Formation Mechanism of Barium Titanate by Solid-State Reactions

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Abstract

The solid state reactions of $BaTiO_3$ formation from a mechanically activated $BaCO_3$-TiO_2 powder mixture have been investigated. Thermogravimetric TGA, thermomechanical TMA, scanning electron microscopy SEM, X-ray diffraction XRD and reactions thermodynamic analyses have been used in the present study. The results of these analyses showed that, the formation of $BaTiO_3$ proceeds through a direct reaction between $BaCO_3$ and TiO_2, not through the decomposition of $BaCO_3$ to BaO neither through the formation of Ba_2TiO_4 intermediate phase. The agglomerated nature of the milled powder, its rearrangement during the course of the reaction, the particle size of $BaCO_3$ and TiO_2 and the effect of the evolved CO_2 gas in the reaction zone are the major factors affecting the mechanism of reaction between $BaCO_3$ and TiO_2.

Index Terms: Barium Titanate, TG; TMA, reaction mechanism, formation.

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1 INTRODUCTION

Barium titanate ($BaTiO_3$) ceramics have been extensively studied during the last few decades because of its excellent electrical and electromechanical properties. A substantial number of synthetic methods have been developed for the preparation of barium titanate powders. Both the conventional solid state reaction methods and the chemical methods such as sol gel, coprecipitation, hydrothermal and mechanochemical used to prepare barium titanate have been reviewed by Vigalovic et al.[1]. Studies on the preparation of nano-size barium titanate have been carried out in the last decade and are still done by a number of authors; [2-4]. Large scale production is frequently based on solid-state reactions of mixed powders $BaCO_3$ and TiO_2 at high temperatures [5]. However, this procedure can result in a ceramic with compositional inhomogeneities and formation of secondary phases which harms the electrical properties of $BaTiO_3$. Hence the intimate mixing of the starting powders is of paramount importance for $BaTiO_3$ preparation. The mechanical activation using high energy milling process is a very effective method for obtaining highly mixed powders [6-9]. Several assumptions were made to explain the formation mechanisms of barium titanate from $BaCO_3$ and TiO_2 precursors. According to Pavlović et al.[9], the following reactions sequence was proposed:

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2 \qquad (1)$$
$$BaTiO_3 + BaCO_3 \rightarrow Ba_2TiO_4 + CO_2 \qquad (2)$$
$$Ba_2TiO_4 + TiO_2 \rightarrow 2BaTiO_3 \qquad (3)$$

Meanwhile Seveyrat et al.[10], emphasized on the reaction: $BaCO_3+TiO_2 \rightarrow BaTiO_3+CO_2$ as a major contributor to the formation of $BaTiO_3$ with a trace amount of Ba_2TiO_4. On the other hand, Kong et al.[6], proposed the following scheme which had been proposed long ago by Gallagher et al.[17],

$$2BaCO_3 + TiO_2 \rightarrow Ba_2TiO_4 + 2CO_2 \qquad (4)$$
$$Ba_2TiO_4 + TiO_2 \rightarrow 2BaTiO_3$$

On the other hand, Beauger et al.[11] proposed another two schemes, the first scheme was:

$$BaCO_3 \rightarrow BaO + CO_2 \qquad (5)$$
$$2BaO + TiO_2 \rightarrow Ba_2TiO_4 \qquad (6)$$
$$Ba_2TiO_4 + TiO_2 \rightarrow 2BaTiO_3$$

While the second one was:

$$BaCO_3 \rightarrow BaO + CO_2$$
$$BaO + TiO_2 \rightarrow BaTiO_3$$
$$BaTiO_3 + BaCO_3 \rightarrow Ba_2TiO_4 + CO_2$$
$$Ba_2TiO_4 + TiO_2 \rightarrow 2BaTiO_3$$

From the above assumptions it can be seen that, the transformation of the reactant to the final product ($BaTiO_3$), could take place by using different paths; i.e. different reaction formulas. Studying the thermodynamics of these reactions is of fundamental importance to understand the mechanism by which this important material is formed. The thermodynamic approach could be a useful tool in examining whether a certain reaction could take place under certain conditions, while another could not. This could be done through the calculation of the change in the

Gibbs free energy (ΔG) of the different reactions at different temperatures.

