The International Journal of Engineering and Science (IJES)
|| Volume || 7 || Issue || 12 Ver.I || Pages || PP 01-07|| 2018 ||
ISSN (e): 2319 – 1813 ISSN (p): 23-19 – 1805

Synthesis of Barium Titanate from Aqueous Solution of Barium Acetate and Titanium Dioxide Precursors

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--***ABSTRACT:*** ---

In this study, $BaTiO_3$ has been prepared from aqueous solution of barium acetate and titanium dioxide mixture. After drying, the barium titanate was obtained through solid state reaction. The thermal analysis TG-DTA and XRD techniques were used to study the formation of $BaTiO_3$ and the mechanism of formation as well. The effects of powder activation, calcination temperature and time on the formation of barium titanate were studied. It was found that, the use of barium acetate retarded the formation of $BaTiO_3$ and increased the temperature at which the reaction is completed. However, the coating process offered by this synthesis method for unmilled powder might be very useful in producing $BaTiO_3$ powder having core shell morphology, where the $BaTiO_3$ core is surrounded by a thin layer of Ba_2TiO_4 as a shell.

KEY WORDS: *Barium Titanate, Barium acetate, preparation and characterization*

Date of Submission: 24-10-2018 Date of acceptance: 31-12-2018

I. INTRODUCTION

Barium titanate ($BaTiO_3$) is a very important advanced ceramic material for the electronic industry. $BaTiO_3$ having both ferroelectric and piezoelectric properties was used in numerous and important applications. Among these applications, we can find the positive temperature coefficient (PTCR) thermistor, gas lighters, resonators, ultrasonic cleaners, multilayer ceramic capacitors (MLCCs), actuators, buzzer, ferroelectric film memory and electro-optic devices [1-3]. Since its discovery, it has become a subject of tremendous research and development in the synthesis methods to enhance its properties and to develop new applications [4-6]. Various methods, such as the solid state reaction method, spray pyrolysis, hydrothermal method, sol-gel method, high energy ball milling and others, has been used for synthesizing $BaTiO_3$ powder [7-14].

The objective of the present work is to study the formation of barium titanate powder from aqueous solution of barium acetate and titanium dioxide powder in order to prepare a homogeneous powder mixture through coating the titanium oxide particles by the barium acetate solution. This coating process might be very useful in producing powder having core shell morphology. The effect of milling using high energy planetary mill, calcination temperature and time will be studied as well.

II. EXPERIMENTAL PROCEDURE

Stoichiometric proportion of $Ba(CH_3COO)_2$ (Fisher ChemAlert® Guide, USA) and titanium dioxide (TiO_2: BDH Chemicals Ltd. Poole, England) powders were used as precursors. $Ba(CH_3COO)_2$ was completely dissolved in distilled water and then the TiO_2 powder was added and mixed using magnetic stirrer hot plate. The mixture was then dried (in NEY Furnace, M-525) at 90°C for 24h. The dried powder was divided into two parts. One part was mixed with ethyl alcohol and milled in a planetary mill (Retsch PM400-Fritsch, Germany) for 7.5h and designated as milled powder. The other part was left as dried and designated as unmilled powder. Both powders were then calcined (in a Carbolite Furnace, GPC 1300, UK) at different temperatures (600-950°C) for different calcination times, with a heating rate of 3°C/min, then furnace cooled. Thermal analyses were conducted in static air at a heating rate 10°C/min using the thermal analyzer (DTA-50, Shimadzu-Japan) and the thermo-gravimetric analyzer (TGA-50, Shimadzu-Japan). The morphology of the synthesized powders was examined by scanning electron microscopy (SEM: JEOL, JSM 5400, Japan). The crystalline phases were characterized using an X-ray diffractometer (XRD-3A, Shimadzu-Japan, CuKα-Ni filter). The crystallite sizes (t_c) of different samples were estimated from the broadening of the line (110) of XRD patterns, using Scherer's formula [15]:

$$t_c = k\,\lambda/ß\cos\theta$$

Where: k is a constant equal to 0.9, λ is Cu K_α wave length (λ =1.5404) and ß is the corrected broadening at the 2θ angle.

