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Evidence of a Dissolution–Precipitation Mechanism in Hydrothermal Synthesis of Barium Titanate Powders

Pascal Pinceloup,[a]* Christian Courtois,[a†] Jean Vicens,[b] Anne Leriche[a] and Bernard Thierry[a]

[a]LAMAC, Université de Valenciennes et du Hainaut-Cambrésis, 59600 Maubeuge, France
[b]LERMAT-ISMRA, Caen, France

Abstract

In our study of the system barium hydroxide-titanium tetraisopropoxide–water–isopropanol between 85 and 150°C, we have observed the following evidence of a mechanism by dissolution-precipitation: (1) when varying the water/isopropanol ratio in synthesis at 150°C, the grain size of barium titanate decreases when the amount of alcohol increases, i.e. when the solubility of the precursors decreases; (2) TEM observations of incompletely reacted powders showed that the grains are either amorphous or entirely crystalline $BaTiO_3$*, which means that homogeneous nucleation and growth is occurring instead of heterogeneous nucleation; (3) high resolution TEM observations of fully reacted powders revealed the presence of necks between particles. These three experimental observations in the same reaction system provide strong evidence of dissolution-precipitation as the primary reaction mechanism. © 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

The hydrothermal synthesis of barium titanate powders is an important industrial process because it leads to fine, crystalline and deagglomerated powders which are suitable for the fabrication of thin ceramic layers used in the manufacture of multilayer ceramic capacitors (MLC technology). For this reason, the hydrothermal synthesis of barium titanate has been investigated by many authors with various synthesis conditions. Its thermodynamic stability in hydrothermal conditions has been modelled and is well understood.[1,2] However, its study is still largely a matter of trial and error, mainly because very little is known about the nature of the formation mechanism of the barium titanate and the species present in hydrothermal conditions. The various kinetic and morphology studies reported in the litterature have opposite conclusions concerning the predominant mechanism. As reviewed by Eckert *et al.*,[3] the different mechanisms can be grouped either as in-situ transformation or as dissolution–precipitation, all of which being based on the more general nucleation-growth process. In a very detailed study, Hertl concludes on an *in-situ* mechanism where the barium reacts at the surface of the titania particles (anatase) to form an inwardly growing shell of barium titanate.[4] Two growth regimes are observed, depending whether the limiting step is the reaction at the interface or the diffusion of the barium ions through the existing barium titanate layer. Another type of *in-situ* mechanism is suggested by Vivekanandan *et al.* and involves the diffusion of barium ions within the amorphous titania particles and the subsequent dehydration and rearrangement of the titania network while heterogeneous nucleation of barium titanate occurs.[5,6] The dissolution–precipitation mechanism has been suggested by Ovramenko *et al.*[7] and recently by Eckert *et al.*[3] In fact, these last authors observe that the mechanism evolves from a dissolution–precipitation process at the beginning of the reaction to an *in-situ* mechanism for longer reaction times.

Present address: Department of Ceramics, College of Engineering, Rutgers, The State University of New Jersey, Piscataway NJ 08855-0909, USA.

[†] To whom correspondence should be addressed. Fax: +33-03-2764-6654; e-mail: christian.courtois@univ-valenciennes.fr

In our study of the system barium hydroxide–titanium tetraisopropoxide–water–isopropanol between 85 and 150 °C, we have observed various evidence of a mechanism by dissolution–precipitation.[8] It is the purpose of this paper to present this evidence.

2 Experimental

The syntheses started from an alkoxide–hydroxide system of precursors. The precursors are commercially available $Ba(OH)_2.8H_2O$ (Merck, 99%) and $Ti(OPr^i)_4$ (titanium tetraisopropoxide = TIPT) (Merck, > 97%). The syntheses were conducted by first preparing a clear aqueous solution of barium hydroxide. Heating in a closed bottle was necessary to dissolve all the hydroxide. A filtration in nitrogen atmosphere was then carried out to eliminate the traces of $BaCO_3$ from the precursor. Separately, a known amount of TIPT was diluted in isopropanol. The respective amounts of barium hydroxide and TIPT were determined so that Ba/Ti = 1·00 to 1·08 during synthesis. The solutions were mixed by slowly dropping the TIPT solution into the clear $Ba(OH)_2$ solution under vigorous stirring and in a CO_2-free atmosphere. Upon contact of the TIPT solution with the highly basic barium hydroxide solution, an instantaneous precipitation occurred via hydrolysis–condensation of the TIPT molecules into hydrous oxide $TiO_2.xH_2O$ nanometric particles. The isopropanol used to dilute TIPT and that produced during the hydrolysis–condensation of TIPT into $TiO_2.xH_2O$ remains in solution and is part of the solvent. By varying the respective quantities of isopropanol and water in the preparation of the two initial solutions, the composition of the solvent (water/isopropanol vol%) could be varied between 37/63 and 86/14.

