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Continuous hydrothermal synthesis of nanometric $BaZrO_3$ in supercritical water

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Abstract

Nanocrystalline barium zirconate ($BaZrO_3$) was synthesized using a hydrothermal synthesis process working in supercritical conditions and in a continuous way. By this method, we succeeded in the continuous and rapid production of nanopowders. As a preliminary work three barium precursors have been investigated: barium hydroxide ($Ba(OH)_2$), barium acetate ($Ba(CH_3COO)_2$) and barium nitrate ($Ba(NO_3)_2$). Two of them ($Ba(CH_3COO)_2$ and $Ba(NO_3)_2$) led to the pure perovskite phase. Then an experimental design has been conducted in order to determine the influence of the experimental parameters on the crystallinity and the grain size of the final product.

Keywords: Powders-chemical preparation; Grain size; $BaZrO_3$; Supercritical water synthesis

1. Introduction

Nanostructured ceramic materials are particularly interesting because of their physical properties depending on grain size [1]. Moreover, surface energy allows stabilizing phases outside the usual limits and new materials, very innovative, can be obtained [2]. Soft chemistry routes, high-energy dry grinding and hydrothermal synthesis have been developed during the last decades in order to obtain nanometric powders [3,4]. Most often, these techniques are developed in batch reactors. Continuous synthesis technologies, allowing several tens of grams of nanoparticles per hour production, are then very interesting to be developed at industrial level. In this perspective, a continuous production prototype of hydrothermal synthesis in subcritical and supercritical water has been developed in our group [5–7]. Recent papers summarise the specific characteristics of supercritical fluid processes for material synthesis and processing [8–12]. Two key features have been found: formation of nanoparticles, and ability to control particle morphology. This technology has also the advantage of being easy to use compared to closed reactors, and to have a high productivity.

Barium zirconate ($BaZrO_3$) is an interesting material for the refractory industry. Indeed, it is a high melting ceramic material (mp $\approx$2600 °C) with extensive functional utility as an inert crucible material for reaction and sintering of superconductors [13]. $BaZrO_3$ could also be a dopant in $BaTiO_3$ matrix [14]. It has also been tested as a thermal barrier coating for supersonic jets [15] and for sensor applications at high temperature in H_2 containing atmosphere [16].

Conventionally, zirconates have been synthesized through solid-state reaction of zircon with carbonates, oxides or nitrate elements of group IIA. Ultrafine powders of ZrO_2 have been converted into $MZrO_3$ (M = Ba, Sr, Ca) by the batch hydrothermal method [17]. The co-precipitation/calcination method was also used [18]. $BaZrO_3$ nanoparticles with diameter in the range of 30–40 nm were synthesized by sol–gel process [19]. A urea-induced precipitation process led to $BaZrO_3$ nanoparticles with a diameter around 90 nm [20].

In a recent study, Kolen'ko et al. [21] have obtained nanocrystalline ZrO_2 (8–12 nm), amorphous $ZrO(OH)_2$ or microcrystalline $BaZrO_3$ (2–5 μm) powders, depending on

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the synthesis conditions, by an hydrothermal route in supercritical conditions at 673 and 783 °C but in a batch reactor . A previous publication showed for the first time the synthesis of nanocrystalline $BaZrO_3$ using the continuous hydrothermal synthesis process, from barium nitrate ($Ba(NO_3)_2$) and $ZrO(NO_3)_2$, in strong basic conditions at 500 °C [5]. In this new paper, we investigated the preparation of $BaZrO_3$ powders with the same process but using three different barium precursors: barium hydroxide ($Ba(OH)_2$), barium acetate ($Ba(CH_3COO)_2$) and $Ba(NO_3)_2$. Then an experimental design has been developed in order to study the influence of different operating parameters and establish the optimal conditions for obtaining a pure crystalline perovskite phase with the smallest grain sizes.

2. Experimental procedure

2.1. Apparatus

The experimental apparatus used for these hydrothermal syntheses was a continuous process described in Fig. 1. In one stream was fed the metal salt solution containing Zr and Ba source materials. This reactive solution was pressurized and combined with a pre-heated water stream (and eventually a basic solution fed in a third way) in a mixing point just before the reactor, which led to a rapid heating and subsequent reaction. The reactor was an inconel serpentine with a length of 2 m and an inner diameter of 2.3 mm, which led to a very fast reaction (around 10 s) that depended on the pumps flows. After the reactor, the solution was rapidly quenched. Filters retained agglomerated particles that were added to the suspension obtained after the backpressure regulator.