III. RESULTS AND DISCUSSION

Thermal analysis of barium acetate Ba $(CH_3COO)_2$ is shown in Fig. 1 The DTA curve shows endothermic peak at 80°C corresponding to a weight loss of 3% on the TG curve due to the removal of adsorbed water. Then the TG curve showed weight loss of 22.7% which ended at 500°C corresponding exactly to the difference between the molar weight of barium acetate and its decomposed product barium carbonate. This weight loss occurs in two steps; in the first one the acetate decomposes to barium oxalate (BaC_2O_4) and in the second the oxalate decomposes to barium carbonate. Fig. 2 shows the X-ray diffraction patterns for the barium acetate calcined at 395°C and 500°C as well as the XRD patterns of barium acetate $Ba(CH_3COO)_2$-as received-precursor and $BaCO_3$ for comparison. It can be seen that the pattern of barium acetate calcined at 395°C corresponds to that of BaC_2O_4, while the pattern of the acetate calcined at 500° shows that it has completely decomposed to barium carbonate. These results concord with that obtained from the thermal analysis. The two DTA exothermic peaks at 405°C and 430°C correspond to the oxidation of gaseous decomposition products, in agreement with results obtained by Zhou L et al., 2006 [16]. Hwang U-Y. et al., 2004 [17] was one of the few investigators who pointed out that the decomposition of barium acetate to barium carbonate takes place through barium oxalate. They found barium oxalates as intermediate product during the formation of barium titanate from barium acetate precursor. Wang Z-m. et al., 2013 [18] proposed the following equation as decomposition mechanism for barium acetate, after detailed DTA, TG, DSC, XRD, and FTIR analysis.

$$Ba(CH_3COO)_2 \rightarrow BaC_2O_4 \rightarrow BaCO_3.$$

On the other hand, Kodera T. et al., 2006 [19] and Sonia et al., 2009 [20] showed in their DTA analysis the exothermic peaks for barium acetate decomposition without comment on it. Zekaj D. C. et al., 2017 [21] showed that, when preparing barium strontium titanate, they got two DTA exothermic peaks at 410 and 440°C, which they attributed to intermediate phase's crystallization. Bera J. and Sarkar D., 2003 [22] showed an exothermic peak in their DTA analysis similar to the second exothermic peak shown in Fig. 1, which they attributed to the thermal decomposition of barium titanyl oxalate to barium titanium oxycarbonate.

At 810°C, Fig. 1 shows a small endothermic DTA peak which corresponds to the polymorphic transformation of barium carbonate from witherite orthorhombic (γ) to rhombohedral (β) structure. The same endothermic peak but at a relatively higher temperature, have been reported by S- Seveyrat L. et al., 2007 (830°C) [7] and Pavlovnić V et al. 2008 (~820°C) [12]. This discrepancy might be a result of using different heating rates.