The resulting suspension was placed in a 2 l stirred autoclave flushed with nitrogen and the hydrothermal treatment was performed at 150 °C for 2 h (Autoclave Engineers). Two syntheses were performed directly in the glove-box by heating the suspension at 85 °C for 15 min and 90 °C for 2 h. After synthesis, the powders were filtered in a pressure filter under nitrogen and freeze-dried (FINN-AQUA, Lyovac GT-2).

The powders were characterized by X-ray diffraction (Siemens D5000) for phases and ICP-AES (Jobin Yvon, JY 38 S) for chemical composition. Observations of the barium titanate particles were made by transmission electronic microscopy with a Siemens Elmiskop 101 on carbon precoated copper grids. High Resolution Transmission Electron Microscopy were performed at LERMAT, Caen, on a Topcon 002B. The specific surface areas were measured by a single point method using adsorption of N_2 (Micromeritics Flowsorb II 2300). The equivalent average particle size Ø, in nm, were calculated with the expression $Ø = 1/S$, where the particles have been considered spherical and equisize; S is the specific surface area in $m^2\,g^{-1}$ (the density of the particles was taken equal to $6\,g\,cm^{-3}$). The calculated values were confirmed by TEM observations.

3 Results and Discussion

1. X-ray diffraction of the powders showed the characteristic peaks of $BaTiO_3$ only. The absence of splitting of the (h00)/(00h) peaks showed that the powders were stabilized in the metastable cubic form at room temperature. Such a stabilization is common in hydrothermally synthesized barium titanate powders and is explained by the entrapment of hydroxyl groups in the perovskite lattice.[5] An unexpected result was obtained from the powders synthesized at low temperatures. The chemical analyses showed that they are highly barium deficient (Ba/Ti = 0·62 and 0·88 for synthesis conditions of 85 °C/15 min and 90 °C/2 h, respectively), due to an incomplete reaction, but their respective diffractograms were not different from that of completely reacted powders, as shown in Fig. 1. The unreacted hydrous oxide $TiO_2.xH_2O$, amorphous in nature as revealed by TEM investigations, did not lead to any broad peak as is usually observed in X-ray diffraction of amorphous materials. This result confirms that X-ray diffraction is not a proper tool to investigate the reaction advancement of the formation of barium titanate powders and that only careful chemical analysis can provide this type of information. Nonetheless, the unreacted powders were used to gain insights concerning the reaction mechanism, because they reflect the state of a powder during reaction. TEM

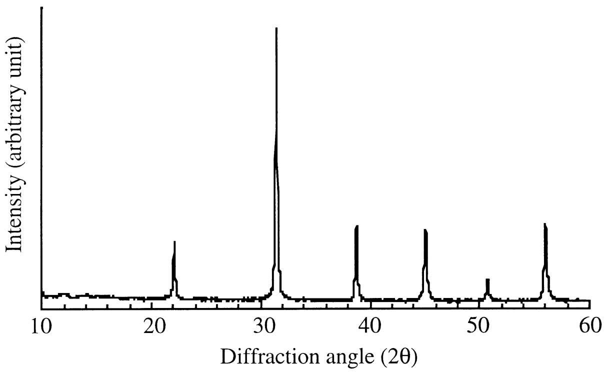

Fig. 1. Typical X-ray diffraction pattern of hydrothermal $BaTiO_3$ powders.

and HRTEM observations revealed that the particles are either crystalline $BaTiO_3$ or amorphous $TiO_2.xH_2O$ [Fig. 2(a) and (b)], i.e. $BaTiO_3$ crystallites were not found within or at the surface of the amorphous $TiO_2.xH_2O$ particles. Amorphous $BaTiO_3$ needs not be considered here since it has been shown by Hennings *et al.*[9] that the barium ions only adsorb at the surface of the amorphous hydrous oxide particle but do not enter the bulk of the particles, hence any amorphous region can be considered as having the composition $TiO_2.xH_2O$. These results show that the *in-situ* mechanism (heterogeneous nucleation), as suggested by Vivekanandan *et al.*,[5] is not observed. This mechanism describes the formation of barium titanate by adsorption and diffusion of the barium ions inside the amorphous titanium oxide particles and subsequent *in-situ* nucleation and growth of barium titanate crystallites until all the initial $TiO_2.xH_2O$ particle is transformed "from inside" into $BaTiO_3$. Instead, our TEM results suggest that a homogeneous nucleation by a dissolution–precipitation mechanism occurs.

