Morphological mapping of high-pressure solvothermal synthesis of BaTiO₃ particles

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Abstract

In this paper BaTiO₃ particles were synthesized by an additive-free solvothermal technique. Different combinations of temperature, holding time and, especially, pressure by gas injection were studied to evaluate the effect of the synthesis parameters on particle morphology. Powders were obtained by using titanium(IV) isopropoxide, barium nitrate and potassium hydroxide as reactants and water/ethanol as solvent. The results showed that from 80 °C to 180 °C and 6 h to 24 h at inherent pressure, amorphous rough spheres, assembled nanocubes and irregular particles were formed. Dendritic and flower-like particles were synthesized at high pressures (20–80 bar). Oriented agglomeration and Ostwald ripening were the main crystal growth mechanisms observed.

1. Introduction

Barium titanate (BaTiO₃) is a perovskite type ceramic extensively used in multilayer ceramic capacitors and also microwave and electro-optical devices due to its high dielectric permittivity and ferroelectric properties [1]. Previous works on BaTiO₃ powders suggest that dissimilar morphologies may determine if the material is more appropriate to be applied either as an electronic part or as an optical component, for example [2,3]. This material is regularly produced by reacting BaCO₃ and TiO₂ at temperatures above 1000 °C. However, under such conditions, it is difficult to control the shape of particles. Among the other synthesis techniques, the solvothermal method is widely used for the preparation of different types of materials under mild conditions without requiring post thermal treatment at high temperatures, yielding powders with well distributed particle sizes and superior morphological and compositional control [4]. The method has been significantly improved and a number of hardware modifications have been proposed, e.g., microwave heating, electrochemical and sonochemical developments [5]. Previous studies corroborated that the solvothermal synthesis of BaTiO₃ particles must provide appropriate control of its characteristics, however, no detailed mapping of the particle architecture evolution has been proposed taking into account the pressure of the system as process variable.

In order to bridge this gap, this work aims at providing a detailed morphological evolution of BaTiO₃ particles as a function of temperature, time and pressure by gas injection during solvothermal synthesis.

2. Experimental

The first solution was made by dissolving 0.98 g of barium nitrate (Ba(NO₃)₂, >99%, Vetec) into a mixture of 75.2 mL of deionized water and 6.6 mL of ethanol under vigorous stirring at room temperature. Considering the ratio Ba/Ti = 1.1, a second solution was made by adding 1.0 mL of titanium(IV) isopropoxide (TTIP, 97%, Sigma-Aldrich), into a mixture of 2.2 mL of ethanol and 0.1 mL of acetic acid and then added dropwise to the first solution to form a white precipitate. 15 mL of a 1 M KOH aqueous solution was used to adjust pH = 14. After 2 h stirring, the solution was sealed into a PTFE-lined stainless steel autoclave and then solvothermally synthesized at 80–180 °C, during 6–24 h under relative pressures that ranged from the autogenous pressure (0.5–10.5 bar) to (20–80 bar) by the injection of pressurized argon. All combinations of parameters used are shown in Table 1. Samples BT1-17 where synthesized at autogenous relative pressures of 0.5, 2.0, 3.9, 6.3 and 10.5 bar which correspond to temperatures of 80, 120, 140, 160 and 180 °C, respectively.

The obtained powders were washed several times with acetic acid, deionized water and acetone until pH = 6. The materials were characterized by X-ray diffraction (XRD, D8 Advance Eco, Bruker) using Cu-Kα radiation (λ = 1.5418 Å). The morphologies were observed using a field-emission gun scanning electron microscopy (FESEM, Auriga 40, Carl Zeiss).
3. Results and discussion

XRD patterns of samples synthesized at different temperatures, times and pressures are presented in Fig. 1a. The occurrence of a single peak at $2\theta \approx 45^\circ$ is usually related to the (2 0 0) diffraction of the cubic symmetry. However, all crystalline samples were indexed to a tetragonal type perovskite structure and were also free from contaminations such as BaCO$_3$. According to Hongo et al. [6], this is typical for the solvothermal synthesis of BaTiO$_3$ particles once OH groups fill certain oxygen sites in the lattice, promoting the formation of barium vacancies, thus changing the unit cell parameters and forming a pseudocubic symmetry (check supplementary data). Hongo et al. also observed a split of the major peak for the tetragonal phase related to (1 1 0) and (1 0 1) which were observed for all samples depicted herein (Fig. 1b).

An amorphous profile may be observed in Fig. 1c for sample BT1. Any treatment at temperatures lower than 80 °C and times shorter than 24 h is not enough to promote the crystallization of BaTiO$_3$ particles. It can be seen in Fig. 2a that amorphous materials have spherical but rough morphology at about 100–200 nm in diameter which improves its dissolution followed by crystallization. Fig. 2b of sample BT2 portrays this conversion into crystalline BaTiO$_3$ mesocrystals of faceted nanocubes that are in a lower content than the amorphous phase. When time increased up to 24 h (BT5 – Fig. 2c), the content of mesocrystals also increased and exceeded that of the amorphous phase. The amorphous band cannot be observed for samples partially crystalline once it is suppressed by a scale factor due to the high intensity of diffraction peaks.