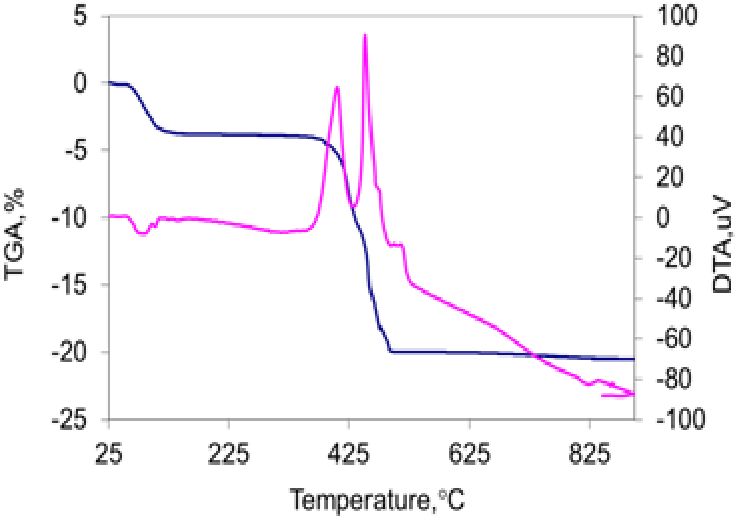


Fig. 1: TG-DTA curve for the Ba $(CH_3COO)_2$ powder

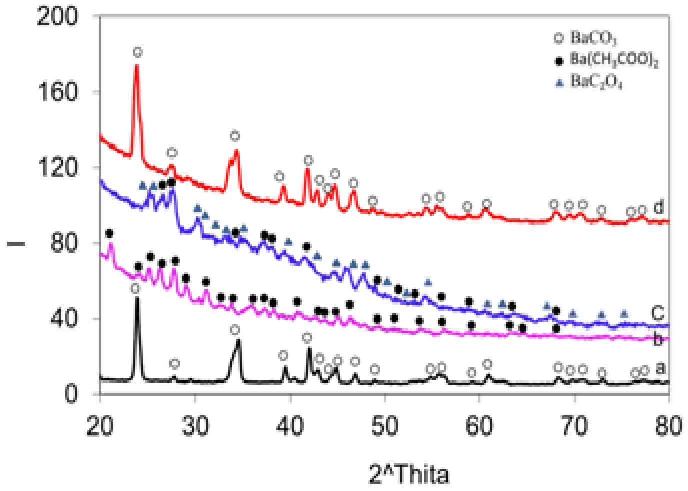


Fig. 2: XRD patterns of the: a)$BaCO_3$; b)$Ba(CH_3COO)_2$ powder; c)$Ba(CH_3COO)_2$ powder calcined at 395°C d)$Ba(CH_3COO)_2$powder, calcined at 500°C

Fig. 3 & 4 show the thermal analyses upon heating the $Ba(CH_3COO)_2$ and TiO_2 powder mixture, the milled and the unmilled respectively. For the *milled* powder, Fig. 3 shows a total weight loss of 28.7% on the TG curve. The DTA curve does not show the endothermic peak that corresponds to the removal of the adsorbed water from the acetate, since the powder was dried prior to the analysis. The decomposition of barium acetate to barium oxalate and barium carbonate, took place in two steps as mentioned earlier between 330–500°C. The corresponding two exothermic peaks were overlapped in one peak which may be a result of dilution by titanium dioxide.

In the temperature range from 500 to 633°C the TG curve does not show any weight loss because the barium carbonate particles resulting from the decomposition of barium acetate might have suffered from bad contact with the TiO_2 particles due to the existence of decomposition gases evolved. Later the particles of barium carbonate and titanium dioxide will go through rearrangement process to establish new contacts and then solid state reaction will take place. However, the DTA curve shows extra small exothermic peaks which might be due to dissociation of small amounts of isolated oxalate inside the agglomerates and/or anatase to rutile phase transformation [13, 23, 24]. Upon increasing the temperature the weight loss starts at relatively higher rate due to the reaction between $BaCO_3$ and TiO_2 to form $BaTiO_3$. This progresses gradually with the increase in temperature. The small DTA endothermic peak detected at 812°C stands for the polymorphic transformation of $BaCO_3$ as mentioned before. This might indicate that small amount of $BaCO_3$ still existed at temperature as high as 1000°C, which might explain the consequent appearance of intermediate Ba_2TiO_4, or the TiO_2 phases in the XRD patterns of the calcined powders.

For the *unmilled* powder, Fig. 4 shows a similar behavior to the milled powder except for the first decomposition peak of the barium acetate, which appeared explicitly in the milled powder pattern (Fig. 3) rather than in the unmilled powder pattern.

