In Situ Preparation of $Ba_{0.75}$ $Ca_{0.25}$ Tio_3 Nanoparticles by Hydrothermal Method

Aqeel A. Al-Taie, Emad K. Al-Shakarchi, and Mazen Kamel

Al-Nahrain University, College of Science, Physics Department, Baghdad/ Iraq.

Corresponding Author: *Emad K. Al-Shakarchi, Al-Nahrain University, College of Science, Physics Department, Baghdad/ Iraq.email:eks2000@hotmail.com.*

ABSTRACT

The system of $Ba_{0.75}$ $Ca_{0.25}TiO_3$ had been synthesized by hydrothermal method under a certain condition. The produced sample was examined by X-ray diffraction (XRD). It showed a tetragonal phase with lattice constants (a=b=4.0173 Å, c=4.048Å). The surface morphology was analyzed by Scanning Electron Microscopy (SEM).It was exhibited the grains possessed a spherical form with an average grain size (1.5μm). The shape and size of nanoparticles were measured using Transmission Electron Microscopy (TEM). It was clear that there was homogeneity in a spherical particle shape and the size range was (30-50 nm). The dielectric measurements were done by using LCR meter in a temperature range (50-200 ^0C) for selected frequencies (1,100and 1000 kHz), it was clear that the values of dielectric constant decreases with increasing frequency.

Keywords: *hydrothermal method, tetragonal phase, ferroelectric behavior, perovskite structure.*

INTRODUCTION

After the previous successive preparation of nanoparticle for $BaTiO_3$ by different technique [1,2], the attention was directed toward the producing nanostructure that might be investigated by another preparation method and different materials. Secondly, the effect of substitution by Ca-ions with respect to Ba-ions was very interesting in producing a new composition like $BaTiO_2$, known as BT [3,4]. The system of $Ba_{1-x}Ca_xTiO_3$(BCT) was considered one of the perovskite ferroelectric materials by calcium partially inserted barium. This solid solution of BCT had been known in 1955 when it was prepared a conventional ceramic method [5]. It is well known, BT shows different phase transitions, rhombohedra, orthorhombic, tetragonal, and cubic at different temperature ranges [1]. Partially introducing of calcium in the structure tend to tetragonal phase, non-centro symmetric structure at low temperatures, it becomes piezoelectric at room temperature. It had very interesting materials in many applications such as Multilayer capacitors (MLCs) [6],and also it shows an appreciable appliances used in optical interconnections, advanced laser systems and optical or electronic storage systems [7]. The applying of hydrothermal is the aim to produce a nanostructure of $Ba_{0.75}Ca_{0.25}TiO_3$ rather than the other methods like sol-gel chemical reaction [8], and microwave-hydrothermal processing [4,9]

The development in dielectric properties of those materials was successfully achieved by substituting the isovalent ions in the system. The Ca-ions substituted in $BaTiO_3$ leads to reduce the high cost and getting a variation in physical properties from the origin [10]. The researches about barium calcium titanate had a controversial result like phase transition, unit cell size, the effect of Ca-ions substituted on the variation of Curie temperature, and the ferroelectric-para electric transition incomparable with of $BaTiO_3$ [11]. It was clear that the BCT-material showed a decreasing in Curie temperature through the substitution of Ca-ions, recently, they showed increasing in Curie temperature through the substitution of Ca-ions. Generally, it depends on the on the preparation conditions and the site of Ca-occupancy [12]. In this research, the preparing conditions of both compounds $BaTiO_3$,and $CaTiO_3$ are necessary to produce $Ba_{0.75}$ $Ca_{0.25}$ TiO_3.The mixture of both compounds with a certain ratio was the way to produce $Ba_{0.75}Ca_{0.25}TiO_3$.The new thing represented by the substituting operation done in situ from the precursors during the synthesis by hydrothermal method by using homemade autoclave design [13].