Fig. 2d illustrates sample BT6. Amorphous spheres are no longer observed and two morphologies, mesocrystals and irregular shaped particles are present roughly at the same extent. Fig. 2e shows the effect of increasing the synthesis time to 24 h (BT9), suggesting an increase in the content of irregular particles while that of mesocrystals decreased. This suggests Ostwald ripening by the dissolution of high surface energy mesocrystals followed by mass transportation and recrystallization on the surface of irregular particles, as responsible for their growth. In addition, another mechanism plays a role in particle growth. This is shown in Fig. 2d and is related to oriented aggregation, in which high surface energy particles undergo sintering by aggregation and re-crystallization, developing a neck-like region (red dashed).

The morphology of sample BT10, as it can be seen in Fig. 2f, is fully irregular with traces of mesocrystals. The growth mechanisms are still active for these synthesis parameters and can be also observed in Fig. 2g, corresponding to sample BT13, synthesized during 24 h. Elongated aggregation by preferential orientation (red dashed) and volume by Ostwald ripening, i.e., dissolution of smaller irregular particles and growth of bigger ones were noticed.

By increasing the synthesis temperature to (BT14), the morphology of BaTiO$_3$ particles is similar to that of sample BT10, i.e., fully irregular with traces of mesocrystals (Fig. 2h). However, BT14 revealed an increase in particle size in comparison to BT10. This means that growth mechanisms are more active at this temperature. The sample synthesized at (BT16) depicted significant growth (Fig. 2i). Continuous and intense particle growth by oriented aggregation (red dashed) and Ostwald ripening resulted in a morphology suggested as an undeveloped coral-like structure, presented by Zhao et al. [7].

Sample BT18 (Fig. 2j) indicates that the synthesis at 20 bar formed dendrites along with a limited content of flower-like particles. The main structure is irregular with the presence of traces of mesocrystals. These irregular particles are slightly different from the samples obtained at autogenous pressure, as it can be better

Table 1
Table 1 Combines temperature, time and pressure adopted on the solvothermal synthesis of BaTiO$_3$ particles.

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Fig. 1. X-ray diffraction patterns taken from (a) BaTiO$_3$ synthesized at different conditions, (b) peak split at $2\theta = 31.5^\circ$ and (c) amorphous BT1.
seen in Fig. 2k for sample BT19, synthesized at 50 bar. The red-dashed magnification shows oriented aggregation and more compacted particles, compared to those seen in BT16, for example. These differences may be related to the high pressure. As pressure increased from 20 to 50 bar, the content in dendrite and flower-like shaped particles increased, but the irregular particles still prevailed along with traces of mesocrystals. When synthesized at 80 bar (BT20), it is possible to establish fully dendritic BaTiO₃ particles with mesocrystals and traces of flower-like ones. These morphologies indicate that the reaction occurred far from the equilibrium induced by gas injection.

A detailed morphological evolution of the synthesized BaTiO₃ particles as a function of pressure-assisted solvothermal synthesis is shown in Fig. 3. Reddish zones indicate the combinations of temperature and time below which crystalline BaTiO₃ cannot be obtained and amorphous materials are formed. At 120 °C, it is possible to observe the formation of BaTiO₃ mesocrystals as a result of the solubilization of amorphous phase followed by crystallization. The same mechanism took place at 140 °C but mesocrystals dissolved and converted into irregular shaped particles. Increasing the temperature to 160 °C, morphology changes were no longer observed and particles growth took place. The growth rate at 160 °C was lower than that of 180 °C which means that the increase in temperature increased the growth rate of particles. The increase in pressure at 180 °C for 18 h (greenish zone) increased the content of dendrites.

4. Conclusions

BaTiO₃ particles were successfully synthesized by the solvothermal method at different temperatures (120–180 °C), times (6–24 h) and pressures (0.5–80 bar). Ostwald ripening and oriented aggregation were the main growth mechanisms resulting in the formation of mesocrystals of nanocubes and irregular shaped particles at autogenous pressures. At 120 °C, amorphous particles were converted into mesocrystals, which were subsequently converted into irregular particles at 140 °C. Growth rate increased with increasing temperature from 160 °C to 180 °C. Fully
dendritic with traces of flower-like morphologies were obtained by the injection of compressed argon without any surfactant at 180 °C for 18 h and 80 bar.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2019.126597.

References


Fig. 3. Morphological mapping of solvothermally synthesized BaTiO3 particles as a function of temperature, time and pressure.