2. Figure 3 shows the evolution of the specific surface area and particle size in function of the amount of isopropanol in the solvent for $BaTiO_3$ powders reacted at 150 °C for 2 h (Ba/Ti≈1). For increasing amounts of isopropanol in the reaction medium, there is a significant increase of the specific surface area, i.e. a decrease of the particle size. This behavior can be explained by considering that the solubilities decrease strongly for increasing alcohol content (the dielectric constant of the solvent decreases), therefore the rate of nucleation increases, which leads to a much greater number of particles. For a given amount of matter to precipitate, which is the case in our experiments, each particle reaches a smaller size because more particles are growing at the same time. Hence, this result cannot be related to a precipitation by heterogeneous nucleation but is instead consistent with a precipitation process by dissolution-precipitation, as previously observed by Kiss *et al.*[10]

3. A high resolution TEM photograph of a fully reacted powder is presented in Fig. 4. It shows that the grains are fully crystallized and single-crystal in nature. TEM investigations showed that some particles tend to aggregate, forming strongly bound complex structures. Figure 4 shows that the region of contact between two particles is not punctual but forms a neck which can extend over 10 to 40 nm and where the crystallographic orientation gradually changes when passing from one grain to the other. The powder in Fig. 4 has not been annealed in any way, hence the necks must have formed during the hydrothermal synthesis. The configuration of the necks resembles that of particles starting to sinter during the first stage of sintering. The formation of such a morphology is usually attributed to two mechanisms, namely surface diffusion and evaporation–condensation, which is the equivalent in gas phase of the dissolution-precipitation process in the liquid phase. The mechanism by surface diffusion usually occurs at much higher temperature than those considered

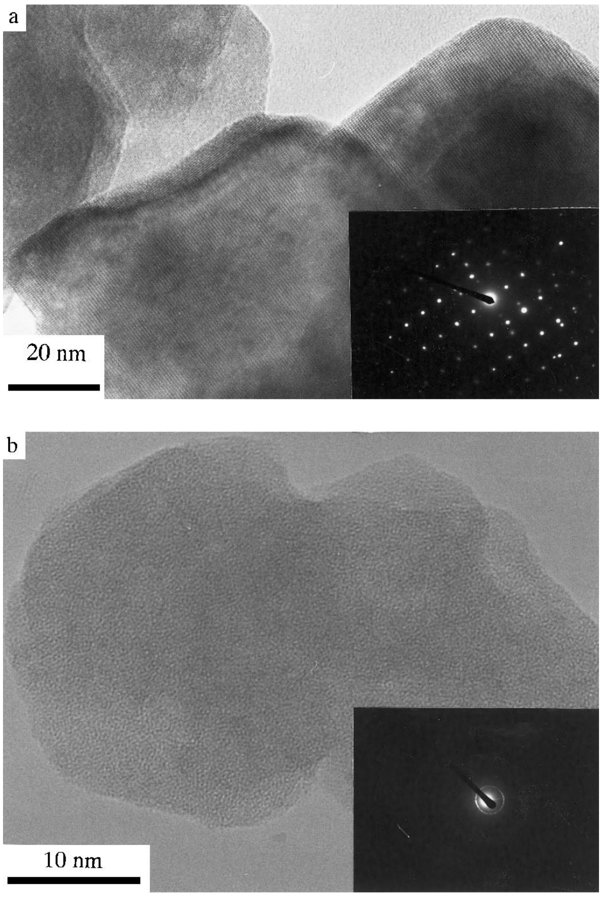

Fig. 2. HRTEM photographs of a powder incompletely reacted (Ba/Ti = 0·88): (a) fully crystallized particle of $BaTiO_3$; (b) fully amorphous particles of $TiO_2.xH_2O$.

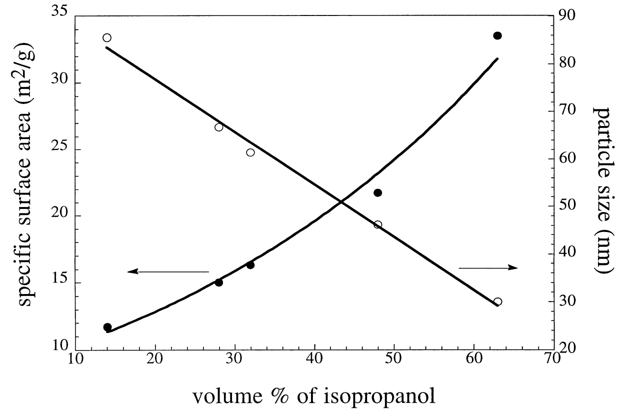

Fig. 3. Evolution of the specific surface area and particle size for powders synthesized with various isopropanol contents in the reaction medium.

