Synthesis of barium titanate improved by modifications in the kinetics of the solid state reaction

E. Brzozowski, M.S. Castro

Institute of Materials Science and Technology (INTEMA), Universidad Nacional de Mar del Plata, CONICET, Juan B. Justo 4302, (7600) Mar del Plata, Argentina

Abstract

In this work, the synthesis of $BaTiO_3$ powder from $BaCO_3$–TiO_2 reaction at high temperatures is studied. In order to improve the kinetics of this reaction, successive modifications on the powder processing have been implemented. The contribution of the mechanochemical activation to the $BaTiO_3$ formation is analysed. It was found that the use of a mechanochemical activation favours the decomposition of $BaCO_3$ at low temperatures and improves the barium ion diffusion through the $BaTiO_3$ layer. In consequence, a $BaTiO_3$ product free of secondary phases can be obtained at lower temperatures. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: $BaTiO_3$ and titanates; Milling; Powders-solid-state reaction

1. Introduction

Barium titanate is a compound widely used in the preparation of components for electronic applications, such as piezoceramic devices, electro-optic elements, ceramic capacitors and PTC resistors. It is known that barium titanate ceramics present a high dielectric constant and exhibit interesting semiconducting properties when they are modified with suitable additives.[1–3]

It has been established that the reproducibility of $BaTiO_3$ ceramics strongly depends on some phenomena that result from ceramic manufacturing technology.[4–8] Titanates are usually synthesized by solid-state reaction at high temperatures, and the successful production of powders for advanced electronic ceramics requires the control of the synthesis process. This can be achieved from the reaction between TiO_2 and $BaCO_3$.[9–12] The reactants are mixed in order to reduce agglomerates, to increase the homogeneity and to reduce the particle size. After mixing, the raw materials are fired at high temperatures and then, the $BaTiO_3$ is produced.

According to Beauger et al.,[9] the reaction between $BaCO_3$ and TiO_2 may be broken down into the following stages.

i. Formation of $BaTiO_3$ by reaction in air between $BaCO_3$ and TiO_2 at the expense of TiO_2:

$$BaCO_3 \rightarrow BaO + CO_2 \qquad (1)$$

$$BaO + TiO_2 \rightarrow BaTiO_3 \qquad (2)$$

According to the model, TiO_2 particles act as catalyser in the $BaCO_3$ decomposition. At first, such reaction proceeds rapidly at the surface of contact between the reactants. Then, $BaTiO_3$ appears.

ii. When $BaTiO_3$ is formed, the reactants are separated by a product layer; then the course of the reaction becomes diffusion controlled. Barium ions must diffuse through $BaTiO_3$ and penetrate into TiO_2 grains. However, when reaching the $BaTiO_3$ interface, barium can react according to:

$$BaTiO_3 + BaO \rightarrow Ba_2TiO_4 \qquad (3)$$

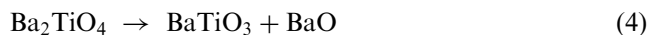* Corresponding author. Fax: +54-223-4810046.
E-mail address: mcastro@fi.mdp.edu.ar (M.S. Castro).

Hence, the formation of Ba_2TiO_4 proceeds by the reaction between BaO and the prior-formed $BaTiO_3$.

iii. Finally, TiO_2 and Ba_2TiO_4 react to produce $BaTiO_3$, which is the final phase:

$$Ba_2TiO_4 \rightarrow BaTiO_3 + BaO \qquad (4)$$

$$TiO_2 + BaO \rightarrow BaTiO_3 \qquad (5)$$

Powders produced in solid-state reactions are often aggregated, affecting the grain growth during sintering. In order to avoid or minimise this problem, it is important to select an appropriate milling method. Unfortunately, chemical impurities are frequently introduced into the powders from the grinding medium (Al_2O_3, ZrO_2, etc.). Also, it is not easy to mix and to maintain chemical homogeneity in the final product, especially when one of the reactants is present in a minor proportion. It is known that mechanical activation alters the physicochemical properties of mixed polycrystalline oxides, and then the synthesis mechanism.[8]

In this work we present a synthesis process of $BaTiO_3$ powders that can be carried out at lower temperatures to obtain a product free of secondary phases.