1.1. Thermodynamics of the chemical reactions:

Gibbs free energy change (ΔG_T) is defined in equation (1) as a function of temperature;

$$\Delta GT = \Delta H_T - T\Delta S_T \quad \text{….(1)}$$

Where: ΔH_T is the enthalpy change for the different chemical precursors taking part in the reaction, calculated as given in Equation (2):

$$\Delta H_{\mathbf{T}} = \Delta H^{\circ}_{\mathbf{298}} + \int_{\mathbf{298}}^{\mathbf{T}} C_{\mathbf{P}} dT \qquad (2)$$

Where: $\Delta H^{\circ}298$ is the standard heat of formation at 298K and CP is the heat capacity [12]. Cp can be calculated from equation (3):

$$CP = a+b*10\text{-}3\ T – c*105/T2 \quad \text{….(3)}$$

Where: a, b, and c are constants.

The entropy change ΔS could be calculated from the following equation:

$$\Delta S_{\mathbf{T}} = \Delta S^{\circ}_{\mathbf{298}} + \int_{\mathbf{298}}^{\mathbf{T}} \frac{C_{\mathbf{P}}}{T} dT \qquad (4)$$

These calculations should be made for the reactants and the products involved in the proposed reactions that could possibly occur. The enthalpy and entropy change for the reaction were given by euations (5) and (6):

$$\Delta HR = \sum \Delta H_{Product} - \sum \Delta H_{Reactant} \qquad (5)$$

$$\Delta SR = \sum \Delta S_{Product} - \sum \Delta S_{Reactant} \qquad (6)$$

The thermodynamic data for the standard values ΔH_{298}, ΔS_{298} and the heat capacity Cp for the chemical precursors used as reactants, as well as for the reaction products were obtained from Kubaschewski et al.[12], and Karapetyants [13] and presented in Table (1).

Table (1): The standard thermodynamic data for ΔH_o, ΔS_o, and C_p.

Substance	Constants a	b	c	Entropy S_{298}, kJ/mole	Enthalpy H_{298}, kJ/mole
$BaCO_3$**	21.5	11.06	2.96	0.112024	-1218.888
BaO**	11.79	1.88	0.88	0.0702658	-553.432
$BaTiO_3$*	20.03	2.04	4.58	0.1079276	-1659.7944
$Ba2TiO_4$*	43	1.6	6.96	0.1966272	-2242.988
CO_2**	10.57	2.16	2.06	0.2134726	-394.00262
TiO_2	17.83	0.5	4.23	0.0502854	-943.844

** O. Kubaschewski and C. B. Alcock, "Metallurgical Thermochemistry", Pergamon press, 1979.*

*** M. Kh. Karapetyants, "Chemical Thermodynamics", MIR Publishers-Moscow, 1978.*

2. Experimental Procedure:

An equimolar mixture of $BaCO_3$ (99% purity, Aldrich Chemical Company, USA) powder and a very fine titanium dioxide (TiO_2) were used as the starting materials. The fine TiO_2 powder was prepared from $TiCl_4$ (Aldrich Chemical Co. Ltd., Gillingham-Dorset-England) by oxidation and hydrolysis. Slurry of $BaCO_3$-TiO_2 powder mixture in alcohol was milled in the planetary mill (Retsch PM400-Fritsch, Germany) for 7.5h. The milling speed was set at 200 rpm. The milling was stopped for 5 min every 30 min of milling to cool down the mill. After milling the slurry was dried at 90oC for 20h in the drying Furnace (NEY Furnace, M-525). The dried powder was then crushed in agate mortar (Fritsch, Germany) followed by sieving using 112 µm sieve. The sieved powder was calcined in Carbolite Furnace, GPC 1300, UK at temperatures from 600 to 900°C for different times, with a heating rate of 10°C/min. The thermal analysis was studied using differential thermal analyzer (DTA-50), the thermo-gravimetric analyzer (TGA-50) and the thermo-mechanical analyzer (TMA-50) from Shimadzu-Japan. X-ray diffractometer (XRD-3A, Shimadzu-Japan, CuKα-Ni filter) was used for phase analysis. Powder morphology, agglomerations, grain size and the as-fired surfaces of the sintered bodies were examined using a Scanning Electron Microscope (JEOL, JSM 5400, Japan).

