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Lowering the synthesis temperature of high-purity $BaTiO_3$ powders by modifications in the processing conditions

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Abstract

In this work, the influence of the $BaCO_3$:TiO_2 ratio and milling conditions on the solid-state barium titanate formation at high temperature has been studied. An excess of TiO_2 improved the $BaTiO_3$ formation when the TiO_2 reactivity was low. Besides, long milling time and an excess of fine grained titanium led to agglomerate formation. In addition, mechanochemical activation performed by rigorous milling and the employment of fine particles of anatase-rich TiO_2 powder allowed the reaction to go to completions at temperatures about 150 °C and below than traditionally need.

Keywords: Powders: solid-state reaction; Planetary milling; $BaTiO_3$ and titanates; Secondary phases; Particle size; TGA and DTA

1. Introduction

The studies of $BaTiO_3$ and its related compounds have intensified because of their excellent electric and electromechanical properties [1], such that, they are extensively used in the preparation of high-permittivity capacitors, PTC resistors, transducers, and ferroelectric memories [2,3].

In order to produce ceramics with dense and uniform microstructures, it is essential to control the properties of the initial $BaTiO_3$ powder. Ideal characteristics of the $BaTiO_3$ powders include high-purity of the final product, fine particle size, unagglomerated particles and narrow particle size distribution [4]. Also, the availability of raw materials for the $BaTiO_3$ preparation and the economic viability of the synthesis are vital for the success of a specific process.

During the last decade a wide number of synthetic methods have been developed for the preparation of barium titanate powders, but large scale production is frequently based on solid-state reactions of mixed oxides [5–14]. In this process, barium titanate is obtained from the reaction between TiO_2 and $BaCO_3$ at high temperatures (1100–1400 °C) [7,8]. Beauger et al. [8,13,14] have studied the solid-state reaction that takes place between these starting materials, and proposed an empirical model for the reaction with the following sequence:

(a) Formation of $BaTiO_3$ by reaction of $BaCO_3$ and TiO_2 in air:

$$BaCO_3 \rightarrow \text{“BaO”} + CO_2 \quad (1)$$

$$\text{“BaO”} + TiO_2 \rightarrow BaTiO_3 \quad (2)$$

Particles of TiO_2 act as a catalyst for the $BaCO_3$ decomposition. Following the decomposition, a layer of $BaTiO_3$ appears around the TiO_2 particles.

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(b) After the initial formation of $BaTiO_3$, TiO_2 and $BaCO_3$ are separated by a product layer, and subsequent $BaTiO_3$ formation is controlled by the diffusion of barium ions through the $BaTiO_3$ layer. Therefore, secondary phases such as Ba_2TiO_4 can appear:

$$BaTiO_3 + \text{“BaO”} \rightarrow Ba_2TiO_4 \quad (3)$$

(c) Finally, the secondary phase reacts with the TiO_2 nucleus to form $BaTiO_3$:

$$Ba_2TiO_4 + TiO_2 \rightarrow 2BaTiO_3 \quad (4)$$

Despite the multiple advantages of the solid-state method for preparing $BaTiO_3$, is that it is a single process and a low cost technique, there are some problems with it to be solved. In fact, high calcination temperatures lead to coarsening of the $BaTiO_3$ particles that are unsuitable for manufacturing fine grained ceramics. Also, even if the nominal ratio of $BaCO_3/TiO_2$ is 1, intermediate phases or $BaCO_3$ can persist as an end-product and a complete reaction between the starting materials is not achieved.

On the other hand, it is well known that tribophysics and tribochemistry (or mechanical and mechanochemistry) can deal with physical, chemical or physico-chemical changes due to the influence of mechanical energy. This influence can be expressed as the increase of total free surface and internal energy of materials, changes in crystal lattice and in some cases, as chemical changes [15,16]. In this work, the influence of the reactivity of the raw materials ($BaCO_3$–TiO_2) and their ratio on the effectiveness of the mechanochemical activation in the $BaTiO_3$ formation has been studied.

