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Preparation of $BaZrO_3$ nanopowders by spray pyrolysis method

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Abstract

Barium zirconate based solid solutions of various compositions become ionic and/or electronic conductors and they are potential candidates for numerous types of applications in the field of electroceramics. This work investigated application of ultrasonic spray pyrolysis method based on thermal decomposition of barium and zirconium nitrate solution for preparation of fine barium zirconate powders. The aerosols of nitrate solutions of 0.1, 0.01 and 0.001 M were thermally treated at 800, 1000 and 1200 °C. The prepared powders were composed of the spherical particles which sizes, from 90 to 500 nm, were mainly depended on the concentration of nitrate solution and less depended on the pyrolysis temperature. The particles consisted of the crystallites of 25–60 nm in size. Their sizes strongly depended on the pyrolysis temperature and to the lesser extend on the solution concentration.

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1. Introduction

Barium zirconate of perovskite structure, $BaZrO_3$, is well known refractory material with very high melting point (2600 °C), small thermal expansion coefficient, poor thermal conductivity, good mechanical properties, thermal stability and low chemical reactivity towards corrosive compounds.[1] Barium zirconate is a good candidate for many structural applications such as crucible material for synthesis of barium based high-T_c superconductors, substrate for thin films deposition, thermal barrier coatings in aerospace industries and material for interface engineering of alumina fiber–alumina matrix composites.[2–4]

Barium zirconate based solid solutions become ionic and/or electronic conductors and they are potential candidates for numerous types of applications in the field of electroceramics. Doped barium zirconate is known to dissolve protons in its lattice and can acts as proton conducting material in steam electrolyzers, humidity sensors, hydrogen pumps and particularly in solid oxide fuel cells (SOFC).[5–9]

A traditional method of barium zirconate synthesis consists in high-temperature solid state reaction usually between zirconia and barium carbonate preceded by powder homogenization often connected with particle size reduction. The powders prepared by such a way keep several drawbacks like a lack of reproducibility, a large particle size, wide size distribution, strong agglomeration and chemical inhomogeneity. To overcome the processing difficulties of existing solid-state methods, "soft chemistry" methods are increasingly important in barium zirconate powder synthesis. Generally, in these methods, the powder is obtained after a low temperature decomposition of different precursors. The co-precipitation technique is a useful method for the preparation of such precursors. In this case ammonium oxalate,[10] ammonia and ammonium carbonate[11] or urea[12] were used as a precipitating agent. The organometallic compounds were also applied as barium zirconate precursors with citric acid,[13] ethylene glycol[14] or polyacrylamide[15] as the complexing agent. Some other methods for barium zirconate synthesis were successfully practiced: thermal decomposition of nitrate[16] or mixture of nitrate with urea as a fuel[15] in combustion mode, hydrothermal reaction[17] or radiation assisted synthesis.[18]

The spray pyrolysis technique was one of the major techniques, used during last decade to prepare fine particles and to deposit a wide variety of materials in thin film form.[19,20] Synthesis through aerosols enables preparation of multicomponent powders with improved compositional homogeneity provided by a higher surface reaction in the absence of compositional segregation. Compared to other synthesis techniques, spray pyrolysis has many advantages such as: simple and continuous operation, controlled shape and size of the particles from nano- to micro-meters, uniform particle size distribution, high

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purity, and control of chemical uniformity and stoichiometry in a mixed oxide system.

The aim of the present paper is to study an application of spray pyrolysis method for preparation of barium zirconate nanopowders.

2. Experimental

The starting aqueous solution was prepared by dissolving appropriate amounts of zirconyl and barium nitrates (Merck, p.a.) in distilled water to prepare the 0.1 M solution expressed in cations concentration. Assuming that the precursor stoichiometry persisted in final particles, the cation ratio of Ba:Zr = 1:1 was established. The starting solution was diluted 10 and 100 times to obtain solutions with concentration of 0.01 and 0.001 M, respectively. The nitrate solution was atomized by an ultrasonic nebulizator at the frequency of 2.6 MHz and aerosol was transported into the horizontally fixed tubular quartz reactor. Oxygen was used as a carrier gas with the flow of 150 $dm^3 h^{-1}$. Two hot-zones tubular furnace was used to heat the quartz reactor. The droplets of the aerosol were dried and decomposed in the first zone of the furnace at temperature of 800, 1000 and 1200 °C. The formed particles were separated from the gas using an electrostatic filter placed in the second zone of the furnace at about 200 °C.

