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Rapid synthesis of submicron crystalline barium zirconate $BaZrO_3$ by precipitation in aqueous basic solution below 100 °C

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Abstract

Pure crystalline $BaZrO_3$ powders can be produced by precipitation in highly basic aqueous solution. The influence of several synthesis parameters is studied. At high OH^- concentration ([NaOH] = 20 mol/l), it is possible to obtain the well-crystallized stoichiometric perovskite phase at relatively low temperature (~80 °C), after a short reaction time (15 min) and without requiring any precaution to avoid the presence of CO_2. This synthesis method yields spherical particles, whose size can be controlled by changing the concentration of the Ba + Zr solution. No calcination treatment is necessary since the precipitate is crystalline. Suitable choice of the synthesis parameters ([NaOH] = 20 mol/l, [Ba + Zr] = 1 mol/l, reaction time = 15 min) yields a sub-micron precipitate with excellent densification behaviour. Corrosion tests in BaO–CuO melt show that ~98% dense $BaZrO_3$ obtained by sintering at 1650 °C for 13 h could be used for crucibles in the synthesis of $YBa_2Cu_3O_7$ superconducting single crystals.

Keywords: Perovskites; Powders-chemical preparation; Refractories

1. Introduction

The barium zirconate perovskite is of interest for various fields of applications. $BaZrO_3$ has excellent mechanical properties, such as high fracture toughness, and can be used as refractory up to very high temperatures ($T_m = 2600$ °C). Barium zirconate also shows high corrosion resistance with respect to the molten phases formed during the synthesis of copper oxide–based superconducting single crystals [1–4] and was found to behave as an inhibitor of macrocrack formation in zirconia substrates.[5] $BaZrO_3$–$BaTiO_3$ solid solutions are ferroelectric[6,7] while other $BaZrO_3$-based materials are high-temperature proton conductors.[8]

It is well known that the synthesis of multicationic oxides by classical solid state reaction suffers from several drawbacks, which have stimulated tremendous research into alternative “low temperature” methods. An abundant literature reports successful synthesis routes for a large range of compounds. In the case of $BaZrO_3$, sol–gel oxalate or citrate routes produce powders with very small grain size but many of these methods require organic solvents which have to be recycled.[9–12] It is also possible to synthesise perovskite compounds from aqueous solutions by homogeneous precipitation with urea or ammonia.[13,14] However, most of these syntheses still require a calcination treatment to transform a homogeneous precursor into a crystalline oxide phase. Besides, these precursors often contain carbonaceous species, which are released as CO_2 during calcination. In the present context of energy saving and CO_2 emission reduction, synthesis methods where the crystalline oxide is formed directly at low temperature are especially desirable. For example, crystalline $BaTiO_3$ can be prepared by controlled double jet precipitation (CDJP)[15,16] or by hydrothermal methods.[17–21] The possibility to upscale coprecipitation syntheses to mass production has been examined by several authors.[16,22]

In this paper we report experimental results on the precipitation of barium zirconate in highly concentrated sodium hydroxide aqueous solution. We study the influence of several synthesis parameters on the composition, crystallization and grain size distribution of the precipitates. The densification behaviour of the optimized powder is examined and the quality of the sintered pieces is ascertained by corrosion tests in BaO–CuO flux at high temperature.

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2. Experimental procedure

$BaZrO_3$ is prepared by coprecipitation of $BaCl_2.2H_2O$ (99% pure, Mel) and $ZrOCl_2.8H_2O$ (98% pure, Avocado) in a concentrated NaOH (99% pure, J.T Baker) solution. Deionised water is used without decarbonatation. In a typical experiment, stoichiometric amounts of zirconium and barium salts are dissolved in 50 ml water. This solution is added to 100 ml of NaOH solution at a constant flow rate (25 ml/min). The reactor is kept at 80 °C during the whole experiment and constant stirring is applied. The precipitate is then centrifuged at 4000 rpm, washed twice with 300 ml of water and dried at 110 °C overnight. The coprecipitation experiment was carried out with several NaOH concentrations (7.5, 10, 12.5, 15, 20 mol/l), reaction times (1, 5, 10, 15, 30 min) and total concentration of reactants [Ba + Zr] (0.2, 0.5, 1 mol/l).

