافات تعتبر مادة هشة اى غير متصلبه ولا يمكن أن تستخدم فى الأغراض التطبيقية كمادة تتميز بالكهربية الضغطية مثلاً. يمكن تحسين خواص تيتانات الرصاص باستخدم شوائب عديدة ومتنوعة فى صورة أكاسيد أو كربونات وغيرها. إضافة هذه الشوائب بنسب معينة يكسبها خواص متميزة للأغراض التطبيقية . والهدف الرئيسى من هذه الدراسة هو تحسين خواص تيتانيات الرصاص. ونتائج هذه الدراسة تختص بدراسة تغير تركيز ايونات الباريوم فى المنظومه $[(Pb_x\ Ba_{1-x})_{0.81}La_{0.125}]TiO_3$ السيراميكيه المدعمه بعنصر اللنثانيوم و معرفه أفضل تركيز لأيونات الباريوم التى تمد هذه النمظومه السيراميكيه بالخواص البلوريه و الفروكهربيه المثاليه والتى يمكن الأستفادة منها فى التطبيقات العملية التى تتميز بها هذه الماده وهذه الخواص التي شملها البحث الحالي هي ثوابت الشبكيه البلوريه – حجم الحبيبات – درجة التبلور.