2. Experimental procedure

Barium titanate was obtained from $BaCO_3$ (Lennox Lab., specific area 1.8 m^2/g, and medium particle size 1.2 μm) and TiO_2 (Degussa P25, specific area 42.4 m^2/g, and medium particle size 0.21 μm). Reactants were mixed in 1:1 relation. The reactants were mixed in a planetary mill (Fritsch "Pulverisette 5", ZrO_2 balls) during 2–10 h or in an alumina ball mill for 2 h, see Table 1 for details. After drying, powders were thermally treated in the range of 600–1200°C, with a heating rate of 10°C/min. In order to analyse the existent phases, the samples were held at each temperature for 1 min and air-quenched.

Crystallographic phases and the structural analysis were carried out in an X-ray diffraction (XRD) with a Phillips PW1830 diffractometer, using CuK_α radiation and Ni filter at 40 kV and 30 mA. Differential thermal analysis were carried out in a DTA-50 Shimadzu, with a heating rate of 10°C/min. Size particle distributions of the raw materials, milled products and calcined samples were determined by the Sedigraph technique with a Micromeritics. The surface area measurements were carried out using the BET method with a Monosorb Quantachrome, employing a mixture of He/N_2 gasses in a relation 70/30.

3. Results and discussion

Fig. 1 shows the diagrams of XRD of samples S1, and S2 after different thermal treatments are shown. TiO_2 used in this system exhibits low crystalline content and the anatase/rutile ratio is 7.5. This relation is responsible for the high reactivity. From Fig. 1, we can see that the 2 h planetary milling process applied produces a small diminution in the crystallinity of the reactants. The milling effect is to destroy agglomerates and to produce the homogenisation of powders. However, from the diagrams the apparition of secondary phases with the planetary milling is also observed. Gomez-Yañez et al.[13] observed an increase in the secondary phases content with the milling process. They determined that an intensive milling in an attritor decreases the rate of Ba_2TiO_4 decomposition, probably due to the previous production of large Ba_2TiO_4 crystals.

It was determined that the presence of secondary phases such as Ba_2TiO_4 in $BaTiO_3$[14] could produce a deterioration of the dielectric properties. On this matter, it was established that the reproducibility of the electrical properties is strongly influenced by the purity of the $BaTiO_3$ employed. Therefore, is necessary to obtain a final product free of secondary phases.

From the Beauger mechanism,[9] it is possible to see that the reaction between TiO_2 and $BaCO_3$ and the diffusion of barium through $BaTiO_3$ layer controls the barium titanate formation. In particular, when a mechanochemical activation is used, both mechanisms can be modified. Then, in order to improve the kinetic of the process, it is necessary to produce the decomposition of $BaCO_3$ at low temperatures. For this reason, an increase in the milling time could increase the $BaCO_3$ reactivity.

Table 2 shows data from particle size distributions corresponding to mixtures S1, and S3, obtained after the milling step and after calcination at 1150°C during 2 h. We considered that D80, D20 and D50 are the corresponding diameters of 80, 20 and 50% volume respectively, and $W = (D80-D20)/D50$ is a measure of the distribution width of particle size. Two facts are observed after each step. A decrease in the medium particle size of the samples milled in a planetary mill was observed. This phenomenon was more important in the particles of high size, which correspond to $BaCO_3$.