The precipitates were characterized by X-ray powder diffraction (Siemens D5000, Cu Kα radiation), IR spectrometry (PerkinElmer FT-IR) and scanning electron microscopy (ESEM Philips XL 30). Thermogravimetric analysis was performed in flowing air with a heating rate of 10 °C min^{-1} (STA 449C, Netzsch). The barium and zirconium contents of the synthesized powders were checked by atomic emission spectroscopy with inductively coupled plasma as atomic emission source (ICP-AES); in order to do so, 0.1 g of dry powder was dissolved in 3 ml of hot nitric acid and then diluted with cold de-ionized water. Particle size distribution (Malvern Mastersizer 2000) was measured on powder dispersed by sonication in 0.1 mol/l acetic acid aqueous solution. The dilatometric curves (TMA92, Setaram) were collected on rods which were isostatically pressed at 200 MPa. The dilatometric measurements were performed with 10 °C/min heating rate. The apparent density was measured by the Archimedes technique in water. The relative density was calculated based on a theoretical density value of 6.23 g cm^{-3} for $BaZrO_3$.

3. Results and discussion

3.1. $BaZrO_3$ precipitation

In a first series of experiments, the NaOH concentration was varied from 20 to 7.5 mol/l while all other experimental parameters were kept constant ([Ba + Zr] = 0.5 mol/l, reaction time = 15 min). After washing and drying, the precipitates were characterized by X-ray diffraction, IR spectroscopy, ICP-AES and thermogravimetric analysis.

The diffractograms of the powders obtained after precipitation in 20 mol/l or 15 mol/l NaOH correspond to single-phase $BaZrO_3$ perovskite (Fig. 1a). The patterns of the powders prepared with 12.5 mol/l or 10 mol/l NaOH reveal the presence of traces of a $BaCO_3$ secondary phase (Fig. 1b). The $BaCO_3$ reflections become more intense after storing the powder for several months (Fig. 1c). Powders precipitated with 7.5 mol/l NaOH are poorly crystallized (Fig. 1d).

IR spectroscopy (Fig. 2) confirms the presence of significant amounts of $BaCO_3$ in all powders precipitated with NaOH concentrations of 12.5 mol/l or less, as shown by the relative intensity of the strong carbonate absorption (at ~1440 cm^{-1}) with respect to the metal-oxygen absorption of the perovskite phase (at ~560 cm^{-1}).

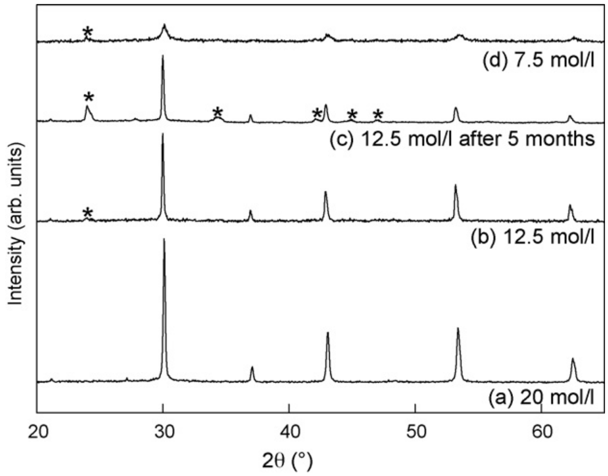

Fig. 1. Powder X-ray diffraction patterns of the powders precipitated in NaOH solutions of various concentrations. Patterns (b) and (c) correspond to the same powder and were measured just after the precipitation and after 5 months, respectively. $BaCO_3$ reflections are marked by an asterisk.

ICP-AES analysis was used to measure the barium/zirconium ratio in the precipitates. Powders precipitated in 20 mol/l or 15 mol/l NaOH possess the expected stoichiometry, i.e. Ba/Zr = 1. On the contrary, precipitates obtained with lower NaOH concentrations display Ba/Zr < 1. The non-stoichiometry increases when the NaOH concentration decreases (Ba/Zr = 0.89, 0.60 and 0.53 for [NaOH] = 12.5, 10 and 7.5 mol/l), indicating that some barium is left in solution or lost during washing. By comparing the ICP-AES and XRD results, it becomes clear that some Zr-rich amorphous phase must be present in the powders prepared with [NaOH] $\leq$ 12.5 mol/l, since the Zr excess cannot be accommodated as a non-stoichiometry in the $BaZrO_3$ perovskite phase (see[23] for a phase diagram).