3. Results and Discussion

3.1. Thermal Analysis

Figure (1) shows the DTA-TG curves for the $BaCO_3$-TiO_2 milled powder mixtures. It can be seen from the figure that, the DTA curve does not show any endothermic or exothermic peaks during heating up to 1000°C, while the thermo-gravimetric (TG) curve shows a weight loss of 18.5%. First a weight loss of 2.46% starting from the room temperature and ending at 220°C, this is represented by differential thermo-gravimetric (DTG) peak (Figure-2) at 40°C, which corresponds to the elimination of the remainder of the ethanol used in the wet milling. Another 2% weight loss occurred in the temperature range 220-430°C, Which corresponds to a DTG peak at 293°C and represented the release of absorbed water from the TiO_2 powder. Then in the temperature range from 430 to 1000°C, the TG curve showed a weight loss of 15.8%, corresponding to the formation of one mole $BaTiO_3$ as a result of the reaction of one mole $BaCO_3$ and one mole TiO_2. This value is equivalent to the release of one mole CO_2, in agreement with the published results [7, 8, 10, 14]. On the other hand, Kong et al.,[6] used a planetary milled $BaCO_3$-TiO_2 powder mixture from Aldrich Chemicals, showed relatively lower value of weight loss of 12.1%, which might be due to deficiency in the carbonate proportion in their powder mixture.

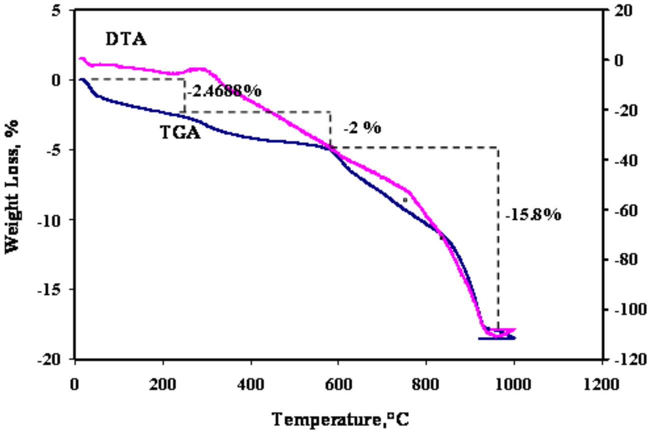

Fig.1. DTA-TG for BaCO3-TiO_2 powder mixture milled for 7.5h.

The TG curve shows that the formation of $BaTiO_3$ takes place in three consecutive stages; characterized by three DTG peaks at 612, 729, and 915°C. The first one (corresponding to DTG peak at 611.8C) in the temperature range 550-670°C, corresponds to the beginning of the reaction between $BaCO_3$ and TiO_2 to form $BaTiO_3$ phase and release of CO_2 (according to the reaction: $BaCO_3+TiO_2 \rightarrow BaTiO_3+CO_2$). The second stage (corresponding to DTG peak at 728.8 °C) proceeded at a slower rate than the first one, in the temperature range 670-820°C and might stand for the Ba_2TiO_4 intermediate phase formation. The third stage took place in the temperature range 820-950°C, and is characterized by a very large DTG peak at 914.7°C. This may stand for the reaction between the unreacted $BaCO_3$ and TiO_2 and as well for the reaction of tiny amount of the intermediate phase Ba_2TiO_4 and the unreacted TiO_2 to form $BaTiO_3$ phase.