Table 1
Nomenclature of the samples. D50 is the particle size of 50% volume

Sample	Milling method
S1	Ball mill, 70 rpm, 2 h.
S2	Planetary mill, 2700 rpm, 2 h
S3	Planetary mill, 2700 rpm, 10 h
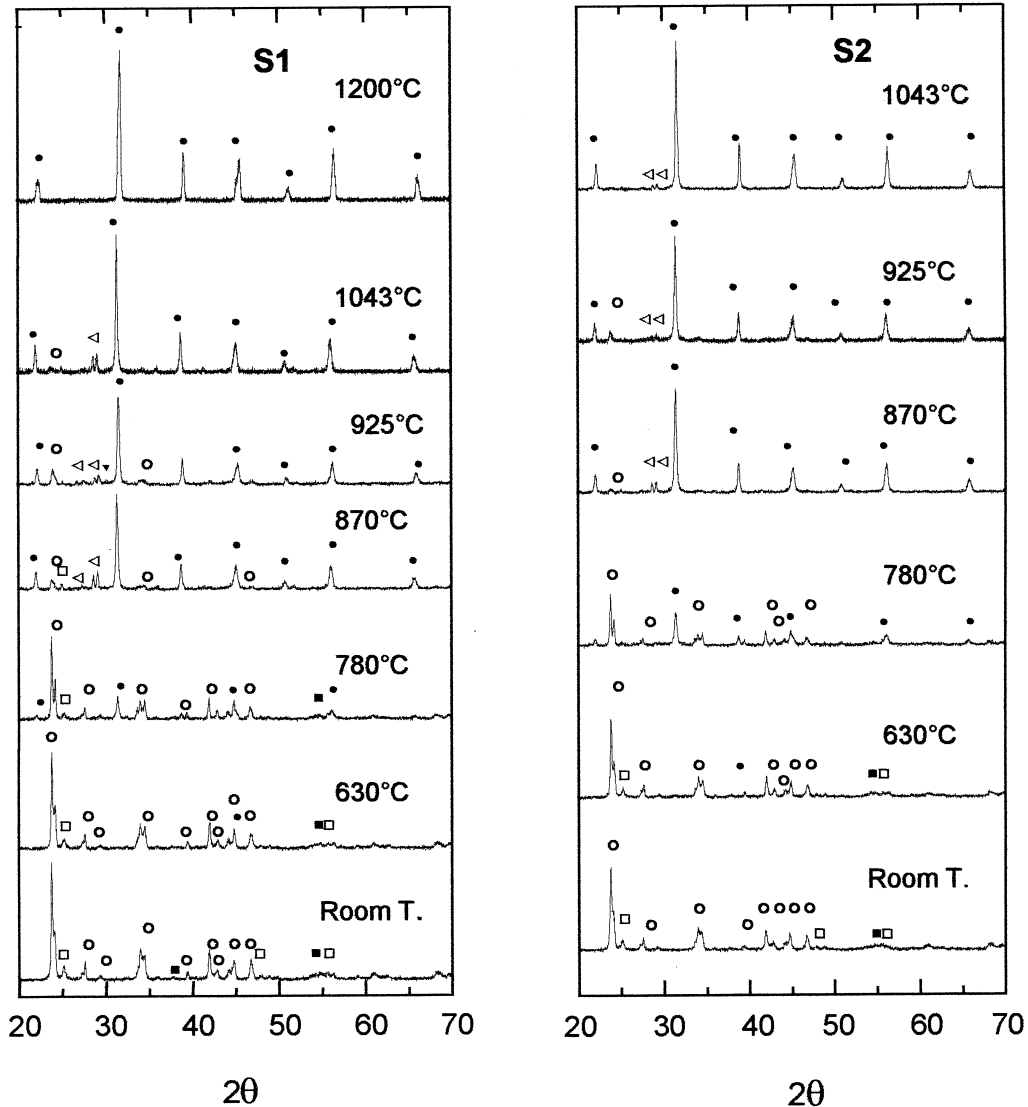
Fig. 1. X-ray diffraction patterns of samples S1 and S2. ○ $BaCO_3$, □ TiO_2 anatase, ■ TiO_2 rutile, ● $BaTiO_3$, ◁ Ba_2TiO_4, ▼ Ba_2TiO_5.