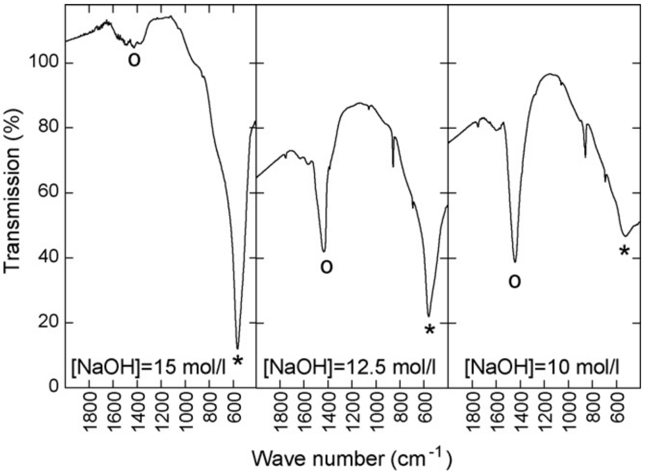

Fig. 2. 400–2000 cm^{-1} IR spectra of powders precipitated in NaOH solutions of various concentrations. The main peaks of $BaCO_3$ and the perovskite phase are marked by o and * symbols, respectively.

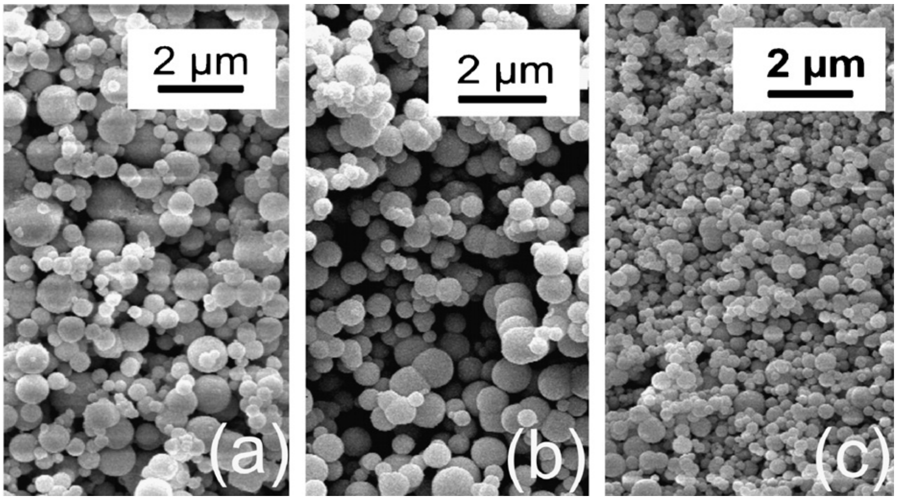

Fig. 3. Electron micrographs of powders precipitated from solutions with Ba + Zr concentration of (a) 0.2 mol/l, (b) 0.5 mol/l and (c) 1 mol/l. (Other synthesis parameters: [NaOH] = 20 mol/l, reaction time = 15 min).

As could be expected from the above results, the mass loss at 1300 °C tends to increase when the NaOH concentration used for precipitation decreases. The total mass loss does not exceed 5% for the powders prepared with [NaOH] ≥ 15 mol/l while it is higher than 10% for all the powders precipitated in [NaOH] ≤ 12.5 mol/l. The mass loss *vs.* temperature curves (not shown) are similar to published data for $BaZrO_3$ or $BaTiO_3$ syntheses[17–19,24] and correspond to the decomposition of hydroxyl and carbonate groups.

In summary, pure stoichiometric $BaZrO_3$ is obtained only by precipitation in the most concentrated NaOH solutions (15 or 20 mol/l). In order to discuss the formation of $BaZrO_3$, it is necessary to consider which barium and zirconium species are present in such highly basic solutions. When added into a basic solution, zirconyl chloride immediately hydrolyzes to form an oxyhydroxide gel $ZrO_{1+x}(OH)_{2-2x}$.[25] However, at high OH^- concentration, the zirconium solubility is increased by formation of the $Zr(OH)_5{}^-$ complex.[26] Concerning barium insoluble salts,[27] barium carbonate is much more insoluble than barium hydroxide. In highly basic solution, soluble barium is mainly found as $Ba(OH)^+$. The precipitation of the barium zirconate in presence of a large concentration of OH^- can occur through progressive dissolution of the zirconium gel in the solution, yielding $Zr(OH)_5{}^-$ ions which react with the $Ba(OH)^+$ ions (Equation (1)). Similar results are reported in the literature for the formation of barium titanate by precipitation from barium and titanium salts.[20,21]