EXPERIMENTAL PART

The hydrothermal method was used to prepare a nanostructure of Ba$_{0.75}$Ca$_{0.25}$TiO$_3$; it was designed and homemade manufacture. It is operated under high pressure, and high temperature. The procedure was applied by the block diagram mentioned in Figure 1. A morality amounts of barium acetates (0.75) and calcium acetates (0.25) was dissolved separately in distilled water, while an amount of titanium tetrachloride was added to isopropanol which cooled down to (0 ^{0}C). Then the solution was heated to room temperature, a strong base NaOH added to raise the pH-value more than (13). Later, the solutions of barium acetates & calcium acetates were added to titanium solution, then the temperature of the entire solution rised to (80 ^{0}C) for (20 min.) for more homogenization.

Then, the mixture was transferred into a Teflon vessel which occupied 40% of its volume. The vessel was settled inside the autoclave, and the temperature adjusted to (200 ^{0}C) for (24 hrs.) at a pressure of about (20 bar), then cooled to room temperature. The mixture washed five times by distilled water to remove the salts and unwanted materials to purify the mixture. The mixture was dried at (80 ^{0}C) for (12 hrs.), then the powder compacted into a pellets with a diameter (10 mm), using a stainless steel die and an electrical press. The samples were pressed with a pressure (127 MPa). The compacted pellets were sintered at a temperature (900 ^{0}C) for (4 hrs.) to solidify them. The pellets then were polished to increase the surface hardness. Finally, the pellets used for dielectric measurements, by applying the electrodes coated with gold by plasma sputtering process.
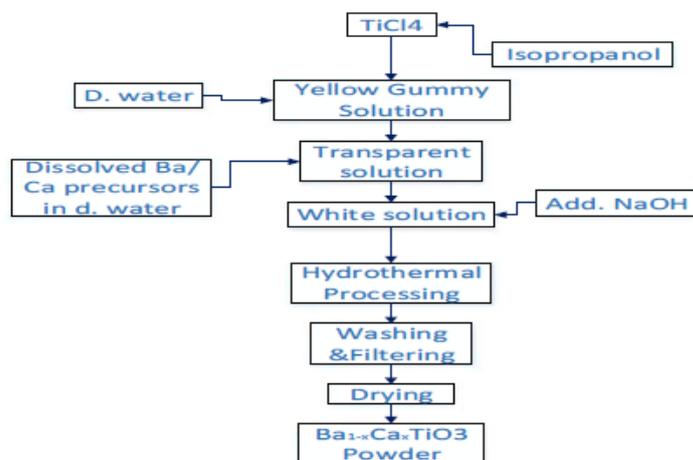
Figure1. *Block diagram of the preparation.*

RESULTS AND DISCUSSION

After the successive preparation Ba$_{0.75}$Ca$_{0.25}$TiO$_3$, as mentioned before. The optimum conditions were dependent on the measurements and analysis for the prepared sample. The crystalline phase was analyzed by X-ray diffraction (XRD) using a PAN alytical XPert PRO diffractometer with a Cu-K $_a$ source (λ =1.540 Å), the applied voltage (40 kV) and current (30 mA). The X-ray diffraction pattern, as shown in Figure 2, was analyzed with aid of COD databases 98-007-1368 [14]. The compound showed a tetragonal phase with lattice constants (a=b=4.0173 Å, c=4.0480 Å) with space group (p4mm). The approaching in the lattice constants tend to make a low degree of tetragonality and the structure approach to the perovskite cubic structure because the ratio of (c/a) equal to 1.0076. Besides, the low tetragonality could be explained by the occurring of titanium

isopropoxide in the preparation instead of using TiO$_2$ as a titanium precursor [15]. The presence of the planes (002),(020) are related to co-existence of cubic and tetragonal phases by the splitting in the intensity of both peaks at room temperature. Depending on the ratio, I (002) /[I (020) +I (002)], for cubic phase the ratio is zero that means there is no splitting. For a mixture of tetragonal and cubic phases, the ratio will have values between 0.33 and zero [6]. That is in contradiction with the result showed a ratio of about 0.66, which means a more stability in the phase production. The reason is return to high intensity of the peak (002) rather than the peak (020). This reversal in the intensity is due to the preferred orientation of the domains with their c-axis perpendicular to the surface [6].