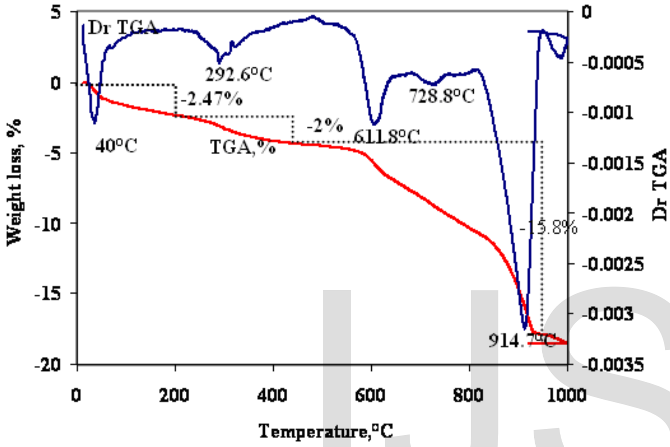

Fig. 2. The DTG curve for the $BaCO_3$-TiO_2 powder mixture milled for 7.5h.

Figures (3), (4) show the relative linear shrinkage and the linear shrinkage rate versus temperature and time, respectively, for a compact made from the as milled $BaCO_3/TiO_2$ powder mixture. From Figure (3) it can be seen that, the shrinkage took place in two stages: the first one started at ~654°C and ended at 895°C. Then upon further heating, no shrinkage could be observed until the second stage of shrinkage started at ~1135°C and continued with an increasing rate during the heating up to ~1320°C. Figure (4) showed that, in the first stage of shrinkage there were two maxima in the shrinkage rate; the first one at 714°C and the second at 836°C. The thermomechanical analysis is in agreement with the DTG results mentioned previously, but lag behind by about 100°C. This comes from the difference in nature between the compact and the powder and as well between weight loss and dimension changes in the compact during the course of the reaction where CO_2 gas will be evolved or released. This could result in competition between swelling (expansion) and contraction due to particle rearrangement at the beginning. Then upon increasing the temperature and the continuous release of CO_2 from the sample, contraction in the compacts showed the two shrinkage peaks mentioned above (at 714.2 and 836°C). The slowing down in rate of weight change (DTG-Figure 2) during the second stage of the reaction might be a result of an increase in CO_2 pressure released in large quantities at the first stage in the vicinity of the reactants. The presence of CO_2 gas thermodynamically suppresses the reaction until paths for CO_2 release are created through microcracks formation caused by CO_2 pressure build up.

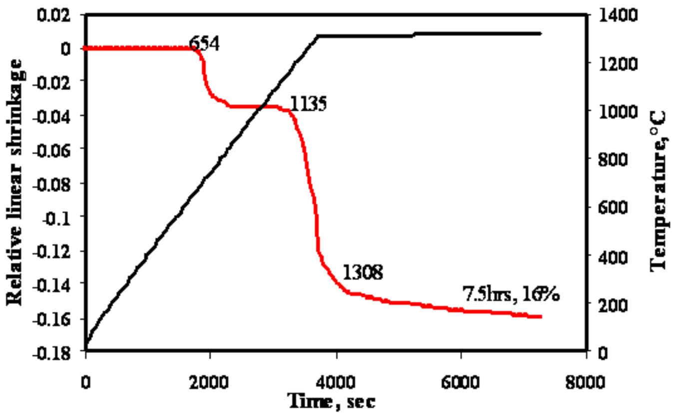

Fig. 3. Linear shrinkage of the $BaCO_3$-TiO_2 compact.

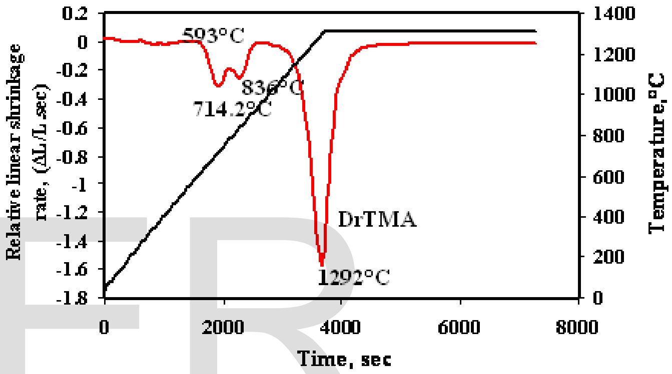

Fig. 4. Linear shrinkage rate of the $BaCO_3$-TiO_2 compact.

