Low-temperature aqueous synthesis (LTAS) of BaTiO$_3$: a statistical design of experiment approach

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Abstract

The effect of a selected number of parameters of the Low-Temperature Aqueous Synthesis (LTAS) on BaTiO$_3$ particle size was investigated by the statistical design of experiment approach. Different syntheses were carried out changing the value of six physico-chemical parameters involved in the process, following the scheme of a 2^{6-2} fractional factorial design. The characterisation of the submicron powders produced shows variations of the average size in the range 30–55 nm, deduced from specific surface area measurements. The statistical analysis of experimental results, performed by the ANOVA method, allows to ascribe such variations to the effect of solutions concentration, stirring energy and precursors mixing conditions. The significance of such parameters, together with the apparent ineffectiveness of the ageing time, is discussed. Also the XRD measurement of barium carbonate amount is presented and its dependence on experimental conditions is discussed. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ceramic materials based on Perovskite-like oxides are of large interest because of their applications in electric and electronic devices. Due to its high dielectric constant, barium titanate (BaTiO$_3$) is probably the most studied compound of such family and still represents the basis for the preparation of Multi-Layer Ceramic Capacitors (MLCC) and thermistors with Positive Temperature Coefficient of Resistivity (PTCR). During last decades special attention has been paid to different aspects of the producing cycle of this material, particularly to powders synthesis, dense greens formation and sintering of compacts.[1–15] This large amount of work has demonstrated that the quality of final products is strongly determined by starting powders properties, as the chemical composition, the particles size and the surface reactivity, that can be only slightly improved in last stages of preparation. Owing to such considerations, a great effort is being devoted to the development of new methods aiming at the preparation of powders with better and, especially, reproducible quality. Consequently several chemical routes,[1–10] sometimes

leading to strikingly different powder characteristics, have been experimented; one of these routes, called Low-Temperature Aqueous Synthesis (LTAS),[16] has been applied not only to the preparation of Barium or Strontium Titanate and relevant solid solutions, but also to that of Zirconates, Hafniates and Stannates with perovskite structure.[17] When compared to other techniques this methodology brings about some advantages like the possibility to design primary particle size in the range from 30 to 300 nm and to introduce dopants directly with precursors. Nevertheless, as for many other methods, the mechanisms which determine powders morphology, though of great importance, are still unknown. Previous experiences on LTAS synthesis and similar works on different systems[18,19] suggest that liquid-phase precipitation of powders can be unpredictably affected by slight variations in processing conditions, like the reaction temperature, the concentration of precursors solutions and the amount of product. Moreover, such parameters are likely to interact, that is the characteristics of final powders can be expected not only to be a simple superposition of the effect of each parameter, but also to depend on their combination. In order to acquire information about such interactions, it is therefore necessary to study the influence of various

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parameters together: this can be achieved by the realisation of factorial experimental designs,[20] widely adopted for production quality control and quick testing of complex processes. The present work reports the results of a series of LTAS experiments consisting in the preparation of $BaTiO_3$ powders with different synthesis conditions, obtained by changing the value of six parameters, in the frame of a factorial design.

2. The factorial design approach

Experiments are usually performed to investigate the effects of some variable on a physical quantity G, that is to find a functional dependence of the general form

$$G = f(\chi_j) \quad j = 1, \ldots, k \tag{1}$$

where the x_j represent variables or parameters involved in the experiments.

Such a problem is commonly faced by means of a series of experiments where only one x_j is varied, keeping the others fixed to a reference value and, if necessary, repeating the procedure for another parameter. This approach, called the *one-parameter-at-a-time* approach, is adequate when deep inspection is only desired on very few (one or two) variables and when the system is simple. On the contrary, when dealing with more parameters or with poorly known systems, as in our case, such method is no longer appropriate because of the increasing number of required experiments and the lack of information about possible interaction among variables. The best way to test the effect of the parameters is then to experiment every combination, that is to change variables together instead of one at a time, by the realisation of a *factorial design*. This approach ensures the widest information with the lowest number of experiments: in fact, considering designs with a fixed number ($k \geqslant 2$) of variables, each at two different levels, a total of 2^k experiments is required to test every combination (2^k designs), considerably less than the $2^{k-1} (k+1)$ needed to obtain the same precision by the one factor at a time method.