It is necessary to mention that the phase created directly with high stability in production before calcinations treatment, even if the heat treatment

applied the phase fixed. That is in contradiction with the previous researches [4,8]. This is the main feature in preparation by hydrothermal process to produce a nanostructure phase. The

peaks with indices (121), (202) and (321), were related to un reacted calcium content which might cause a forming of calcium titanate.
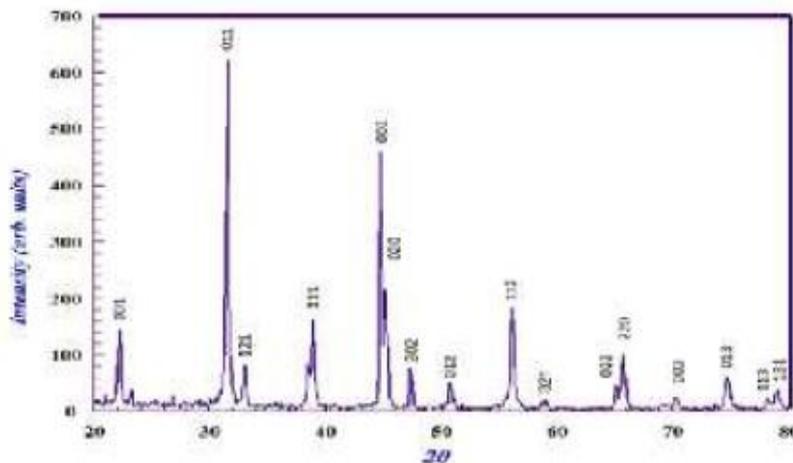
Figure 2: XRD pattern of Ba0.75Ca0.25TiO3 sample

The TEM-analysis was necessary to emphasize the presence of nanostructure. The resultant image, as shown in Figure 3, was obtained from a PHILIPS CM10 microscope using an accelerating voltage of 100 kV. The magnification power was about 64000-92000x, and the magnification calibrated in pixels per nanometer. The image showed the primary particles appears as agglomerate; possess a spherical shape with a range of (30-50 nm) in diameter. It was noted that the clusters of the primary particles were formed according to the high ratio of barium in the compound, which was sensitively polarized during the imaging process. The indication was extremely a small particle size in the range of nanometers.

The surface morphology of the sample characterized by SEM-analysis, as shown in Figure 4. The SEM image was acquired with an Inspect S50 SEM by an accelerating voltage of (30 kV) and magnification 5626x. There is a homogeneity ingrain shape, but not verified in grain size. The average grain size was (1.5 μm), and the grain size distribution as shown in figure 5, there was a greater ratio of grains in the scale of (1 μm), which was the predominate one. This result is better than that concluded by Jayanthi et.al. [16], they investigated the grain size in the ran range (10 μm). The shape of the grain is approach to the spherical form with an existence of some nodes at the edges. The dielectric measurements had been done under different frequencies and temperatures to explain their effect on the phase transition from ferroelectric to paraelectric, as exhibited in Figures 6-8. The first figure represented the variation of electrical permittivity (ε r) and dielectric loss (D) with temperature variations of Ba$_{0.75}$ Ca$_{0.25}$ TiO$_3$