Then, when the decomposition of the carbonate is produced, a diminution in the particle size is observed (see Table 2).

Due to the use of TiO_2 with high specific area, samples S1 and S3 present an elevated value of specific area. Moreover, sample S3 does not present an important increase in the specific area as consequence of the milling step, because in this mixture the activation process presents a diminution in the $BaCO_3$ particle sizes.

Fig. 2 shows the DTA diagrams for samples S1, S2, and S3. Significant differences in the systems appear as temperature is increasing. Sample S2 does not present an important variation in the DTA diagram respect to S1. However, in sample S3, a displacement of the $BaTiO_3$ peak respect to S1 is observed. Moreover, the signal corresponding to the transition $\gamma \rightarrow \beta$ in $BaCO_3$ (827°C)[15,16] does not appear in sample S3. This difference is due to an increase in the reactivity of the $BaCO_3$

Table 2
Particle size distributions and specific area of samples S1, and S3

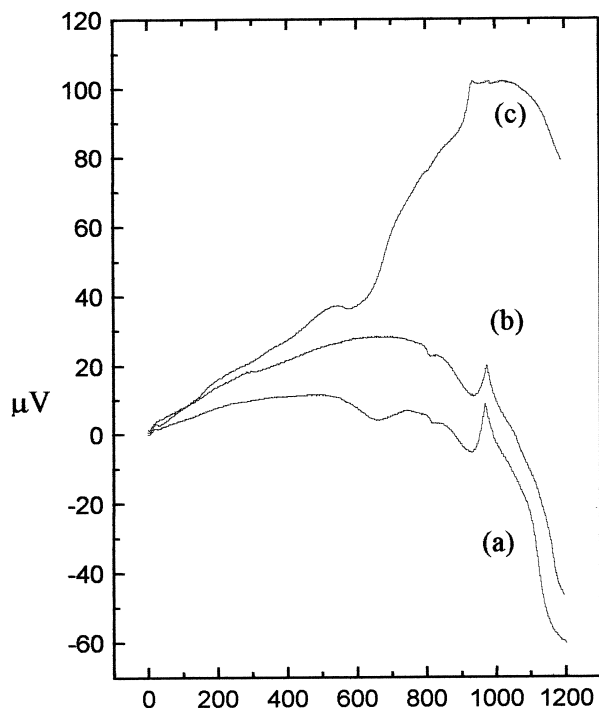|	As milled					Calcined			
Sample	D80 (μm)	D20 (μm)	D50 (μm)	W	Specific area (m²/g)	D80 (μm)	D20 (μm)	D50 (μm)	W
S1	1.95	0.4	1.30	1.19	16.6	2.10	0.74	1.20	1.13
S3	1.5	0.25	0.85	1.47	17.2	1.30	0.52	0.80	0.98

Fig. 2. Diferential thermal analysis diagrams of samples (a) S1, (b) S2 and (c) S3.

after applying the rigorous milling process. In consequence, the $BaCO_3$ decomposition in S3 started before reaching the transition temperature, and the signal corresponding to $\gamma \rightarrow \beta$ cannot be detected by DTA. On the other hand, $BaCO_3$ in sample S3 could present a lower crystallinity than the corresponding for samples S1 and S2 due to the intensive milling process.

In Fig. 3 XRD diagrams for sample S3 at different temperatures are shown. According to the diagrams, prominent differences in the signals corresponding to $BaCO_3$ are present in the samples without thermal treatment. It is specially noted that after the mecano-chemical activation the intensity of the signal corresponding to the plane (200) has diminished with a 500/160 ratio. This indicates that after 10 h of rigorous mill a remarkable decrease in the crystallinity of $BaCO_3$ and in the $BaCO_3$ particle size has taken place.