The central point in factorial designs is represented by a regression model of the form

$$G = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{\substack{i=1 \\ j>i}}^{k} \beta_{ij} x_i x_j + \sum_{\substack{i=1 \\ j>i \\ l>j}}^{k} \beta_{ijk} x_i x_j x_l + \ldots$$

$$+ \beta_n(x_l \ldots x_k) + \epsilon \tag{2}$$

where the β_j are the regression coefficients, the x_j represent the variables and ϵ is a random error variable with normal distribution around zero.

The model Eq. (2), adopted as an approximation of the function $f(x_j)$ in Eq. (1), takes into account both direct effects of variables and all possible interactions among parameters, represented by the various terms $x_i x_j$, $x_i x_j x_l$, and higher order products, with a total of $2^k + 1$ terms.

In this work, a 2^k factorial design was adopted as a factor screening experiment, in order to select most important variables and exclude non relevant ones.

3. Experimental procedure

$BaTiO_3$ powders were prepared following the LTAS reaction,

$$Ba(OH)_2 + TiCl_4 + 4NaOH \rightarrow BaTiO_3$$
$$+ 4NaCl + 3H_2O \tag{3}$$
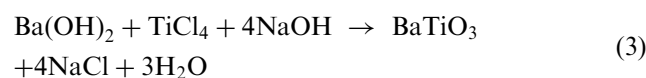
where ionic species react into an aqueous solution, at 80°C under flowing N_2 at atmospheric pressure, to form crystalline perovskite powder. The reaction Eq. (3) was carried out into a batch-type reactor with the addition of distilled water, sodium hydroxide (16 M solution), barium hydroxide and titanium chloride. After precipitation, the powders were aged, at the same temperature but with reduced stirring, for 5 or 10 hours before being washed with distilled water by 20 decantation cycles. It is known that one of the most important sources of contamination for $BaTiO_3$ prepared by wet chemical methods is the formation of $BaCO_3$, through the reaction of Ba^{2+} with CO^{3-} ions coming from air or dissolved in alkaline solutions. In order to reduce the final amount of this secondary phase, that has been demonstrated to be responsible for phenomena like swelling and desintering, very detrimental for ceramics,[21,22] special care was taken in avoiding contact of NaOH solution and $Ba(OH)_2$ powder with atmosphere. Particularly, $Ba(OH)_2$ was stored under a vacuum, while the NaOH solution was passed from the storage bottle to the reactor into closed tubes; similarly the N_2 gas, used to fill both reaction and washing vessels, was purified through soda lime filters and water was always freshly distilled. Commercial reactants, $Ba(OH)_2.8H_2O$ (98%, Sigma-Aldrich), $TiCl_4$ (99.9%, Acros) and NaOH (97%, Sigma-Aldrich) were employed without further purification and the $TiCl_4$ was added to the reaction volume in form of aqueous solution. As the aim of the present work is to study the influence of preparation conditions, a computer controlled laboratory plant was set up, designed to achieve high reliability and precision in the control of process variables. The plant (Fig. 1) comprises the PTFE reactor, kept into a thermostatic bath, where the reactants are fed by means of peristaltic pumps, and several devices which are connected to a personal computer and controlled by

specific codes. The experiments performed in the batch reactor were organised in a multifactorial experimental design (2^{6-2} factorial design), six factors being applied at two levels each. The definitions and levels of the factors are reported in Table 1. Levels were kept within relatively narrow boundaries in order to ensure the linearity of single factors effects, as assumed in the regression model Eq. (2). Factors are: (A) *ageing time*, corresponding to the time of permanency of powders into the reactor after the precipitation at the synthesis temperature, (B) *initial Ti concentration*, that is the concentration of the $TiCl_4$ aqueous solution, (C) *total powder production*, that fix the concentration of Ba^{2+} ions into the solution at the beginning of the precipitation, (D) *injection mode of reactants*, (E) *stirring rate* and (F) *injection time*.