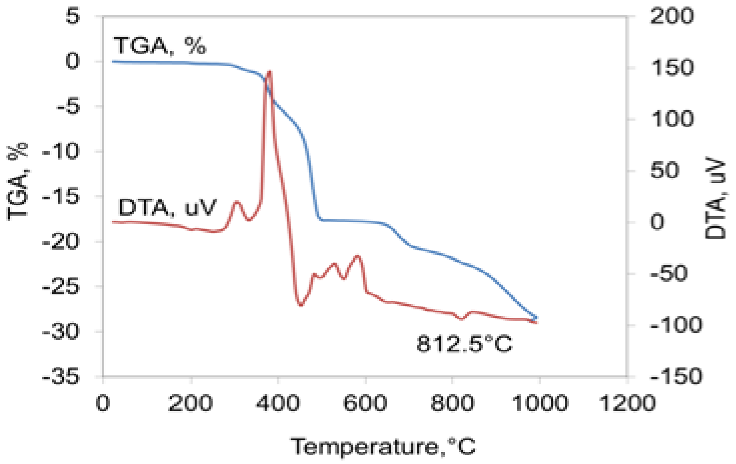


Fig.3: TG-DTA curve for the $Ba(CH_3COO)_2$-TiO_2 powder mixture, milled for7.5h

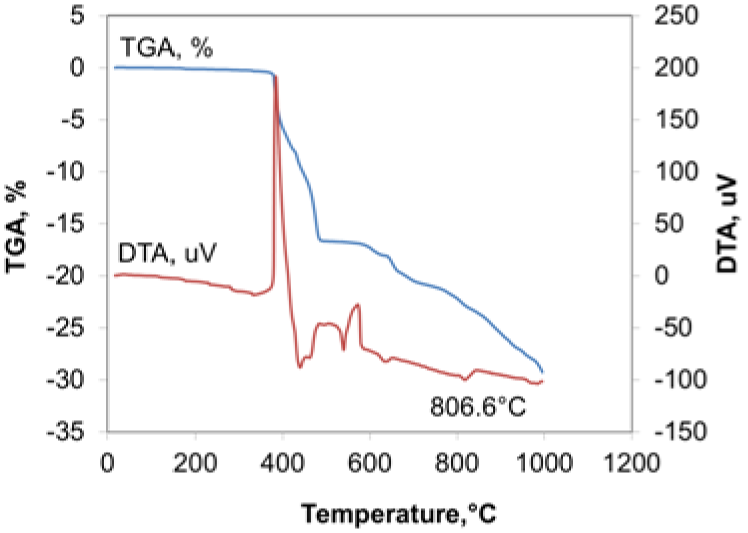


Fig. 4: TG-DTA curve for the unmilled $Ba(CH_3COO)_2$-TiO_2 powder mixture

The XRD patterns for the milled and the unmilled $Ba(CH_3COO)_2$-TiO_2 powder mixtures calcined at different temperatures and times are given in Figures 5 & 6 respectively. As shown in Fig. 5, $BaCO_3$ peaks still existed for the milled powders even after calcination at 850°C, indicating that this calcination temperature was not enough for complete formation of $BaTiO_3$. The XRD patterns for the calcined powders at 950°C for one hour, showed very small amounts of an orthotitanate intermediate phase (Ba_2TiO_4) at 2θ: 29.3°, which coexisted with $BaTiO_3$. However, single perovskite $BaTiO_3$ phase was formed upon increasing the calcination time of powder mixture at this temperature to two hours. This formation temperature is lower than that obtained by Wang W-N et al., 2005 [9] who used low-pressure spray pyrolysis (LPSP) method for the same starting precursors.

The XRD patterns for the unmilled powder, Fig. 6, show a similar behavior to the milled powder up to 950°C. However, increasing the calcination time or temperature did not eliminate the Ba_2TiO_4 intermediate phase from the final product, which might be due to the lower reactivity of unmilled powders. It was found that, the temperature at which this trace amount of Ba_2TiO_4 was formed and the temperature at which this phase transformed to $BaTiO_3$ depends on the reactivity of reacting powders [13]. On the other hand and according to a previous thermodynamic study [25], the elimination of the intermediate phase above 1200°C is not thermodynamically possible.