2. Experimental

Barium titanate was prepared from different analytical reagents, as indicated in Table 1. $BaCO_3$ (Mallinckrodt, calcium $< 0.05\%$ as major impurity) and TiO_2 (Degussa P25 with $Al_2O_3 < 0.3\%$ as principal impurity, or Baker Chem with Pb $< 0.02\%$ as principal impurity) were mixed in a ratio of 1:1 or 1:1.01, as listed in Table 1. Reactants were milled in a planetary mill (Frisch “Pulversisette 7”, ZrO_2 balls) for 4 or 10 h and dried to constant weight.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out in flowing air with a Shimadzu D-50 analyser used to control the heating rate at 10 °C/min up to 1200 °C. The characteristics of the powders including particle morphology and agglomeration were examined by SEM (Philips 505). Measurements were made on powders calcinated at 1200 °C for 2 h. Particle size distributions of the raw materials and milled products were determined using a Sedigraph particle analyser. In order to identify the crystalline phases, samples were subjected to several heat treatments from 600 to 1200 °C at a heating rate of 10 °C/min, holding the sample at the selected temperatures for 1 min and air-quenched. X-ray diffraction (XRD) patterns were recorded on these powders using a Philips PW1830 X-ray diffractometer with Cu Kα radiation and Ni filter at 40 kV and 30 mA.

3. Results and discussion

It was established that a high proportion of the anatase phase gave a low packing density to the TiO_2 lattice and a high reactivity in the reaction with $BaCO_3$ at high temperature [14]. Samples labelled as S2 and S3 were prepared from TiO_2 with the highest parti-

Table 1
Nomenclature of the samples

Sample	$BaCO_3$[a]			$BaCO_3$:TiO_2 ratio	TiO_2[a]			Anatase/rutile ratio
	D20	D50	D80		D20	D50	D80	
S1	1.25	1.65	2.30	1:1.01	<0.01	0.02	0.32	7.5
S2	1.25	1.65	2.30	1:1.01	0.47	0.65	0.80	6.6
S3	1.25	1.65	2.30	1:1	<0.01	0.02	0.32	7.5
S4	1.25	1.65	2.30	1:1	0.47	0.65	0.80	6.6

[a] Particle size in μm.

Table 2
Particle size of the milled samples

Sample	D20 (μm)	D50 (μm)	D80 (μm)	Milling time (h)
S1-10	0.68	1.55	2.55	10
S2-10	0.84	1.35	2.1	10
S1-4	0.38	1.15	2.0	4
S2-4	0.6	1.2	1.9	4
S3-10	0.42	1.17	2.0	10
S4-10	0.8	1.27	2.0	10

cle size and the lowest anatase/rutile ratio. In samples S1 and S3, a very fine TiO_2 with the highest anatase/rutile ratio was employed (Table 1). The use of two titanium oxides with different reactivity allowed the influence to be measured on the $BaTiO_3$ formation.

Table 2 shows the particle size of S1–S4 after milling in the planetary mill. D20, D50, and D80 are the particle diameters corresponding to 20, 50 and 80 vol.%, respectively.

Two $BaCO_3$:TiO_2 ratios were studied. A $BaCO_3$:TiO_2 ratio of 1:1.01 was used in samples S1 and S2, in order to achieve complete reaction by increasing the catalytic reactive content. In samples S3 and S4, a stoichimetric $BaCO_3$: TiO_2 ratio was employed. Samples S1 and S2 milled for 10 h (called S1-10 and S2-10) did not exhibit any reduction in the particle size with the milling time (see Table 2). On the contrary, in sample S1-10 an increase in particle size at D20 and D80 fractions was detected. This increase was due to TiO_2 agglomerate formation at high milling times. Accordingly, a reduction in milling time was adopted (see in Table 2 samples milled for 4 h). When the milling process was conducted for 4 h, a reduction in particle size was observed (samples S1-4 and S2-4) and thereafter, a milling time of 4 h was employed for the following studies.