The effect of the mecanochemical activation can be detected after carrying out thermal treatments on the samples. For example, after calcination at 630°C, the system S3 presents the signals of $BaTiO_3$ (see Fig. 3), while in the systems S1 and S2 they are not detected. At 660°C, high-intensity $BaTiO_3$ signals in the system S3 are detected. Starting from that temperature, the signals belonging to this specie increase continuously. At 710°C, the differences between the systems are accentuated. At this temperature the amount of $BaTiO_3$ increases in the sample S3, and signals corresponding to $BaTi_2O_5$ and Ba_2TiO_4 are observed. However, the system S2 does not exhibit a great increase in the
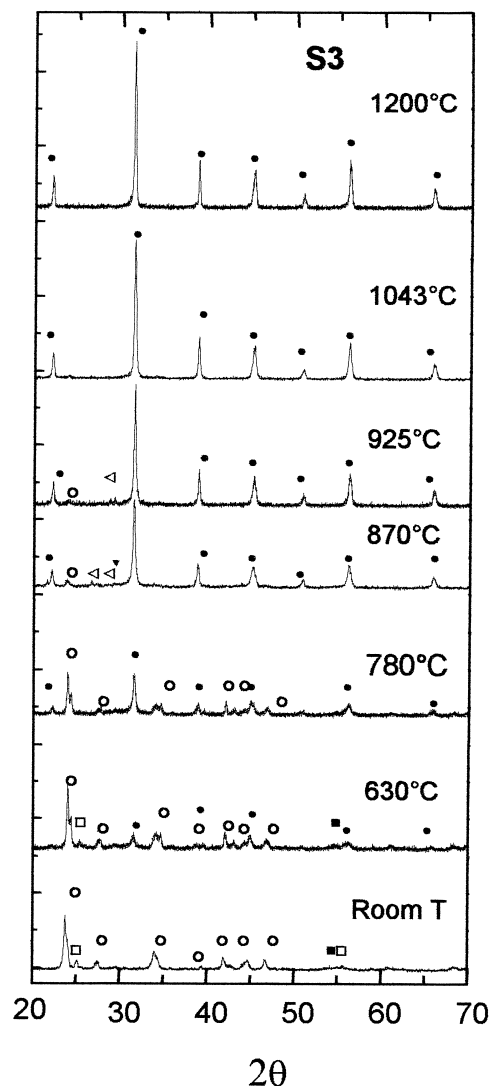

Fig. 3. X-ray diffraction patterns of sample S3. $\bigcirc BaCO_3$, $\square TiO_2$ antase, $\blacksquare TiO_2$ rutile, $\bullet BaTiO_3$ $\triangleleft Ba_2TiO_4$, $\blacktriangledown Ba_2TiO_5$.

$BaTiO_3$ formed. A later increment of the temperature maintains these differences, but at 1043°C in the system S3 only the signals belonging to $BaTiO_3$ are detected. Conversely, at this temperature the systems S1 and S2 even exhibits the signals corresponding to $BaCO_3$, TiO_2 (anatase) and Ba_2TiO_4, and also those of $BaTiO_3$. The increase in the milling time produced a decrease in the $BaCO_3$ crytallinity and in the particle size, improving its reactivity. Then, formation of barium titanate free of secondary phases was observed.

4. Conclusions

According to the considered reaction pattern, the formation of $BaTiO_3$ in the initial stage of the reaction between $BaCO_3$ and TiO_2 depends on the $BaCO_3$

decomposition. This is favoured by the catalytic effect of a very reactive TiO_2. In a second stage, the $BaTiO_3$ formation is controlled by the barium diffusion through barium titanate layer. In this stage, secondary phases are formed. An effective way of limiting the existence of secondary phases consists of departing from a system in which the reactivities of the raw materials are similar. In this work, such goal was achieved by making modifications on the processing of the powders. The application of a rigorous mill step allows an increase of the reactivity of $BaCO_3$. This reactivity avoids that the barium carbonate decomposition and the barium diffusion control the course of the reaction.