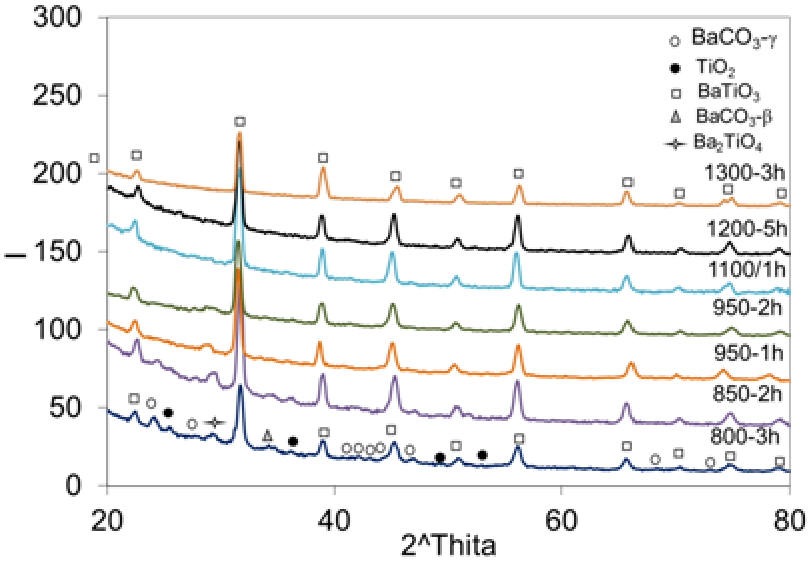


Fig.5: XRD patterns of the $Ba(CH_3COO)_2$-TiO_2 powder mixtures, milled for 7.5h and calcined at different temperatures and times

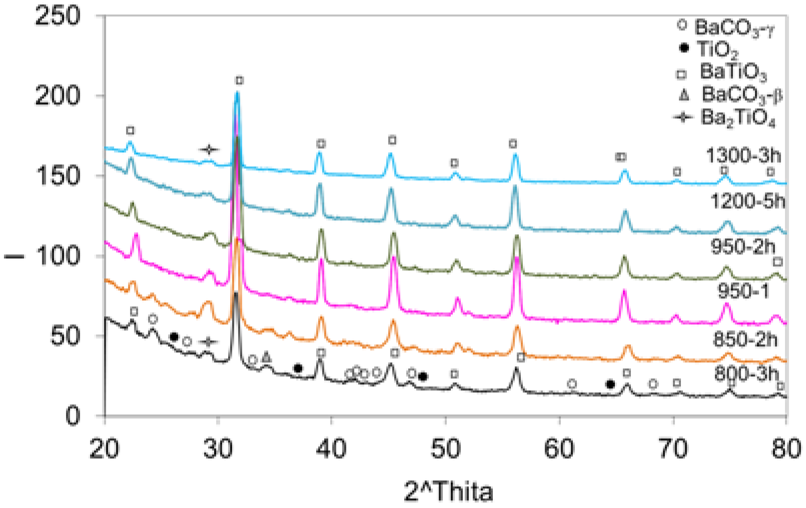


Fig. 6: XRD patterns of the unmilled $Ba(CH_3COO)_2$-TiO_2 powder mixtures, calcined at different temperatures and times

Fig. 7 shows SEM micrographs of the morphology of the $BaTiO_3$ powders prepared from Ba $(CH_3COO)_2$-TiO_2 milled mixtures, and calcined at 950°C for 2h. It can be seen from Fig.7-a that the powders are in the form of nearly spherical agglomerates. Small agglomerates less than 200 nm in size and large agglomerates of an average 2µm or greater could be observed. At higher magnification (8500x), Fig. 7-b shows that large agglomerates are composed of smaller agglomerates. The same observations are valid for the unmilled powder shown in Fig. 8, but with greater proportion of large agglomerates; this might have an effect on the final properties of the prepared $BaTiO_3$. The crystallite sizes were calculated from the XRD line broadening and found to be 14.6 and 14.35nm for the milled and unmilled powders respectively, using Scherrer's formula [15].