3.2. X-ray diffraction

X-ray phase analysis made on the product of the solid state reaction in air between $BaCO_3$ and TiO_2 Figure (5) showed that $BaTiO_3$ is the dominating phase. The amount of $BaTiO_3$ formed after calcination increases with the increase in calcination temperature at constant calcination time of 1h. At 900°C, the reaction between $BaCO_3$ and TiO_2 reaches an end by 100% formation of perovskite single phase $BaTiO_3$.

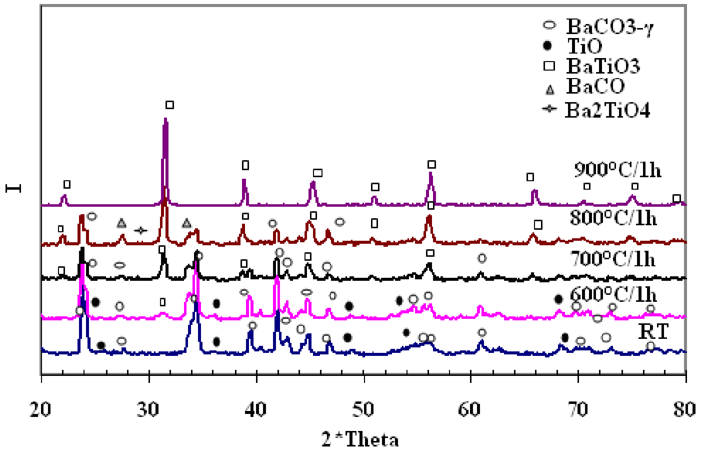

Fig. 5. XRD patterns of powder mixture milled for 7.5 h and cal-

cined atdifferent temperatures.

However, the XRD patterns for the powders calcined at 800°C, showed small amounts of an intermediate phase with a composition Ba_2TiO_4 (orthotitanate phase at $2\theta=28.6°$) in addition to $BaTiO_3$, TiO_2 and $BaCO_3$ phases. This trace amount of Ba_2TiO_4 does not appear on the XRD patterns made for the powders calcined at 600, 700, and 900°C. Seveyrat et al.[10], Berbeni et al.[8], and Brzozowski et al.[7] reported a similar behavior, where a very small amount of intermediate phase was preceded by $BaTiO_3$ formation, in agreement with the present results. They found that the temperature at which this trace amount of Ba_2TiO_4 was formed and the temperature at which this phase retransformed to BaTiO3 depends on the reactivity of TiO_2 powder and on the milling time. On the other hand, Kong et al.[6] came up with a conclusion, telling that the intermediate phase Ba_2TiO_4 was formed before the formation of $BaTiO_3$ at 700°C.

This is not only contradicting with the above results but it contradicts also with their own XRD pattern, which shows that $BaTiO_3$ starts to form at 600°C. This rules out the statement saying that the formation of $BaTiO_3$ should be preceded by the formation of Ba_2TiO_4 intermediate phase. Their results might be attributed to probable in homogeneity of their mixture or may be due to using more $BaTiO_3$ than that required stoichiometrically.

3.3. The thermodynamic Analysis

The thermodynamic calculations of the change in Gibbs free energy (ΔG) versus temperature for the different possible reactions that could take place during the calcination of $BaCO_3$ and TiO_2; showed to be in favor of the direct reaction between $BaCO_3$ and TiO_2 to form $BaTiO_3$. Figure (6) shows the free energy change, ΔG, versus temperature; From the figure it can be seen that, the schemes of reactions based on the decomposition of $BaCO_3$ (A. Beauger et al., 1983, E. Brzozwski et al., 2003) contradict with the thermodynamic data of the decomposition of $BaCO_3$, which occurs at relatively higher temperature than that for the direct reaction between $BaCO_3$ and TiO_2. On the other hand, models based on the formation of Ba_2TiO_4 from the reaction between $BaTiO_3$ and $BaCO_3$ also contradicts with the thermodynamic data. Since this reaction can not take place at 800°C but at rather higher temperature i.e 900°C. The only thermodynamically possible reaction to form Ba_2TiO_4 at 800°C is:

$$2BaCO_3 + TiO_2 \rightarrow Ba_2TiO_4 + CO_2$$

However, this reaction is not geometrically feasible because the previously formed $BaTiO_3$ acts as isolation layer between the reactants $BaCO_3$ and TiO_2. Yet, if somehow a quantity of the intermediate phase Ba_2TiO_4 was formed, most of it will disappear immediately when reacting with CO_2 gas trapped in the reaction zone. This will take place according to a thermodynamically possible reaction as follows:

$$Ba_2TiO_4 + CO_2 \rightarrow BaTiO_3 + BaCO_3, \quad \text{Where: } \Delta G = -20.3 \text{ Kj/mole}$$