These parameters, together with the pH value, completely define the thermodynamic equilibrium among the different ionic species in the aqueous solution, as shown by the model of Lencka and Riman.[23] The values of these parameters has been chosen to obtain a $BaTiO_3$
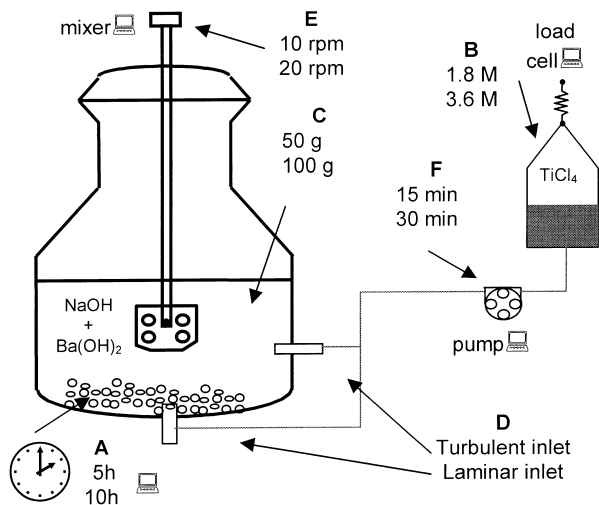

Fig. 1. Plant scheme with the indication of factor related points and computer connected devices (🖥). A = Ageing time, B = Initial Ti concentration, C = Total powder production, D = Injection mode, E = Stirring rate, F = Injection time.

Table 1
Factor definitions (factorial design 2^{6-2})[a]

Factor	Definition	Levels	
		Low	High
A	Ageing time	5 h	10 h
B	$[Ti]_0$	1.8 M	3.6 M
C	Production	50 g	100 g
D	Injection mode	Laminar	Turbulent
E	Agitation speed	10 rpm	20 rpm
F	Ti injection time	15 min	30 min

[a] I = ABCE = BCDF.

yield > 99.9%. In order to reduce the number of tests to 16, one quarter of the complete 2^6 design was effected, factors (E) and (F) being confounded with the second order interactions ABC and BCD, respectively.[20] Table 2 reports the 16 combinations actually experimented; each test is identified by the letters related to factors at *high* level (factors at *low* level are omitted). In order to study the effects of above defined factors some quantities (responses) related to particle size were measured and analysed using the ANOVA technique. Common powder particle size measurement techniques were applied, that is direct observation by scanning electron microscopy (SEM), specific surface measurements by isothermal nitrogen physisorption (B.E.T.), X-ray diffractometry (XRD) and sedimentation analysis (photocentrifuge), while additional information was obtained from thermo-gravimetry (TG). Samples for XRD (Philips PW1710, Co-K_α radiation) were prepared by manual grinding in agate mortar of as-prepared powders. TGA was carried out in laboratory air from room temperature up to 900°C (Mettler-TG50). Isothermal N_2 adsorption measures (Micromeritics-Gemini 2375) were performed at nitrogen boiling temperature on specimens which had been calcined in air at 500°C for 1 h. Diluted and ultrasonicated suspensions were used for the preparation of samples for SEM (Philips 515) observations and for sedimentation (Horiba-Capa700) measures. The responses coming from such techniques were sometimes quite different and hardly comparable. The reason for this has to be ascribed to strong chemical interparticle bonding, coming from surface carbonates present and to the agglomeration of powders due to capillary forces, arising among fine primary particles (approx. 50 nm). Such drawbacks make it difficult to resolve fine aggregated particles in SEM images and deeply affect sedimentation