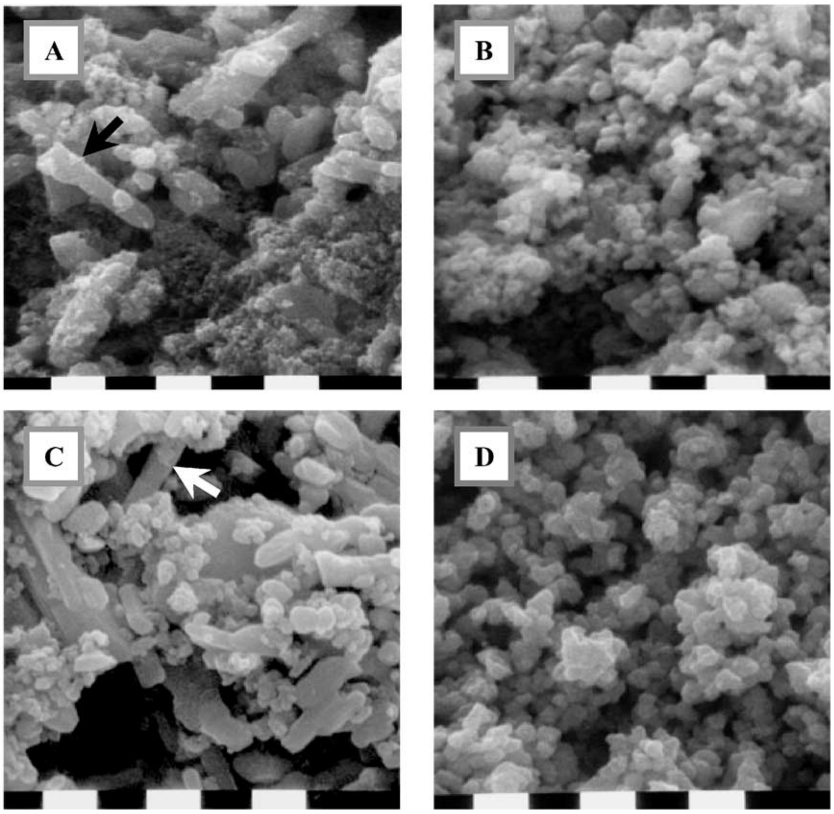

Fig. 1. SEM microphotographs of: (A) mixture S1-4; (B) calcined sample S1-4; (C) mixture S2-4; (D) calcined sample S2-4. Thermal treatment performed at 1200 °C for 90 min; bar: 10 μm.

In Fig. 1A and C, SEM micrographs of mixtures S1-4 and S2-4 are displayed. Analysis of the mixed powders showed that $BaCO_3$ was present as elongated particles, as indicating by the arrow in Fig. 1A and C. Conversely, TiO_2 particles have spherical morphology and in the case of the sample S1-4 they are strongly agglomerated. However, Fig. 1B and D shows the development of rounded particles of barium titanate after calcining S1-4 and S2-4 mixtures at 1200 °C for 90 min. This observation agrees with the model of reaction proposed in this work, in that the TiO_2 particles acted as nucleation sites for $BaTiO_3$ formation. The strong agglomeration of TiO_2 in the mixture S1-4 induced sintering of titania particles as $BaTiO_3$ was forming. Significant particle growth in sample S1-4 was observed.

TGA curves of the overall set of samples are shown in Fig. 2A. A lower decomposition temperature was observed in the S1-4 than in the S2-4 sample. Thermal events detected by DTA are shown in Fig. 2B for the various samples. An endotherm between 800 and 830 °C (peak (1)) indicates the transition from $\gamma \rightarrow \beta$ in $BaCO_3$. The phase transition peak is less significant in sample S1-4 than in sample S2-4 due