From the above discussion, and combining the results of the thermodynamic analysis together with the XRD analyses and the DTA/TGA curves might be useful for better understanding the reaction mechanism of $BaTiO_3$ formation through solid state reaction. Thus a more realistic approach to the reaction mechanism will be given in the following section.

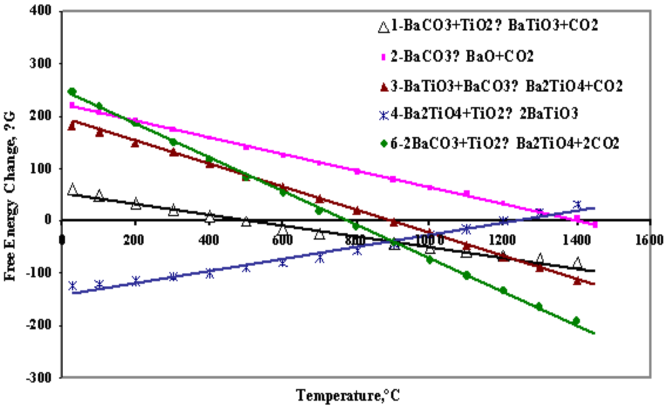

Fig. 6. The change in Gibbs free energy (ΔG) versus temperature for the different possible reactions that could take place during the calcination of $BaCO_3$ and TiO_2

3.4. Realistic approach to the reaction mechanism

The SEM of the as milled powder, Figure (7), showed that the powder consists of large agglomerates of bimodal particles of fine TiO_2 and coarse $BaCO_3$.

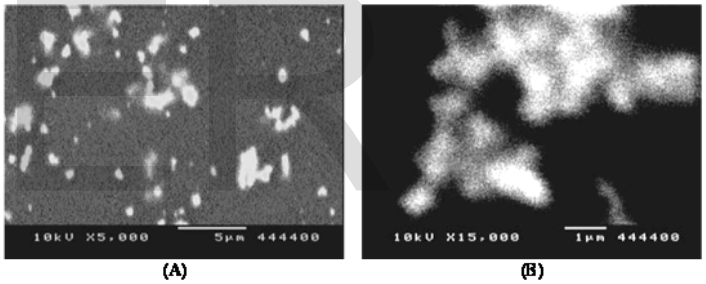

Fig. 7. SEM of dispersed powder of the $BaCO_3/TiO_2$ milled mixture.

When the agglomerated mixture schematically shown on Figure (8-A) is heated up to 600-700°C, a reaction between $BaCO_3$ and TiO_2 to form $BaTiO_3$ will take place at all the dissimilar contacts inside each agglomerate and as well in the contact surfaces between the agglomerates where dissimilar contacts exist as schematically shown on Figure (8-B). The XRD made on $BaCO_3/TiO_2$ mixture calcined at 600°C showed the formation of $BaTiO_3$. This reaction produces CO_2 gas, most of it was trapped inside each agglomerates. The gas will develop pressure which will create slowly a network of microcracks through which it will escape from the reaction zones. This can be seen from the TG curve, Figure (1), which shows a relatively low rate for the weight loss. The thermomechanical analysis TMA showed a shrinkage which occurs as a result of release of CO_2. This shrinkage will be accompanied by particle rearrangement inside each agglomerates as well as agglomerates rearrangement. As a result new dissimilar contacts inside and outside the agglomerates will be created and the reaction proceeds again on the newly created dissimilar contact surfaces and more $BaTiO_3$ was formed. On some of the new surfaces of contacts between the agglomerates which are rich in $BaCO_3$, an intermediate phase of Ba_2TiO_4 may be formed as shown in Figure (8-C). As mentioned before the XRD made on the powder mixture calcined at 800°C showed a trace amount of the intermediate phase, which indicates that the heterogeneities in the powder are very little. This supports the idea that this reaction occurs on few places at the new contact surfaces between the agglomerates, where dissimilar contacts rich in $BaCO_3$ exist. This step also will be accompanied by further shrinkage and rearrangements (reflected on TMA curves), which will create further new dissimilar contacts during the course of heating up. The reaction will then proceed at relatively higher rate as shown on the TG curve, Figure (1), as a result of the increase of temperature and the ease of the CO_2 release. In this range of temperature the TiO_2 will react with both the intermediate phase and the residual $BaCO_3$ to form $BaTiO_3$. This is shown on Figure (8-D), where single phase $BaTiO_3$ fine particles and voids were formed. It should be noted here that the particle size of the initial powder and the homogeneity are very important factors in the determination of the reaction mechanism. Niepce et al.[15] and Buscaglia et al.[16] showed that it is possible to prevent the formation of Ba_2TiO_4 phase by controlling the particle size of both $BaCO_3$ and TiO_2 powders.