Table 2
Experimental results of the statistical design

Treatment	No. Order	S_{bet} (m² g⁻¹)	W_I (%)	$[BaCO_3]$ (wt. %)
'1'	15	20.89	3.32	0.80
a(e)	11	22.72	3.95	1.20
b(ef)	14	26.25	3.99	2.80
ab(f)	12	29.51	4.05	2.70
c(ef)	9	24.24	3.34	1.75
ac(f)	5	27.17	3.49	1.20
bc	13	30.64	3.49	1.40
abc(e)	6	24.20	2.94	3.20
d(f)	4	23.51	3.77	2.50
ad(ef)	2	21.50	3.44	1.70
bd(e)	8	28.75	4.33	2.90
abd	16	35.02	4.60	4.50
cd(e)	1	24.57	3.47	2.70
acd	3	25.52	3.31	2.96
bcd(f)	10	30.00	3.65	2.70
abcd(ef)	7	18.87	2.29	2.30

measures. On the contrary, gas adsorption experiments appear suited for the study of such strongly agglomerated particles and give the possibility to account for surface morphology: specific surface data were therefore taken as reference in this work and used for statistical analysis.

4. Results and Discussion

XRD investigation confirms that $BaTiO_3$ powders produced via LTAS crystallise with a pseudo-cubic structure, with the presence of $BaCO_3$ as a secondary phase. The stabilisation at room temperature of the cubic, instead of the expected tetragonal phase, has been reported by many workers and ascribed to the size of particles below a critical value (≈ 80 nm) or to the presence of OH^- ions trapped into the bulk.[24] The relative amount of titanate and carbonate phases was determined by the Rietveld method as implemented in the DBWS code[25] and all calculations were performed within the Cerius^2 environment (Molecular Simulations Inc., San Diego, CA). The structures of cubic $BaTiO_3$ and of orthorhombic $BaCO_3$ were assumed as reference models; data were taken from the Inorganic Crystal Structure Database[26] (cards nos. 27970 and 15196). Fitting procedure took into account as many as 20 parameters, comprising lattice constants, angle dependent asymmetries and aberrations, peaks profile shape functions and background subtraction. Calculated average carbonate content was 2 ± 1 wt. %, with only two powders out of these limits: detailed results are reported in Table 2. Thermogravimetric curves reveal that the overall relative mass decrease, around 5%, can be divided into three intervals (Fig. 2), $T < 500$, $500 < T < 750$ and $750 < T < 900°C$: the weight losses in such intervals (indicated as W_I, W_{II} and W_{III}) correspond respectively to the elimination of hydroxyl groups, adsorbed at $BaTiO_3$

particles surface or chemically bonded in the bulk (W_I) and, possibly, to a low-temperature decomposition of carbonates (W_{II}, W_{III}), as recently reported[27] for $BaTiO_3$ prepared by the hydrothermal method. In particular the loss registered in all samples at 270°C can be assigned to bulk OH^- elimination. Specific surface data show a distribution around an average value of 25 ± 4 m^2 g^{-1} (Table 2), while SEM observations show powders with equiaxed particles (Fig. 3) and distributed in size around mean values ranging between 30 and 80 nm. Preliminary examination of the results shows that the observed variations of the responses can be interpreted as a consequence of the interplay of the following factors: *initial Ti concentration [Ti]$_0$, injection mode of the reactants*, *agitation rate* and *powder production*. In a first approach of this complex system, the influence of *injection time* and *ageing time* can be neglected.

4.1. S_{bet}

The most influential factors are [Ti]$_0$ and the agitation rate. Fig. 4 shows a general increase of S_{bet} with [Ti]$_0$, except for high agitation rate and powder production. The effect of [Ti]$_0$ is depressed at high agitation rate and high powder production. The highest S_{bet} value (34 m^2 g^{-1}) is observed at high [Ti]$_0$ when introducing the reactant in turbulent mode, at low agitation and low powder production.