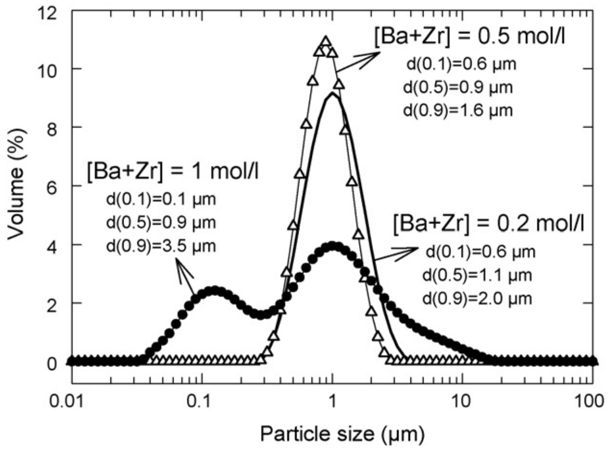

Fig. 4. Particle size distribution of powders precipitated from solutions with Ba + Zr concentration of 0.2 mol/l, 0.5 mol/l and 1 mol/l. (Other synthesis parameters: [NaOH] = 20 mol/l, reaction time = 15 min).

$$\mathrm{Ba(OH)}^{+}_{(aq)} + \mathrm{Zr(OH)}^{-}_{5\,(aq)} \rightarrow \mathrm{BaZrO}_{3(s)} + 3\,\mathrm{H_2O} \qquad (1)$$

When [NaOH] ≤ 12.5 mol/l, residual zirconium gel is present in the precipitate (for the reaction conditions described above, i.e. [Ba + Zr] = 0.5 mol/l, reaction time 15 min). The presence of $BaCO_3$ in these powders results from the adsorption of Ba^{2+} and/or $Ba(OH)^+$ ions on the amorphous zirconia gel or barium zirconate particles. Prolonged exposure of the powder to the air then leads to the formation of $BaCO_3$.

The precipitation mechanism suggested in Eq. (1) was corroborated by characterizing the Ba/Zr ratio in the precipitate after reaction times ranging from 1 to 60 min (with [NaOH] = 20 mol/l, [Ba + Zr] = 0.5 mol/l). In all cases only the perovskite reflections are detected in the X-ray diffraction patterns. After 1 min, the Ba/Zr ratio is 0.75, suggesting the presence of amorphous zirconium gel. The stoichiometric ratio Ba/Zr = 1 is reached after a reaction time of 5 min.

The fact that all equilibria are shifted towards the formation of $BaZrO_3$ in the presence of large concentrations of OH^- is further confirmed by the possibility to use weakly soluble reactants. In such an experiment, $BaCO_3$ powder is added directly to the NaOH solution (15 mol/l). After adding the zirconium solution, stirring for 2 h and washing, pure $BaZrO_3$ perovskite is obtained. When replacing both zirconyl chloride and barium chloride by zirconium oxycarbonate and barium carbonate, $BaZrO_3$ can be obtained if longer reaction time and/or higher NaOH concentration are used, but the resulting powder has poor densification behaviour and this route was abandoned.

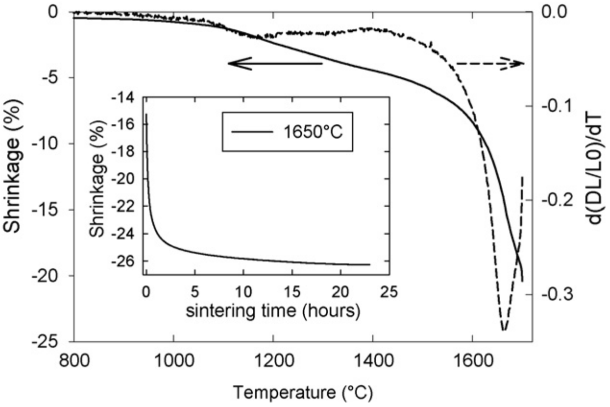

Fig. 5. Temperature dependence of the shrinkage and the shrinkage rate (10 °C/min heating rate). Inset: shrinkage vs. sintering time at 1650 °C (after heating to 1650 °C at 10 °C/min).

3.2. Particle size distribution

The influence of some synthesis parameters on the particle size was studied by electron microscopy and granulometry. All the experiments described in this section were carried out with 20 mol/l NaOH and resulted in spherical particles (Fig. 3). The particle size tends to increase during the first minutes after the addition of the reactants but no further evolution in particle size can be observed for reaction times longer than 15 min.