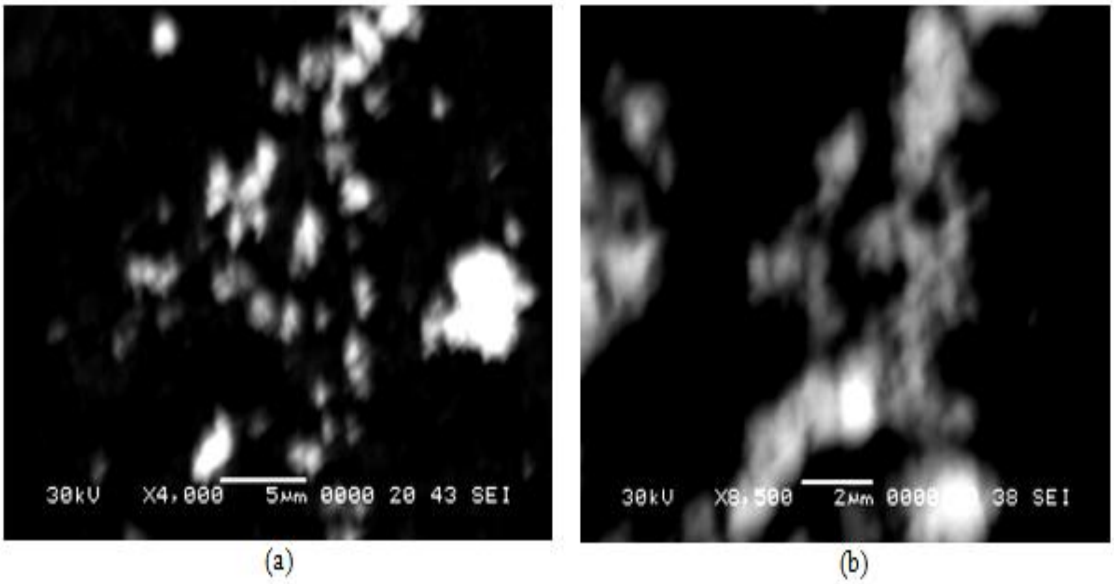
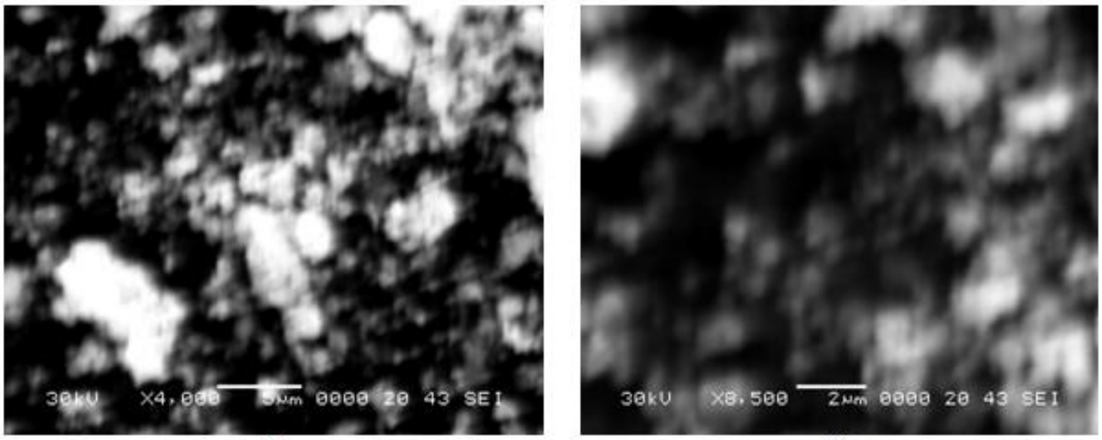


Fig. 7: SEM for $Ba(CH_3COO)_2$-TiO_2, milled powder mixture, calcined at 950°C/2h;
a) 4000x b) 8500x



(a) (b)

Fig. 8: SEM for $Ba(CH_3COO)_2$-TiO_2, unmilled powder mixture, calcined at 950°C/2h; a) 4000x b) 8500x