4.2. ΔW_I

Only powder production has a systematic effect on the gravimetric loss, low losses being generally observed at high powder production. No significant effect of the introduction mode is observed (Fig. 5). The effect of [Ti]$_0$ changes according to the levels of agitation rate and powder production: at low powder production, increasing [Ti]$_0$ increases ΔW_I at low agitation rate, and
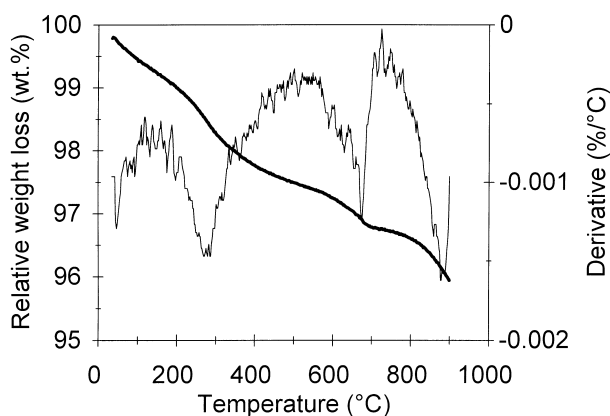

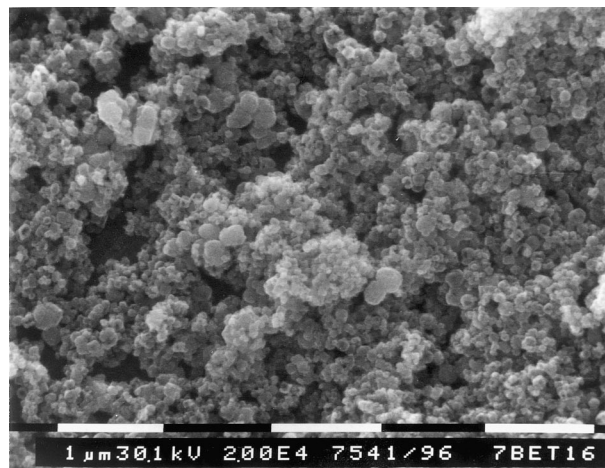Fig. 2. TG curves of as-prepared powder [sample *abcd(ef)*]. Heavy line: weight loss, thin line: derivative.

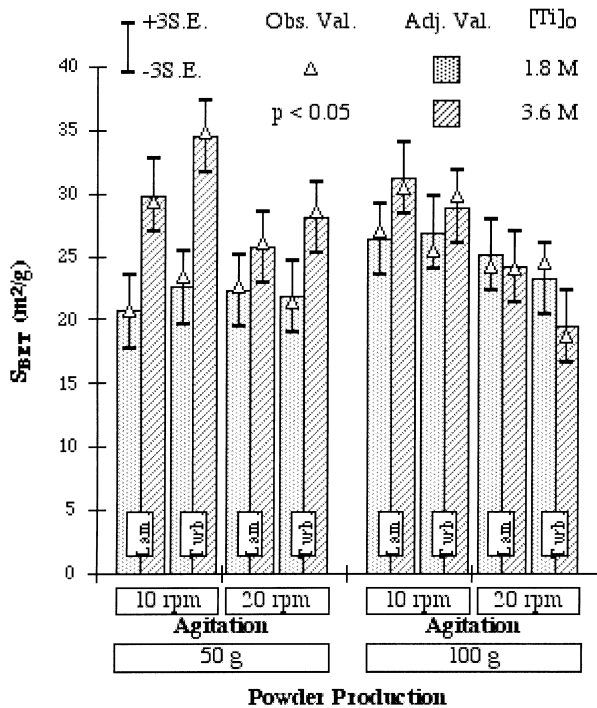Fig. 3. SEM image of sample *abcd(ef)*.