sample. There is increasing the value of (ε r) with increasing temperature during the ferroelectric state till the peak point record at (135 ^{0}C), which is the Curie point, which means the inversion point to paraelectric state. Then the decreasing in (ε r) was happened through the paraelectric state up to (180 ^{0}C).
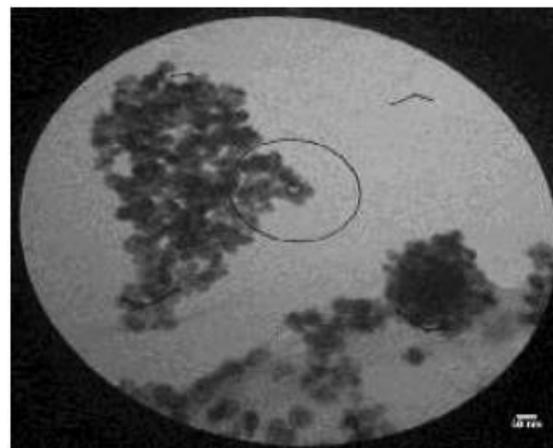
Figure3. *TEM micrograph of Ba0.75Ca0.25TiO3 sample.*
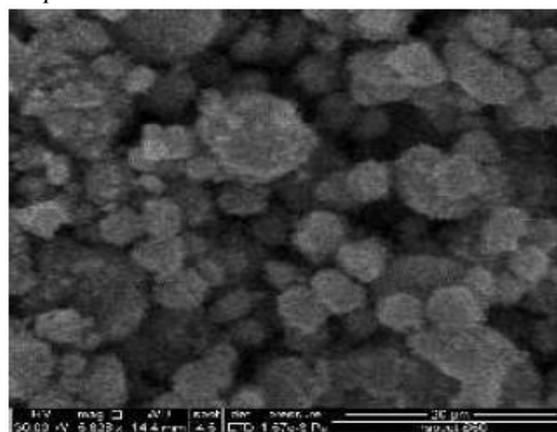
Figure4. *SEM micrograph of Ba0.75Ca0.25TiO3 sample.*
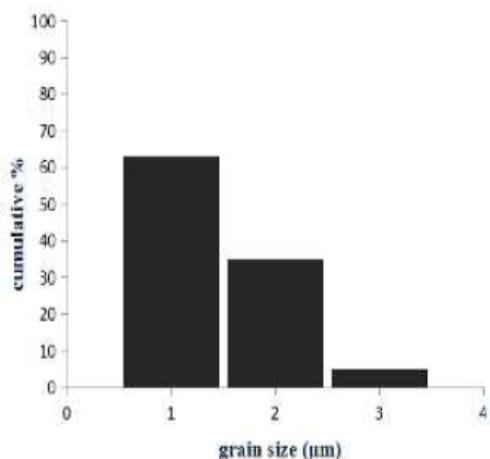
Figure5. *Distribution of particles with micro-scale.*

The dielectric loss decreases to its minimum value at the same transition point and stay less than (0.2%) in that region. This result showed that the effect of addition of calcium caused rising in Curie temperature in comparison with the Barium titanate that was about (120 ^{0}C) [17]. This rising in Curie point related to the existence of a diffusion effect which occurs when Ca-ions occupy the Ba-sites only [12]. In fact, there was approving by Varatharajan et al. [10]. They stated the effect of substitution by Ca +2 causes an increase in the transition temperature, but this increasing may also be affected by the route of preparation. The comparison with pure BaTiO$_3$, the dielectric constant was decreased because of the substitution of anti-ferroelectric by calcium titanate in ferroelectric barium titanate should be reduce the concentration of aligned electric dipole moment in Ba $_{0.75}$Ca $_{0.25}$TiO$_3$ [18].

The dielectric constants, as shown in figure7, exhibited a raisin in the dielectric constants toward the inversion point at 137.4^{0}C, at frequency 100 kHz, but in figure 8, the value of Curie point is about 135 ^{0}C under frequency 1 MHz. Normally, there is approaching in the T c -values because the frequency has no effect on the transition from ferroelectric to paraelectric but there is indicative in there placement of Ba ions by Ca ions [10]. On the other words. The frequency has direct effect on the decreasing of dielectric constants as mentioned in Figures (6, 7 and 8).That was normally noticed due to Ca-ions concentration Ca-ions, which reduces the dielectric constant that is corresponding to previous study [10]. The value of dielectric constant decreases with increasing of frequency, where the maximum value of dielectric constant at frequency 1 kz., is 423, while at 100 kHz., its magnitude decreased to 402, and at 1MHz., the value dropped to 341.