Acknowledgements

References

1. Hill, D. C. and Tuller, H. L., Ceramics sensors: theory and practice. In *Ceramic Materials for Electronics: Processing Properties and Applications*, ed. R. C. Buchanan. Marcel Dekker, Inc., New York and Basel, 1986, pp. 265–372.

2. Hozer, L., *Semiconductor Ceramics — Grain Boundary Effects*. PWN Polish Scientific Publishers, Warsaw, Poland, 1994 pp. 3–41, 109–143.

3. Rae, A., Chu, M. and Ganine, V., Barium titanate—past, present and future. In *Dielectric Ceramic Materials*, ed. K. M. Nair and A. S. Bhalla. The American Ceramic Society, Westerville, OH, 1998, pp. 1–12.

4. Caballero, A. C., Fernández, J. F., Moure, C. and Durán, P., ZnO-doped $BaTiO_3$: microstructure and electrical properties. *J. Eur. Ceram. Soc.*, 1997, **17**, 513–523.

5. Tzing, W. H., Tuan, W. H. and Lin, H. L., The effect of the microstructure on the electrical properties of NiO-doped $BaTiO_3$. *Ceramics International*, 1999, **25**, 425–430.

6. Tzing, W. H. and Tuan, W. H., The effect of NiO addition on the sintering and grain growth behaviour of $BaTiO_3$. *Ceramics International*, 1999, **25**, 69–75.

7. Li, X. and Heng, S. W., Size effects in barium titanate particles and clusters. *J. Am. Ceram. Soc.*, 1997, **80**(11), 2844–2853.

8. Stojanovic, B. D., Pavlovic, V. B., Pavlovic, V. P., Djuric, S., Marinkovic, B. A. and Ristic, M. M., Dielectric properties of barium titanate sintered from tribophysically activated powders. *J. Eur. Ceram. Soc.*, 1999, **19**, 1081–1083.

9. Beauger, A., Mutin, J. C. and Niepce, J. C., Synthesis reaction of metatitanate $BaTiO_3$. Part 2: study of solid–solid reaction interfaces. *J. Matt. Sci.*, 1983, **18**, 3543–3550.

10. Mutin, J. C. and Niepce, J. C., About stoichiometry of polycrystaline $BaTiO_3$ synthesized by solid–solid reaction. *J. Mat. Sci. Letter*, 1984, **3**, 591–592.

11. Hamano, A., Atake, T. and Saito, Y., Succesive phase transitions of $BaTiO_3$ ceramics synthesized by powder calcination. *Int. J. High Tech. Ceram.*, 1988, **4**, 41–50.

12. Amin, A., Spears, M. A. and Kulwicki, B. M., Reaction of anatase and rutile with barium carbonate. *J. Am. Ceram. Soc.*, 1983, **66**, 733.

13. Gomez-Yañez, C., Benitez, C. and Balmori-Ramirez, H., Mechanical activation of the sysnthesis of $BaTiO_3$ from a mixture of $BaCO_3$ and TiO_2 powders. *Ceramics International*, 2000, **26**, 271–277.

14. Beauger, A., Mutin, J. C. and Niepce, J. C., Role and behaviour of orthotitanate Ba_2TiO_4 during the processing of $BaTiO_3$ based ferroelectric ceramics. *J. Mat. Sc.*, 1984, **19**, 195–210.

15. Templeton, L. K. and Pask, J. A., Formation of $BaTiO_3$ from $BaCO_3$ and TiO_2 in air and in CO_2. *J. Am. Ceram. Soc.*, 1959, **42**, 212–216.

16. Fernández, J. F., Durán, P. and Moure, C., Reaction kintetics in the $BaTiO_3$ synthesis: influence of the TiO_3 crystalline structure and morphologies. In *Ceramics Today-Tomorrow's Ceramics*, ed. E. D. Vicenzini. Elsevier Science Publishers, Amsterdam, 1991, pp. 1973–1982.