Fig. 4. Effects of Powder production, Agitation rate, Injection mode and $[Ti]_0$ on the specific surface (S_{bet}) of $BaTiO_3$ precipitates.
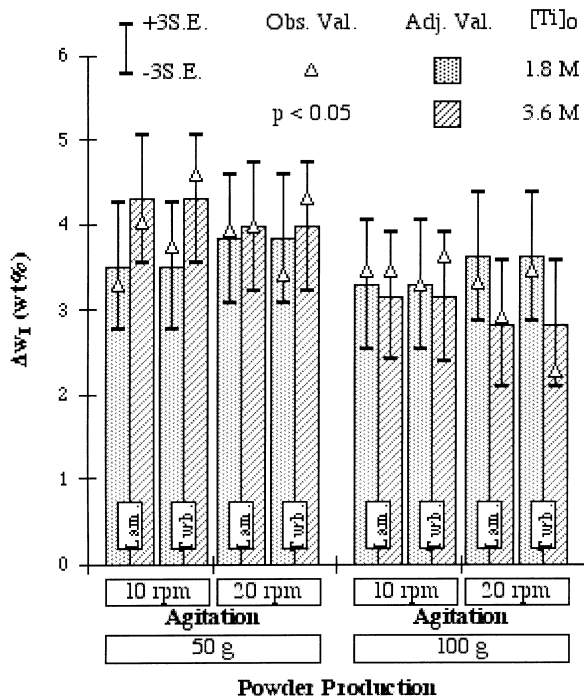

Fig. 5. Effects of Powder production, Agitation rate, Injection mode and $[Ti]_0$ on the first gravimetric loss (ΔW_I) of $BaTiO_3$ precipitates.

has no effect at high agitation rate, whereas at high powder production, increasing $[Ti]_0$ has no effect at low agitation rate, but decreases ΔW_I at high agitation rate.
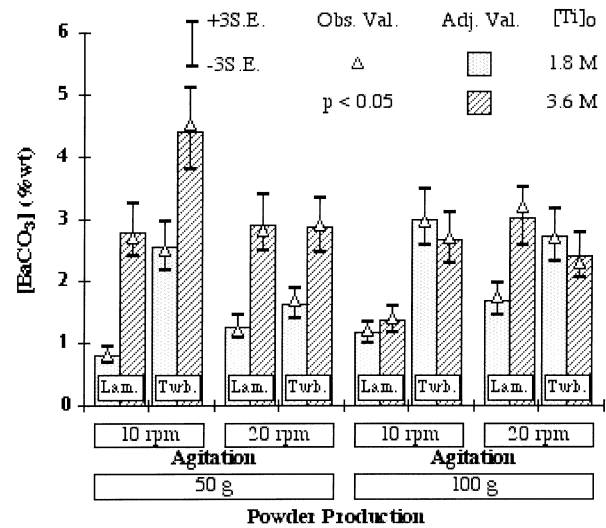

Fig. 6. Effects of Powder production, Agitation rate, Injection mode and $[Ti]_0$ on the $BaCO_3$ content (wt.%) of $BaTiO_3$ precipitates (statistical analysis was performed on log $[BaCO_3]$).

4.3. [BaCO₃]

$[Ti]_0$ and the injection mode are the two main factors affecting the level of carbonate contamination, but their effects are influenced by the level of powder production and agitation rate (Fig. 6). A systematic increase of $[BaCO_3]$ is observed when increasing $[Ti]_0$ at low powder production. At high powder production $[BaCO_3]$ is generally insensitive to $[Ti]_0$ except, at high agitation rate when laminar conditions of injection are used. Turbulent injection of the reactants generally increases $[BaCO_3]$.

5. Conclusions

The best conditions to obtain fine $BaTiO_3$ precipitates with low carbonate contamination are: slow agitation, laminar injection of the reactants, high powder production. Under these conditions a finer precipitate is obtained at the highest initial Ti concentration with no significant increase in carbonate contamination.

The characteristics of the $BaTiO_3$ prepared depend in a complex way on the precipitation factors: particularly the injection mode of the reactants (turbulent or laminar), the agitation rate, and the final amount of precipitated powder. The effect of the initial supersaturation (adjusted via $[Ti]_0$) on the particle size (measured by S_{bet}) is the highest when the precipitation is performed under slow agitation: this effect is depressed, and my even be reversed, when the batch production is increased.

The particle size decrease (as evidenced by an increase in S_{bet}) increases the tendency of the precipitates to adsorb water, as evidenced by the observed increase in gravimetric loss at 500°C. However, no correlation

seems to exist between S_{bet} and the level of carbonate contamination.

Acknowledgements

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