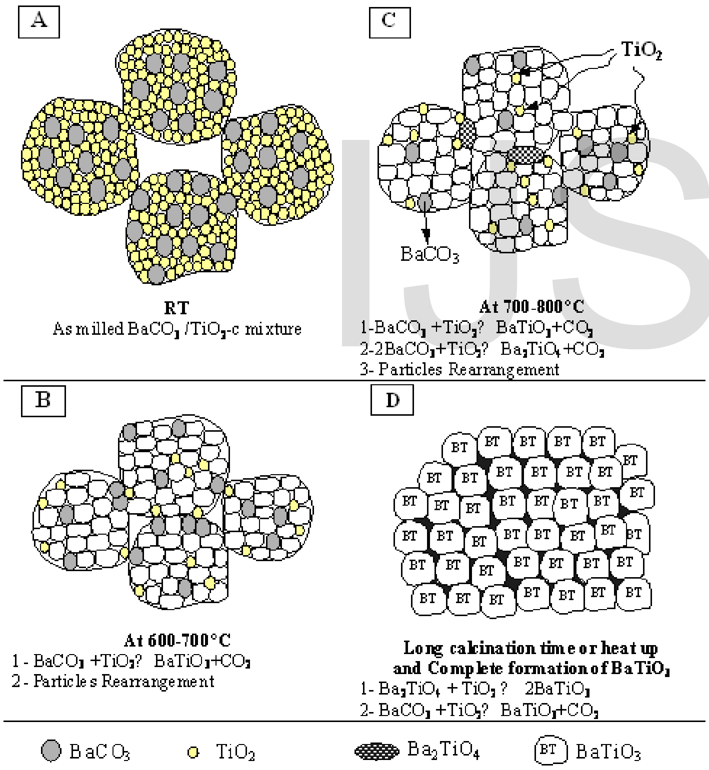

Fig. 8. Schematic diagram for the realistic approach describing the reaction mechanism of formation of $BaTiO_3$ from $BaCO_3/TiO_2$ powder mixture

4. Conclusions

The solid state reaction of $BaTiO_3$ formation from a mechanically activated $BaCO_3$-TiO_2 system has been investigated. An equai molar mixture of $BaCO_3$ and TiO_2 powders was activated in a planetary ball mill for 7.5 h. A reaction mechanism was proposed depending on the morphology of the milled powder and on the experimental results obtained from SEM, TG, TMA and XRD analyses. The agglomerated nature of the milled powder, its rearrangement during the course of the reaction, the particle size of $BaCO_3$ and TiO_2 and the effect of CO_2 gas in the reaction zone are the major factors affecting the mechanism of reaction between $BaCO_3$ and TiO_2. The DTA-TG, XRD and the thermodynamic analyses showed that, the formation of $BaTiO_3$ proceeds through a direct reaction between $BaCO_3$ and TiO_2, not through the decomposition of $BaCO_3$ to BaO, neither through the formation of Ba_2TiO_4 intermediate phase.

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