The particle size depends significantly on the [Ba + Zr] concentration. Fig. 3 shows the electron micrographs of precipitates obtained after 15 min for [Ba + Zr] concentrations of 0.2, 0.5 and 1 mol/l. The particle size decreases when the concentration of reactants increases: addition of a concentrated solution of reactants leads to supersaturation, therefore nucleation is favoured over grain growth.[28,29]

Fig. 4 shows the particle size distribution measured by laser granulometry on these same powders. The precipitates obtained with [Ba + Zr] = 0.2 or 0.5 mol/l have similar average sizes ($d_{0.5}$ ∼1 μm) but the size distribution is somewhat broader for the lowest concentration. In the case of the powder obtained with the largest concentration of reactants (1 mol/l), the particle size distribution is bimodal. Comparison with the electron micrograph (Fig. 3c) confirms that the peak centred at ∼150 nm corresponds to the primary particles while the second peak at ∼1 μm corresponds to agglomerates.

3.3. Densification

The powder used for the densification study is a pure $BaZrO_3$ precipitate with small particle size (∼150 nm). As described above, the synthesis conditions were: [NaOH] = 20 mol/l, [Ba + Zr] = 1 mol/l, reaction time 15 min. Fig. 5 shows the temperature dependence of the shrinkage and the shrinkage rate of a rod pressed isostatically at 200 MPa. The onset of shrinkage occurs at ∼1100 °C. Above ∼1450 °C, the shrinkage rate substantially increases and reaches its maximum around 1650 °C. The inset of Fig. 5 shows the dependence of the shrinkage on the sintering time at 1650 °C. Most of the densification process occurs during the first 2 h but a further improvement of the density can be obtained by extending the sintering time to ∼20 h, although the shrinkage rate decreases strongly. The final relative density is ∼98.4% of the theoretical density.

Densification experiments were carried out with different sintering temperatures and durations. The relative densities were measured by Archimedes' method. Electron micrographs of fractures of some samples are shown in Fig. 6. After 2 h at 1500 °C, densification has hardly started and only necks between particles are formed (Fig. 6a). Particles are cubic and less than 0.5 μm in size. It is possible to reach 98% relative density at 1500 °C by extending the sintering time to 13 h (Fig. 6b) or even 24 h, to promote grain growth (Fig. 6c). At 1650 °C, 98% relative density is achieved after a much shorter sintering time, but extending the thermal treatment to 13 h results in a material with large grains (typically 6 μm, see Fig. 6d).

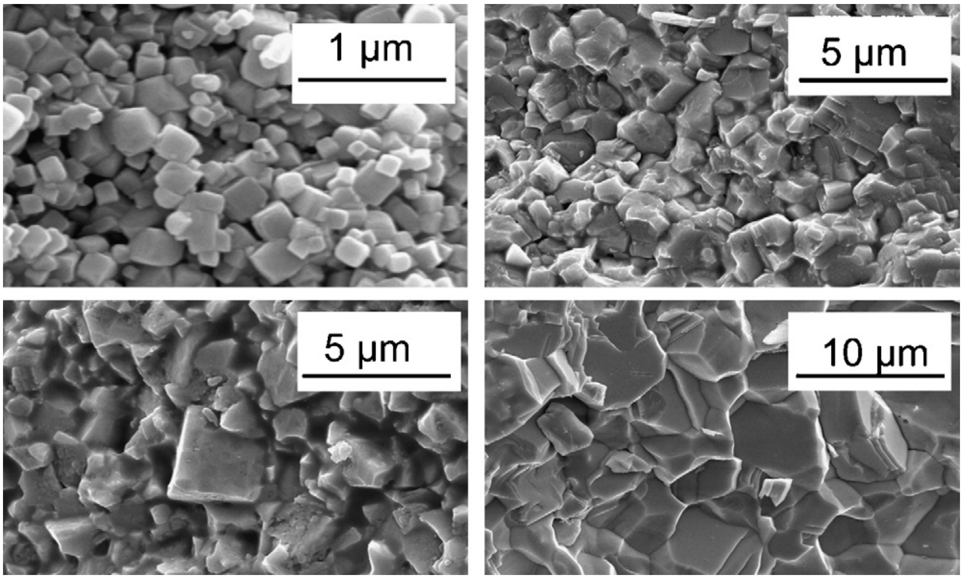

Fig. 6. Electron micrographs of fractures in samples sintered (a) at 1500 °C for 2 h, (b) at 1500 °C for 13 h, (c) at 1500 °C for 24 h and (d) at 1650 °C for 13 h.