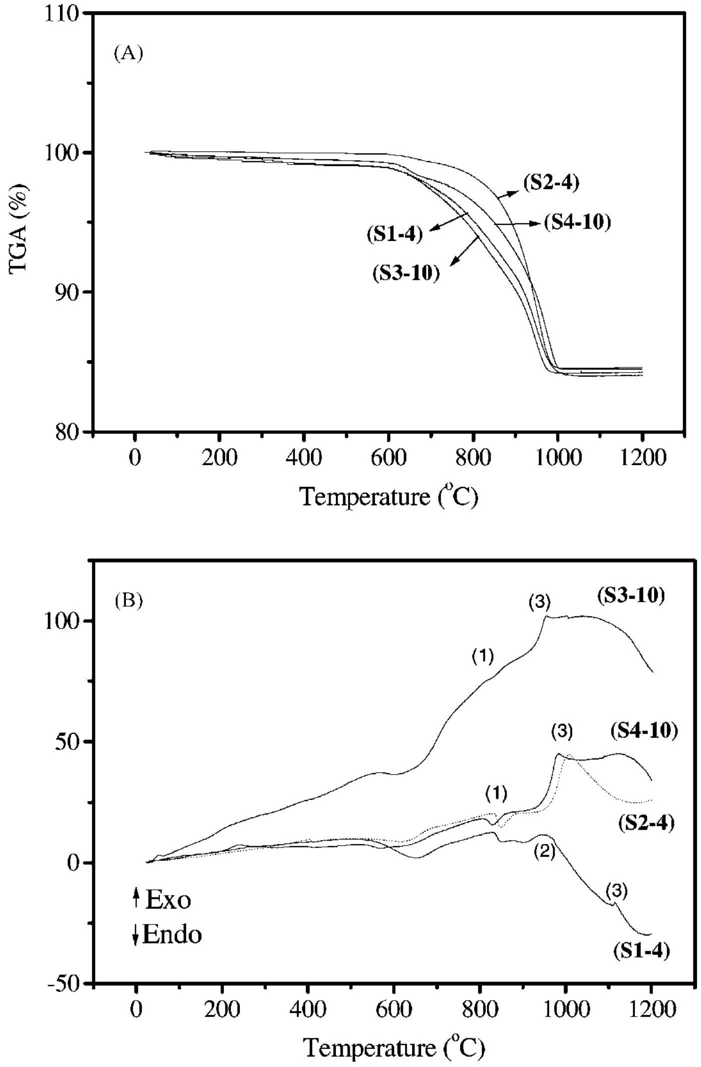

Fig. 2. (A) TGA; (B) DTA curves for samples S1-4, S2-4, S3-10 and S4-10.

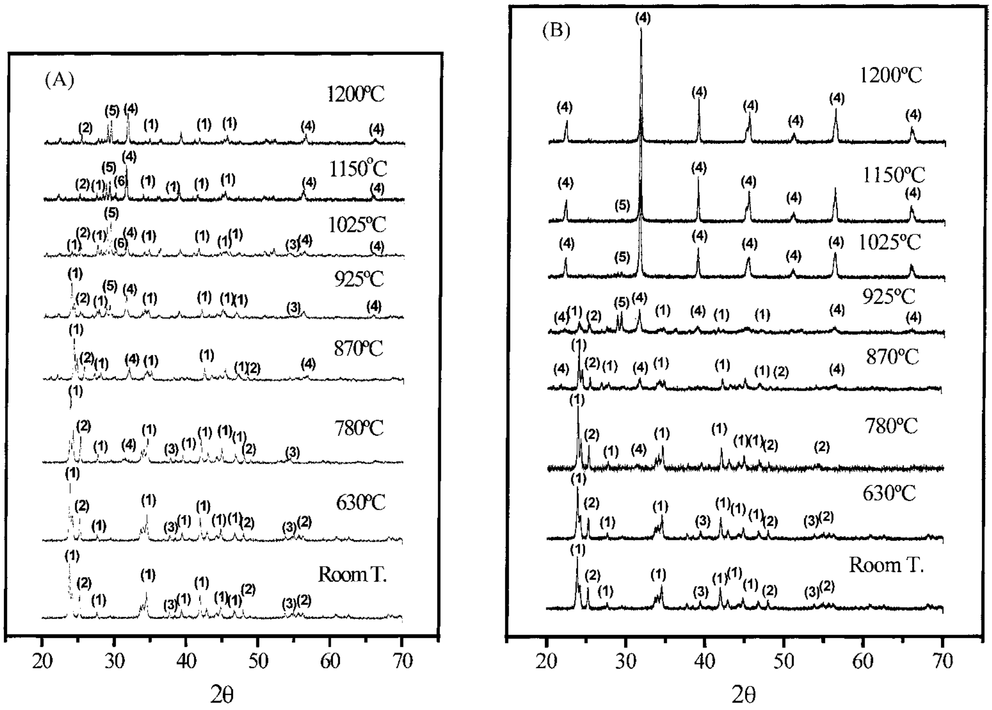

Fig. 3. XRD diagrams of the samples at different temperatures: (A) S1-4; (B) S2-4. (1) $BaCO_3$, (2) TiO_2 anatase, (3) TiO_2 rutile, (4) $BaTiO_3$, (5) Ba_2TiO_4, and (6) $BaTi_2O_5$.

to fast $BaCO_3$ decomposition. This also affected the intermediate phases (peak (2) around 950 °C) and $BaTiO_3$—the large peak (3) at 1115 °C, in S1-4. A more limited formation of the secondary phases in sample S2-4 allowed the $BaTiO_3$ formation to occur at 1009 °C (peak (3) for S2-4).