here, typically in the range 700–1000 °C against 150 °C for the hydrothermal synthesis. Thus, it is unlikely that a surface diffusion process be at the origin of the formation of the necks and we believe that a dissolution process is responsible for this phenomenon. It is suggested that the necks grow only after two particles interact strongly enough to form a punctual contact. Then in a similar way as for the evaporation–condensation process, the region of contact becomes a site of preferential precipitation because of its negative curvature. We believe that the necks form by a preferential precipitation from new nutrient coming from the solution on the site of punctual contact between two particles. Given the high stability of the barium titanate in basic solutions, it is unlikely that barium and titanium ions from already crystallized barium titanate particles would redissolve to nourish the neck region. Instead, we think that the neck can grow from barium ions present in the solution and from freshly dissolved titanium species from amorphous $TiO_2.xH_2O$. Thus the necks can grow as long as unreacted amorphous $TiO_2.xH_2O$ is present in the reaction medium, but not after it has entirely been converted to $BaTiO_3$.

4. Finally, the assumption of *in-situ* transformation can also be ruled out by the following considerations. If *in-situ* transformation occurred, there should be a mathematical relationship between the initial size of the amorphous particles of $TiO_2.xH_2O$ and the final size of the $BaTiO_3$ particles (real sizes can be deduced from Fig. 2). We first assume initial amorphous particles of $TiO_2.xH_2O$ with size d_i and density ρ_i. An *in-situ* mechanism should transform them into $BaTiO_3$ particles of size d and density 6 g cm^{-3} which contain the same number of titanium ions as that of the starting particles. By equating the initial and final numbers of particles in one mole of material, a relation has been derived which gives the size d_i that the initial particles should have in order to lead to $BaTiO_3$ particles of size d. The relation is shown in Fig. 5. It involves the three parameters d, ρ_i, and x the number of water molecules/TiO_2 formula. Figure 5 shows a series of curves derived for various values of ρ_i and x. A value of $d = 80$ mn has been considered from Fig. 2. From the literature, it is known that $TiO_2.xH_2O$ has a density close to 3 g cm^{-3},[11] and x ranging between 3 and 10.[5] Hence, the initial particles should have a size around 80 nm or more to lead to $BaTiO_3$ particles of size 80 nm. From TEM, the observed size of the initial particles is closer to 30 to 40 nm, which is considerably smaller than the calculated value of 80 nm. Hence, we believe that an *in-situ* mechanism cannot account for the mechanism of formation of $BaTiO_3$ powders.

Fig. 4. HRTEM photograph of necks between three $BaTiO_3$ particles.

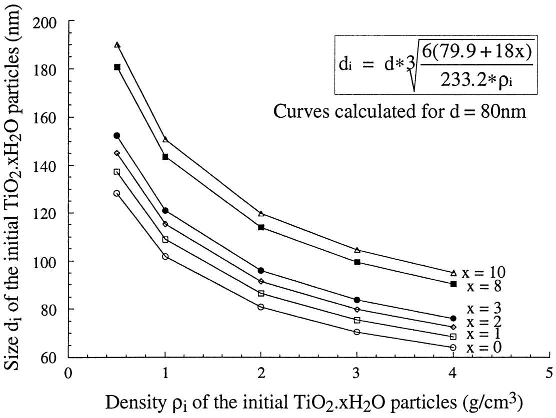

Fig. 5. Calculated values of the initial size (d_i in nm) of the $TiO_2.xH_2O$ particles which would lead to $BaTiO_3$ particles of size $d = 80$ nm, in the hypothesis of an *in-situ* transformation mechanism. The calculations have been performed for various densities (ρ_i) of the initial $TiO_2.xH_2O$ Particles (horizontal axis), and for various values of x in $TiO_2.xH_2O$.

4 Conclusion

From the hydrothermal synthesis of $BaTiO_3$ powders at various temperatures and time and with various contents of isopropanol in the solvent during synthesis, four observations have been collected which cannot be explained by an heterogeneous nucleation (*in-situ* mechanism). These observations are: (1) the absence of partially crystallized-partially amorphous particles in incompletely reacted powders, (2) the evolution of particle size with isopropanol content agrees with a dissolution-precipitation mechanism (homogeneous nucleation), (3) the formation of necks between particles in contact after only 2 h at 150 °C in hydrothermal reaction, (4) the discrepancy between the expected size of the initial particles of $TiO_2.xH_2O$ and the final $BaTiO_3$ Particles, after correcting for volume changes due to reaction, in the hypothesis of an *in-situ* mechanism.

Therefore, an *in-situ* mechanism cannot be attributed to the mechanism of formation of $BaTiO_3$ powders. Instead, our observations agree with a dissolution-precipitation mechanism which takes place until all the amorphous $TiO_2.xH_2O$ is consumed. Until that point, morphology modifications and growth can occur. After complete conversion into $BaTiO_3$ it is anticipated that the kinetic of any particle modification becomes extremely slow.

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