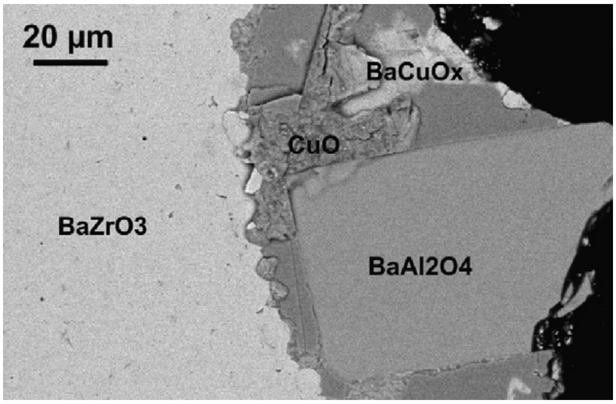

Fig. 7. Back-scattered electron micrograph of a polished cross-section through a $BaZrO_3$ rod sintered at 1650 °C for 13 h and immersed in a molten BaO–CuO flux at 1000 °C for 5 days.

Resistance of $BaZrO_3$ sintered pieces to the corrosion by Ba–Cu–O molten flux requires both a density over 97%[4] and high-quality grain boundaries. As a test of the quality of the samples prepared from the precipitated powder, corrosion tests were made on bulk pieces sintered at 1500 °C for 24 h and 1650 °C for 13 h respectively. The samples were immersed in a molten phase of BaO–CuO at 1000 °C for 5 days. The sample sintered at 1500 °C for 24 h did not resist and was completely destroyed. On the contrary, the samples sintered at 1650 °C for 13 h were not affected. The reactivity observed in samples sintered at 1500 °C might be due to the presence of sodium in the grain boundaries, although no detectable amount of sodium is usually found in the 1500 °C samples. However, the possibility of some sodium being retained as high as 1500 °C is confirmed by the fact that Na_2ZrO_3 traces at 1500 °C were observed by XRD in a few insufficiently-washed samples. Finally, an electron micrograph of a polished section through the 1650 °C sample is shown in Fig. 7. Four phases are identified: bulk barium zirconate, copper oxide, barium copper oxide and barium aluminate resulting from reaction of the flux with the alumina crucible. No reaction and no diffusion layer can be detected between the dense barium zirconate phase and the corrosive liquid phase. The flux does not percolate through the ceramic piece, due to the high density of the material, the large grain size (resulting in fewer grain boundaries) and the low reactivity of the grain boundaries.

4. Conclusion

Pure crystalline $BaZrO_3$ powders can be produced by precipitation in highly basic aqueous solution. The high OH^- concentration ([NaOH] = 20 mol/l) makes it possible to obtain the well-crystallized stoichiometric perovskite phase at relatively low temperature (~80 °C), after a short reaction time (15 min) and without requiring any precaution to avoid the presence of CO_2. This synthesis method yields spherical particles, whose size can be controlled by changing the concentration of the Ba + Zr solution. No calcination treatment is necessary since the precipitate is crystalline, therefore aggregation of the particles by partial sintering is avoided.

Suitable choice of the synthesis parameters ([NaOH] = 20 mol/l, [Ba + Zr] = 1 mol/l, reaction time = 15 min) yields a precipitate with excellent densification behaviour. The primary particle size is around 150 nm and the median grain size of the agglomerates is around 900 nm, thus no grinding step is necessary. In particular, ceramic parts obtained by sintering the isostatically pressed powder at 1650 °C for 13 h reach ~98% of the theoretical density and are not affected by a treatment in a BaO–CuO melt at 1000 °C for 120 h, demonstrating that this powder could be used for making high density ceramic crucibles for the synthesis of $YBa_2Cu_3O_7$ superconducting single crystals.

More generally, our results suggest that coprecipitation in highly basic aqueous solution may be an efficient synthesis method for compounds that cannot be obtained by conventional coprecipitation with low to medium hydroxide concentrations. Possible candidates are other zirconium-containing phases or similar compounds, where the solubility of a weakly soluble cation (such as zirconium) can be enhanced by formation of complexes with OH^-, thereby improving their reactivity towards other solution species.

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