In figure 6, the dielectric loss (D) showed a decreasing in its value to minimum level which is about 0.015% in the region of transition from ferroelectric to paraelectric state, whereas in figure 7, a slight raising in (D) at frequency 100 kHz., to be 0.027% at the Curie transition point, while at 1 MHz., the value of (D) raised to its maximum magnitude and reached 0.033% at Curie region. It is noted that the overall magnitudes of dielectric losses are below 0.05% in the adjacency of the Curie transition zone. That is benefit in the industrial application of multilayer capacitor.
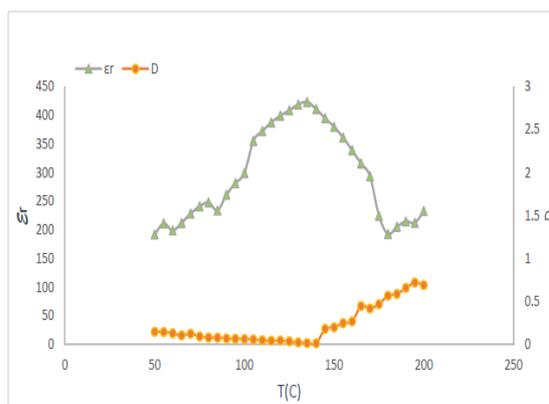
Figure6.*The dielectric measurements of Ba$_{0.75}$ Ca$_{0.25}$ TiO$_3$ sample under 1 kHz.*
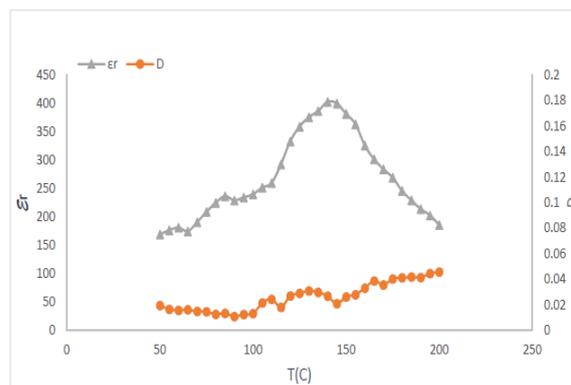
Figure7.*The dielectric measurements of Ba $_{0.75}$ Ca $_{0.25}$ TiO$_3$ sample under 100 kHz.*
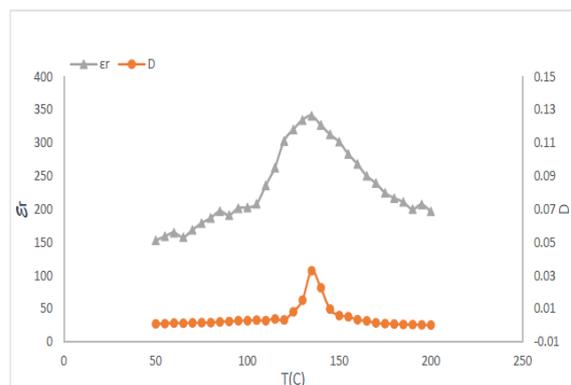
Figure8.*The dielectric measurements of Ba0.75Ca0.25TiO3 sample under 1 MHz.*

CONCLUSION

A homogenized substitution material of $Ba_{0.75}$ $Ca_{0.25}$ TiO_3 had been successfully prepared by using a hydrothermal route from the starting materials of barium and calcium and under a certain conditions of pH-value, pressure and temperature. There is verify a pure tetragonal phase without necessity for calcinations process. That is good in the saving energy for the sample production. The resultant powder showed an anoparticle falls in the range of (30-50 nm) that is agreement with the results of XRD analysis. The nanomaterials of $Ba_{0.75}Ca_{0.25}TiO_3$ had an extending in ferroelectric region. The effect of Calcium substitution causes a limited variation in Curie temperature but the more benefit was the decreasing in dielectric constant with frequency. On the other hand, the smallest value of dielectric losses at a certain frequency is useful in the multilayer capacitor design.

REFERENCES

[1] E.K. Al-Shakarchi, Dielectric Properties of a $BaTiO_3$ Ceramic Prepared by Using the Freeze Drying Method; J. Korean Physical Society, 57 (2), pp. 245-250, (2010).

[2] N.B. Mahmood, E.K. Al-Shakarchi, Three Techniques Used to Produce $BaTiO_3$ Fine Powder; J.Modern Physics, 2, pp. 1420-1428, (2011).

[3] N.B. Mahmood, E.K. Al-Shakarchi, B. Elouadi, X. Feaugas, Crystal Structure of Ba x Sr 1-x TiO 3FinePowder; J. Modern Physics, 6, pp. 70-77, (2015).