The phase composition of the prepared powders was examined by X-ray diffraction analysis (X'Pert Pro, Philips). The Scherrer formula using the full width at half maximum of the (1 1 0) diffraction peak of barium zirconate adjusted by a pseudo-Voigt function enabled evaluation of the crystallite size. Transmission electron microscopy (Philips CM20 with EDAX Phoenix EDS attachment) was used to characterise morphology of the powders and their local chemical composition. The particle size distributions were determined based on the microscopic images of the powders processed with the Aphelion program. The particle size determined by the image analysis denotes the diameter of a circle having area equal to that of the measured particle.

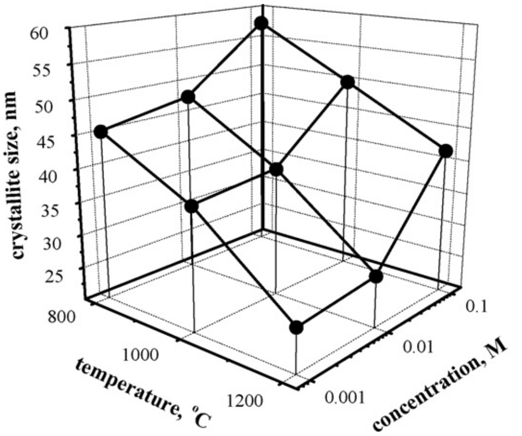

Fig. 1. Influence of the pyrolysis temperature and the solution concentration on the crystallite sizes in all prepared powders.

3. Results

X-ray diffraction analysis shows that all prepared powders are composed of barium zirconate phase only. Fig. 1 presents the changes of crystallite size determined from X-ray peak broadening due to the concentration of nitrate solutions and temperature of the pyrolysis. It can be explicitly concluded that decrease of the solution concentration as well as increase of the pyrolysis temperature cause decrease of barium zirconate crystallite sizes. This effect is most probably connected with kinetics of