XRD analysis of the S1-4 and S2-4 mixtures after each thermal cycle agreed with the thermal analysis results for the formation of $BaTiO_3$ and the occurrence of intermediate phases (Fig. 3). Sample S1-4 showed the greatest content of secondary phases over all temperatures studied. However, in sample S2-4 the secondary phases disappeared at 1100 °C. In analysing the changes observed Beauger's model was adopted. Due to the high reactivity of the TiO_2 (sample S1-4) a layer of $BaTiO_3$ covered the TiO_2 nuclei at lower temperatures. After that, direct contact between TiO_2 and $BaCO_3$ was not possible, the decomposition of the $BaCO_3$ was not catalysed by TiO_2 and the massive decomposition occurred at high temperature. The reaction rate was slowed by the diffusion of barium ions through the $BaTiO_3$ layer. In addition, secondary reactions at the interfaces between TiO_2 and $BaTiO_3$ and between BaO and $BaTiO_3$ took place. As a result, phases with high barium content (such as Ba_2TiO_4) or titanium (such as $BaTi_2O_5$ and $BaTi_4O_9$) were observed. If these persisted at high temperature it was difficult to obtain a final high-purity product, as happened with sample S1-4. When an excess of fine TiO_2 particles were used, the final product with secondary phases was obtained. In these systems, the diffusion of the barium ions through the $BaTiO_3$ layer controlled the formation of the final product at the end of the reaction.

In Table 2 the particle sizes of samples S3 and S4 milled for 10 h are shown. We can see that milling decreased the particle size. This was more important with larger particles of $BaCO_3$. In this case TiO_2 agglomeration was not observed because a $BaCO_3$:TiO_2 stoichiometric ratio was employed.

From the TGA curves of samples S3-10 and S4-10 in Fig. 2A, it can be seen that S4-10 starts to decompose at lower temperature than any other system.

According to the DTA analysis carried out on samples S3-10 and S4-10 (see Fig. 2B), no perceptible variation in the $BaCO_3$ transition temperature at 800–830 °C with the synthesis conditions was detected. However, two phenomena affected the intensity of the signal belonging to the $\gamma \rightarrow \beta$ transition in $BaCO_3$. On one hand, more rigorous milling decreased the intensity of the endothermic peak at 800–830 °C (compare Fig. 2B for S1-4 and S3-10 samples or S2-4 and S4-10 samples). In this case, the diminution of crystallinity and the increasing of $BaCO_3$ reactivity made the $\gamma \rightarrow \beta$ phase transition less significant in this reagent. On the other hand, more reactive TiO_2 catalysed the $BaCO_3$ reaction and consequently, a less perceptible endothermic signal at 830 °C was detected. The mechanochemical activation led to a great formation of $BaTiO_3$ at a lower temperature.

In Fig. 4, XRD spectra of samples S3-10 (A) and S4-10 (B) after different thermal treatments are shown. From these, a decrease in the crystallinity of $BaCO_3$ after the milling process over 10 h was observed. In these samples a more reactive TiO_2 decreased the temperature of $BaTiO_3$ formation and a product free of secondary phases was obtained at 1043 °C (see Fig. 4, sample S3-10). When TiO_2 with a lower ratio of anatase/rutile was employed, barium titanate with Ba_2TiO_4 as a secondary phase at 1100 °C was obtained (S4-10). This can be explained by the reaction model proposed by Beauger et al. [8,13,14]. Sample S3-10 contained a TiO_2 with a greater reactivity, which improved the $BaCO_3$ decomposition. In this case, we can see that the effectiveness of the milling process was affected by the reactivity of the TiO_2 employed.

Based on this experimental evidence, we can assert that a combination of a very reactive TiO_2 with an equimolar $BaCO_3/TiO_2$ ratio and rigorous mechanochemical activation of the reagents led to the lowest temperature for a complete formation of $BaTiO_3$ (sample S3-10: 951 °C).