[4] P. Salcedo-Abraira, E. Morán, M. E. Villafuerte-Castrejón, R. Vivar-Ocampo, and L. Pardo; $Ba_{0.9}Ca_{0.1}TiO_3$: microwave-assisted hydrothermal synthesis and piezoelectric properties, Advances inApplied Ceramics, online printed, 2017

[5] R.C. DeVries, R. Roy; Phase equilibria in the system $BaTiO_3$-$BaTiO_3$,J Am Ceram Soc., 38 (4),142-146, (1955).

[6] S. Jayanthi, T.R.N. Kutty, Extended phase homogeneity and electrical properties of barium calciumtitanate prepared by the wet chemical methods; Materials Science and Engineering B, 110, pp. 202212, (2004).

[7] H. Veenhuis, T. Börger, K. Peithmann, M. Flaspöhler, K. Buse, R. Pankrath, H. Hesse, E. Krätzig,Light-induced charge-transport properties of photorefractive barium-calcium-titanate crystals dopedwith rhodium; Applied Physics B, 70, pp. 797–801, (2000)

[8] J. Moreno, J.M. Dominguez, A. Montoya, L. Vicente, and T. Viveros; Synthesis and Characterizationof $MTiO_3$(M = Mg, Ca, Sr, Ba) Sol-Gel, J. MATER. CHEM., 5(3), pp.509-512,(1995).

[9] S. Komarneni, Q. Li, K.M. Stefansson, and R. Roy; Microwave-hydrothermal processing forsynthesisof electroceramic powders, J. Mater. Res., 8(12), pp. 3176-3183, (1993).

[10] R. Varatharajan, S.B. Samanta, R. Jayavel, C. Subramanian, A.V. Narlikar,P.Ramasamy,Ferroelectric characterization studies on barium calcium titanate single crystals; Materials Characterization; 45, pp. 89-93, (2000).

[11] L. Kadira, A. Elmesbahi, S. Sayouri, Dielectric study of calcium doped barium titanate Ba 1-x Ca x TiO_3 ceramics; Int. j. Physical Sciences, 11(6), pp. 71-79, (2016).

[12] V.S. Tiwari, D. Pandey, P. Groves, The influence of powder processing technique on chemical homogeneity and the diffused phase transition behavior of $Ba_{0.9}$ $Ca_{0.1}$ TiO_3 ceramics; Physics D, 22 (6),pp. 837-843, (1989).

[13] S.H. Lafta, E.K. Al-Shakarchi, A.M. Musa, M.Farle, R.Salikov, Effect of Molar Ratio onStructural Properties of Nanostructure Li-Ni Ferrites Prepared by Hydrothermal Method; IJARPS, 2(9),pp. 5-12, (2015).

[14] P.S.R. Krishna, D. Pandey, V.S.Tiwari, R. Chakravarthy, B.A. Dasannachary; Effect of powder synthesis procedure on calcium site occupancies in barium calcium titanate: A Rietveld analysis; Appt.Phys. Lett. 62 (3), pp. 231-233, (1993).

[15] J.M. Han, M.R. Joung, J.S. Kim, Y.S. Lee, S. Nahm, Y.K. Choi, J.H. Paik, Hydrothermal Synthesis of $BaTiO_3$ Nanopowders Using TiO 2 Nanoparticles, J. American Ceramic Society; 97 (2), pp.346–349, (2014).

[16] S. Jayanthi, T.R.N. Kutty, Extended phase homogeneity and electrical properties of bariumcalcium titanate prepared by the wet chemical methods; J. Materials Science and Engineering, B 110,PP. 202–212, (2004).

[17] Haertling GH., Ferroelectric Ceramics: History and Technology; J. American Ceramics Society,82(4), pp. 797-818, (1999).

[18] Verbitskaya TN, Svetlova LN, Sokolova LS, Laverko EN, Raevskaya EB, Influence of added calcium titanate on the structure and properties of ferroelectric solid solutions based on $BaTiO_3$; Soviet Physics Crystallography, 33, pp. 609– 610, (1988).