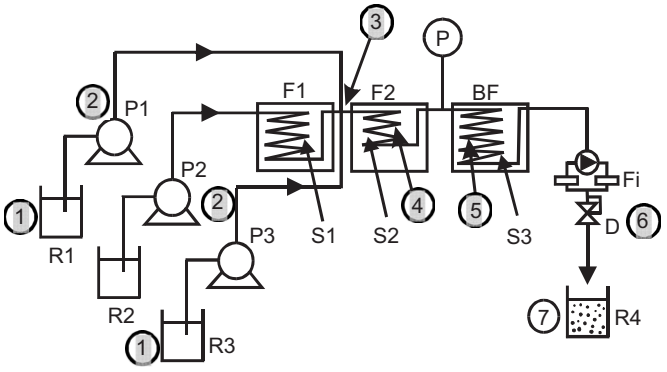

Fig. 1. Continuous hydrothermal synthesis process. Experimental protocol: (1) initial state cations in aqueous solution, (2) fast rise in pressure, (3) mixing point—rise in temperature, (4) conditions of synthesis (supercritical water medium), (5) cooling, (6) fall of pressure, (7) final state sol or suspension. Experimental set-up R1: cations solution, R2: water, R3: basic solution, P1, P2, P3: pumps of cramming, F1, F2: fluidized-bed owens, BF: cold bath, S1, S2: Inconel tubing, S3: stainless tubing, P: pressure gauge, Fi: filters on two parallel lines, D: back pressure regulator, R4: receiver.

2.2. Synthesis

The synthesis conditions are reported in Table 1. $ZrO(NO_3)_2 \cdot 6H_2O$ has been used as the Zr precursor. This solid could dissociate in a solution of nitric acid. Three different Ba precursors have been used, which are $Ba(OH)_2$, $Ba(CH_3COO)_2$ and $Ba(NO_3)_2$. With $Ba(CH_3COO)_2$ as well as $Ba(NO_3)_2$, a basic solution of sodium hydroxide was added. This was necessary in order to release OH^- ions for the neutralisation of protons; otherwise in the supercritical conditions the apparatus could suffer rapidly from acidic corrosion.

Reactions that occur in the apparatus are described as follows:

- Before the reactor, the dissolution of the precursors takes place (due to the high value of ε, the dielectric constant of water):

$$Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^-, \quad (R1)$$

or

$$Ba(CH_3COO)_2 \rightarrow Ba^{2+} + 2CH_3COO^-, \quad (R1')$$

or

$$Ba(NO_3)_2 \rightarrow Ba^{2+} + 2NO_3^-, \quad (R1'')$$

$$NaOH \rightarrow Na^+ + OH^-, \quad (R2)$$

and

$$ZrO(NO_3)_2 \rightarrow ZrO^{2+} + 2NO_3^-. \quad (R3)$$

Table 1
Synthesis conditions of $BaZrO_3$ from different Ba precursors on the continuous hydrothermal synthesis process

Precursors		P (bar)	T (°C)	Residence time (s)	Reaction product	Heat-treated product
$ZrO(NO_3)_2$, $6H_2O$	0.025 mol L^{-1}	300	450	9	Amorphous	$BaZrO_3 + ZrO_2$
$Ba(OH)_2$	0.1 mol L^{-1}					
$ZrO(NO_3)_2$, $6H_2O$	0.025 mol L^{-1}	300	485	15	$BaZrO_3$	$BaZrO_3$
$Ba(CH_3COO)_2$	0.1 mol L^{-1}					
NaOH	1.5 mol L^{-1}					
$ZrO(NO_3)_2$, $6H_2O$	0.075 mol L^{-1}	300	450	31	$BaZrO_3$	$BaZrO_3$
$Ba(NO_3)_2$	0.3 mol L^{-1}					
NaOH	1.75 mol L^{-1}					

The heat treatment has been realised at 900 °C during 2 h under air atmosphere.