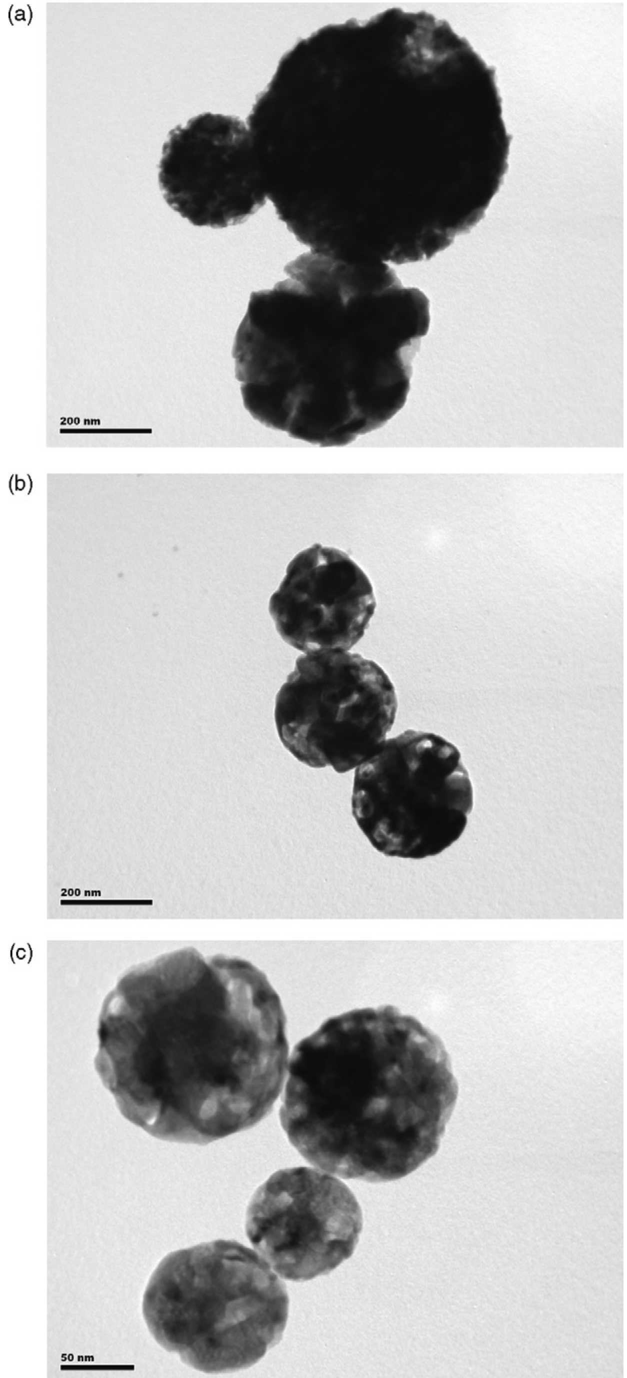

Fig. 2. Morphology of the $BaZrO_3$ powders prepared from solution of 0.1 M at 800 °C (a), 0.01 M at 1000 °C (b) and 0.001 M at 1200 °C (c).