Gómez-Yañez et al. [17] reported the formation of Ba_2TiO_4 at high temperature in samples

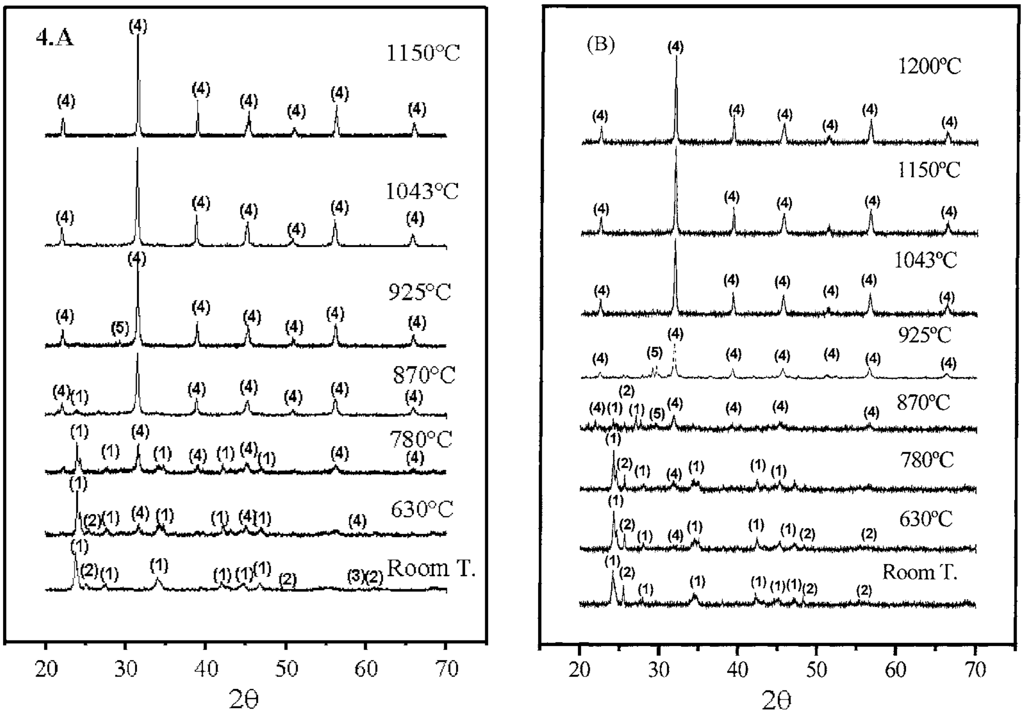

Fig. 4. XRD diagrams of the samples at different temperatures: (A) S3-10; (B) S4-10. (1) $BaCO_3$, (2) TiO_2 anatase, (3) TiO_2 rutile, (4) $BaTiO_3$, (5) Ba_2TiO_4.

with mechanical activation. They attributed this to the TiO_2 allotropic transformations from anatase phase to rutile structure during the milling process. We did not observe this phase transformation, but we noted that the existence of agglomerates in the TiO_2 of small particle size led to an important generation of Ti-rich phases. On the other hand, we observed that the anatase/rutile ratio modified the temperature of $BaTiO_3$ formation free of secondary phases.

4. Conclusions

In this work, we have studied the effect of three parameters on the formation of $BaTiO_3$ by solid-state reaction: (1) $BaCO_3/TiO_2$ ratio, (2) anatase/rutile phases relation, reactivity and granulometry of TiO_2, and (3) mechanochemical activation of the reagents. From these sketches, it has been possible to conclude that:

- Long periods of milling can produce agglomeration of the particles with a detrimental effect on the material homogeneity. This problem was more significant when the ratio of $BaCO_3$:TiO_2 differed from 1:1.
- The optimum $BaCO_3$:TiO_2 ratio showed a dependence on the reactivity of the TiO_2 employed. An excess of TiO_2 improved the $BaTiO_3$ formation when the TiO_2 reactivity was low.
- Two processes controlled the barium titanate formation. One was the $BaCO_3$ decomposition catalysed by the presence of TiO_2. The other one was Ba ions diffusion through the $BaTiO_3$ layer formed surrounding the TiO_2 particles. The second process induced the second phase formation.

Acknowledgements

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