3.1 Formation mechanisms

Based on the thermodynamic studies obtained by, Othman K. I et al., 2014 [25] and the results of the present work we propose that the reaction between Ba $(CH_3COO)_2$ and TiO_2 takes place according to the following sequence:

1- Between 340-440°C:

$$Ba(CH_3COO)_2+TiO_2+7/2O_2 \rightarrow BaC_2O_4+TiO_2+2CO_2+3H_2O \quad \text{….(1)}$$

2- Between 440-500°C:

$$BaC_2O_4+TiO_2+0.5O_2 \rightarrow BaCO_3+TiO_2+CO_2 \quad \text{…..(2)}$$

3- At 630 and above:

$$BaCO_3+TiO_2 \rightarrow BaTiO_3+CO \quad \text{....(3)}$$

4-At about 800°C:

At the heterogeneous points, where the $BaCO_3$ is greater than the nearby TiO_2, the formation of Ba_2TiO_4 intermediate phase becomes thermodynamically more possible to occur according to the following reaction:

$$2BaCO_3+TiO_2 \rightarrow Ba_2TiO_4+2CO_2 \quad \text{….. (4)}$$

5- At 900°C:

The amount of intermediate Ba_2TiO_4 phase increases (Fig. 5, 6) for two reasons; *first*, due to the reaction between the formed barium titanate and the nearby barium carbonate to form this intermediate phase according to Eq.(5). *Second* the rate of spontaneous transformation of this intermediate phase to barium titanate starts to decrease at this temperature.

$$BaTiO_3+BaCO_3 \rightarrow Ba_2TiO_4+CO_2 \quad \text{….(5)}$$

5- Meanwhile, a decrease of intermediate phase can occur spontaneously by the reaction of Ba_2TiO_4 with TiO_2 through interdiffusion process upon increasing temperature to eventually form $BaTiO_3$ according to Eq. 6:

$$Ba_2TiO_4 + TiO_2 \rightarrow 2BaTiO_3 \quad \text{….(6)}$$

This might be the case of reactive milled powder mixture which was composed mainly of small agglomerates and showed less heterogeneity. However, above 1200°C this reaction (Eq.6) is not possible thermodynamically and accordingly any unreacted quantity of the intermediate phase cannot be eliminated above this temperature and will remain in the final product. This explains the appearance of this phase in the XRD pattern for the unmilled $Ba(CH_3COO)_2$ and TiO_2 powder mixture (Fig. 6), where a core shell morphology more probably prevails with $BaTiO_3$ core surrounded by a thin orthotitante barium rich Ba_2TiO_4 shell. This is a great and remarkable difference between the milled and the unmilled powders that can be offered by this synthesis method. Wang Z-m et al., 2013 [18] showed similar core shell approach for the powder prepared by sol gel method relative to that prepared by mechanical activation.

IV. CONCLUSIONS

The formation of barium titanate from aqueous solution of barium acetate and TiO_2 has been studied in detail. Thermal analysis, SEM and XRD have been used to describe the formation process and we found that:

1- The activated powder, by planetary milling, showed better homogeneity than the unmilled one.
2- $BaTiO_3$ powder produced by this method was composed of large and small agglomerates ranging from an average size of 0.2 to 2µm; for the milled powder and could reach 5µm for the unmilled one. Each of these agglomerates is formed of small crystallites of about 14nm.

3- The use of aqueous barium acetate retarded the reaction between the derived $BaCO_3$ with TiO_2 which, in this case, was found to start after the decomposition of the acetate to barium oxalate and then to $BaCO_3$

4- The unmilled powder contains more Ba_2TiO_4 intermediate phase than the milled one even after calcinations at 1300°C for 3h.

5- The calcined unmilled powder is thought to have the morphology of a core of barium titanate and a shell of thin layer of Ba_2TiO_4.

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Kolthoum I. Othman" Synthesis of Barium Titanate from Aqueous Solution of Barium Acetate and Titanium Dioxide Precursors" The International Journal of Engineering and Science (IJES), 7.12 (2018): 01-07