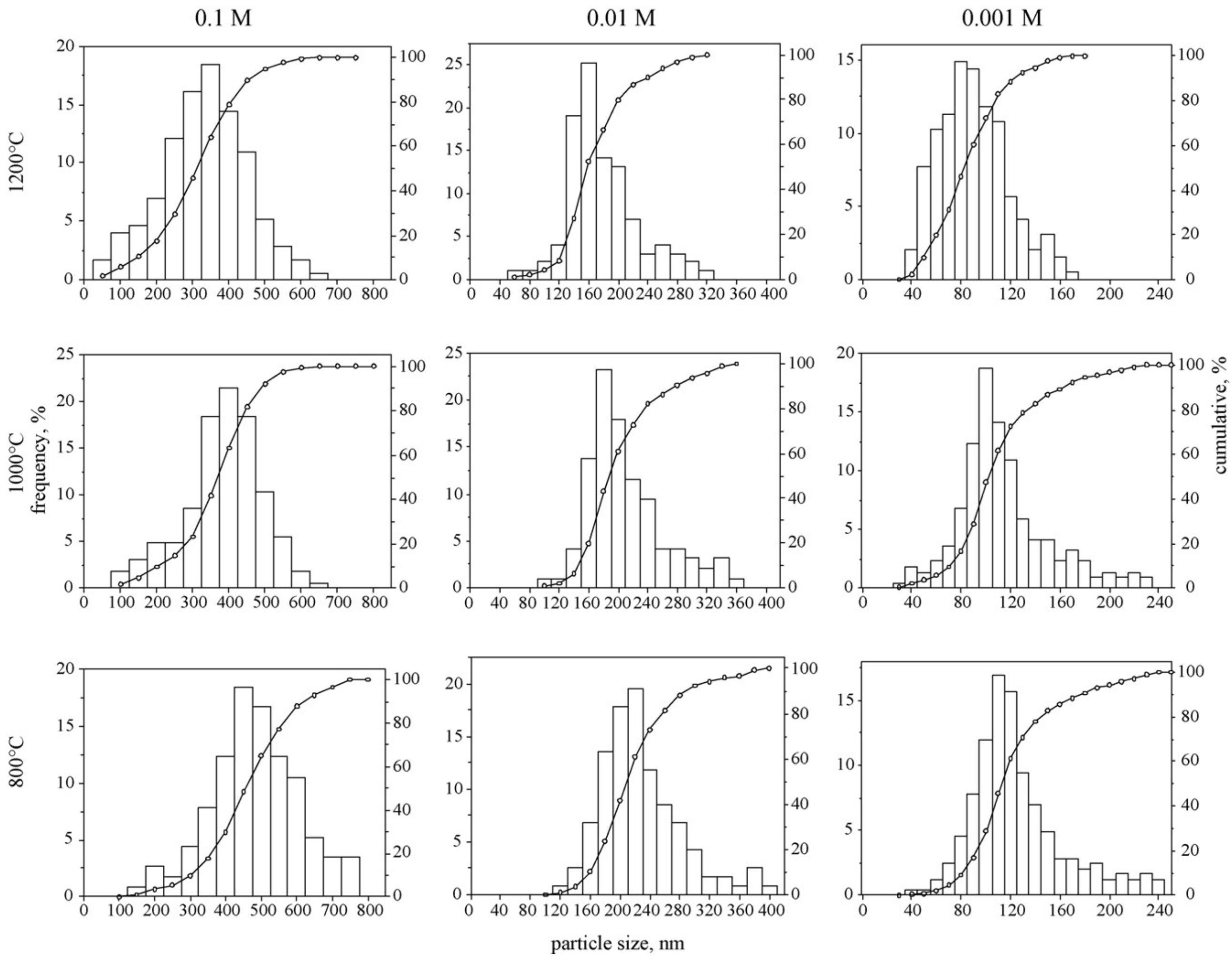

Fig. 3. Particle size distributions of the prepared powders.

the decomposition of the salts and forming of the $BaZrO_3$ crystallites. Increase of the pyrolysis temperature lead to the higher overheating that favours the nucleation process than the crystal growth. On the other hand, lower concentration of the nitrates solution means lower the nominal solid phase amount in the single droplet. It can be stated that influence of the pyrolysis temperature on the crystallite size is much stronger than of the nitrate solution concentration. Generally, there are no essential differences between the crystallite sizes prepared from solutions of 0.01 and 0.001 M concentrations.

TEM observations reveal that particles of all powders are spherical in shape. Fig. 2 presents typical micrographs of powder particles prepared from the solutions of the following concentrations and processed at indicated temperatures: 0.1 M at 800 °C (a), 0.01 M at 1000 °C (b) and 0.001 M at 1200 °C (c). It can be stated that all particles are composed of the smaller crystallites. Comparison of the crystallite size (Fig. 1) with the particle size (Fig. 2) suggests that the latter ones are not single crystals. It was also confirmed by TEM images made in dark field mode.

The particle size distributions in each case were mono-modal and weak tendency to their broadening towards the bigger and bigger particles can be observed (Fig. 3). Increase of the pyrolysis temperature shifts the mode of the distributions, regardless the solution concentration, towards smaller sizes. On the other hand, increase of the solution concentration leads to increased particle sizes. A power of influence of the pyrolysis temperature and the solution concentration on the particle size is good

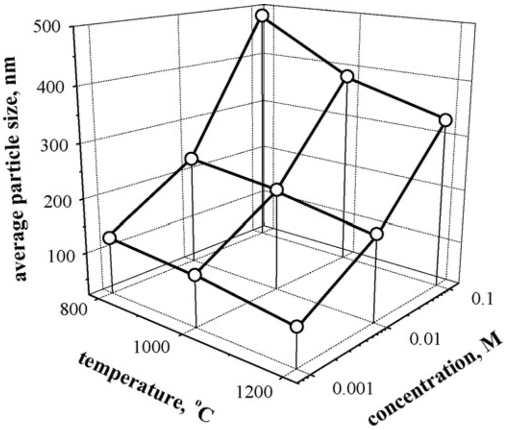

Fig. 4. Changes of the arithmetical average sizes of the barium zirconate particles as a function of the pyrolysis temperature and the solution concentration.

visible in Fig. 4 which presents changes of the mean sizes of the barium zirconate particles as a function of both factors. The barium zirconate particles are formed already at temperature as low as 800 °C and no distinct differences between the particle sizes in powders prepared at different temperatures is observed. Absence of barium and zirconium oxides or other impurities indicates that product of drying and following decomposition of nitrates is very homogenous. The strong influence of the solution concentration on the particle size suggests that individual particles are formed from the single droplets. In such case distribution of the particle size results from the distribution of the droplets size.

4. Conclusions

The ultrasonic spray pyrolysis method based on thermal decomposition of nitrate solution was successfully applied for preparation of fine barium zirconate powders. The powders are composed of the spherical particles which sizes are mainly depended on the concentration of nitrate solution and less dependent on the pyrolysis temperature. The particle size distributions are mono-modal with the average particle sizes varying from 90 to 500 nm in the powders prepared from solution of 0.001 M at 1200 °C and 0.1 M at 800 °C, respectively. The particles consist of crystallites of 25–60 nm in size. Their sizes strongly depend on the pyrolysis temperature and to the lesser extend on the solution concentration.

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