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Solid-state synthesis and spark plasma sintering of submicron $BaY_xZr_{1-x}O_{3-x/2}$ ($x = 0$, 0.08 and 0.16) ceramics

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Abstract

Fine powders (particle size of 100–200 nm) of $BaY_xZr_{1-x}O_{3-x/2}$ ($x = 0$, 0.08, 0.16) were produced by solid-state reaction at 1000–1050 °C using nanocrystalline ZrO_2 and $BaCO_3$ raw materials. The powders were densified by means of the spark plasma sintering process resulting in dense and homogeneous submicron microstructures. Near full density ceramics with grain size < 300 nm were obtained by sintering at 1600 °C for 1–5 min.

Keywords: Powders-solid state reaction; Sintering; Perovskites; ZrO_2; $BaZrO_3$

1. Introduction

Barium zirconate, $BaZrO_3$, is a cubic perovskite (space group: $Pm\bar{3}m$, unit cell edge: 4.193 Å, theoretical density: 6.23 g cm^{-3}) with a high melting point of 2600–2700 °C and no phase transitions up to this temperature.[1] Because of the high relative dielectric constant ($\varepsilon_r = 30$–40) at high frequencies, even at temperatures of ≈500 °C, $BaZrO_3$ was initially investigated as a dielectric for microwave components.[2] In recent years, this material has attracted renewed interest because it was reported to be virtually inert to the attack from the BaO–CuO melt used for the growth of YBCO single-crystals.[3–7] Consequently, crucibles and other parts made of sintered $BaZrO_3$ can be utilized for the processing of high-purity single-crystals of high T_c superconductor oxides.[5,6] New applications of $BaZrO_3$ are currently being investigated. It has been recently shown that the addition of $BaZrO_3$ nanoparticles as pinning centers in YBCO leads to a strong enhancement of the current density in superconducting films.[8] $BaZrO_3$ heavily doped on the Zr site with transition elements has also interesting potential applications. $BaPd_xZr_{1-x}O_3$ can be used as a catalyst for catalytic combustion of hydrocarbons.[9] $BaY_xZr_{1-x}O_{3-x/2}$ is a promising high-temperature proton conductor due to the high proton solubility and the concomitant high proton conductivity.[10–12]

Near full density (≥97%), small grain size, and absence of intergranular phases are key requirements for the ceramics to be used for the realization of $BaZrO_3$ crucibles and of Y:$BaZrO_3$ proton conducting membranes with the required properties. Ceramic powders for the sintering process are usually obtained by solid-state reaction between ZrO_2, Y_2O_3 and $BaCO_3$ at 1200–1400 °C. The resulting powders are usually rather coarse and, consequently, temperatures of the order of 1700 °C are required to attain a good densification (≥90%).[4–6,11,13] At such a high temperature, grain growth is quite fast and sintering often results in coarse-grained materials and inhomogeneous microstructure. Sev-

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eral wet chemical routes for the synthesis of fine $BaZrO_3$ powders were investigated: hydrothermal preparation,[14,15] sol–gel method,[16,17] peroxide process,[18] citrate route,[19] and coprecipitation.[20] The sintering temperature could be lowered to 1400–1500 °C, although good densification (≥95%) was seldom attained[16,17] and significant grain growth was still noticed.

In the present study, $BaZrO_3$ powders were prepared by conventional solid-state reaction between ZrO_2 and $BaCO_3$. The use of nanocrystalline raw materials has allowed a significant lowering of the reaction temperature in comparison to conventional processing resulting in very fine and not agglomerated powders. Spark plasma sintering (SPS) was used for the densification of submicron powders of $BaZrO_3$ and $BaY_xZr_{1-x}O_{3-x/2}$. The ability of SPS in producing dense ceramics and ceramic composites has been verified for a broad variety of structural and functional materials.[21–25] Densification by SPS occurs at lower temperatures than traditional sintering and in a shorter time, typically a few minutes, thus minimizing grain growth and, in the case of composite materials, interfacial chemical reactions.

2. Experimental

2.1. Powder synthesis

For the preparation of pure $BaZrO_3$, stoichiometric quantities of nanocrystalline ZrO_2 (Grade TZ-0, Tosoh, Tokyo, Japan, $S_{BET} = 15.3\ m^2\ g^{-1}$, $d_{BET} = 67$ nm, predominantly monoclinic) and nanocrystalline $BaCO_3$ (Grade BM020, Solvay Bario e Derivati, Massa, Italy, $S_{BET} = 31.2\ m^2\ g^{-1}$, $d_{BET} = 48$ nm) were used. The main impurities contained in the raw materials were Na_2O (78 ppm) and SrO (119 ppm) for $BaCO_3$, Al_2O_3 (<50 ppm), SiO_2 (70 ppm) and Na_2O (200 ppm) for ZrO_2. The powders were mixed in water inside polyethylene jars using partially stabilized zirconia media. A solution of the ammonium salt of polyacrilic acid (Acros Chimica, Italy, MW 2000) was added as a dispersant. After mixing, the slurry was freeze-dried. The dried mixture was heated at 2 °C min^{-1} and calcined for 6 h at 1000 °C in a flowing oxygen atmosphere using platinum crucibles. The burnout of the organic additive was accomplished by 4 h isothermal hold at 300 °C. The final powder was denoted as BZ. The methodology described above was also used to prepare the yttrium-doped compound $BaY_xZr_{1-x}O_{3-x/2}$. In the case of composition $x = 0.08$ (denoted as BZY8), yttrium was added as aqueous solution of $Y(NO_3)_3{\cdot}4H_2O$ (Aldrich Chimica, Milan, Italy, 99.9%). In the case of composition $x = 0.16$ (denoted as BZY16), yttria-stabilized zirconia (Grade TZ8-YS, Tososh, Tokyo, Japan, 8 mol % Y_2O_3, $S_{BET} = 7 \pm 2\ m^2\ g^{-1}$, $d_{BET} = 150 \pm 40$ nm, cubic) was used as raw material. The calcination temperature of BZY16 was increased to 1050 °C. Phase purity of calcined powders was investigated by X-ray diffraction (XRD, Co Kα radiation). The morphology was observed by scanning electron microscopy (SEM). Specific surface area, S_{BET}, was measured by nitrogen adsorption according to the BET method. The density, ρ, of the powders was measured by helium picnometry. The equivalent BET diameter, d_{BET}, was calculated as $d_{BET} = 6/\rho S_{BET}$.

2.2. Spark plasma sintering

The powders were sintered as disks of 1.9 cm diameter and ≈0.2–0.3 cm thickness by SPS (Dr. Sinter 1050, Sumitomo Coal Mining Co., Tokyo, Japan). The powder was poured in a graphite die, heated at 200 °C min^{-1} up to the sintering temperature with an applied pressure of 105 MPa and held at constant temperature (1400–1600 °C) for 0–5 min. The temperature was measured using an optical pyrometer focused on the external surface of the die. The heating was provided by a pulsed dc current which is allowed to pass through the conductive die that directly acts as heating element. The length of the pulses was 3 ms and a pulse pattern of 12:2 (meaning 12 pulses on and 2 off) was used. The electric power was then switched off, the pressure released, and the sample was allowed to cool at about 400 °C min^{-1} to room temperature. The as-sintered ceramics were polished and then annealed in air for 2 h at a temperature of 1000 °C. This treatment was intended to relieve residual stresses (arising either from the SPS process or from polishing) and to remove the surface carbon contamination. Phase composition and unit cell parameter of sintered barium zirconate were determined by XRD. The microstructure was observed by SEM on fracture or thermally etched surfaces. The grain size was measured as the mean intercept length. The density of the ceramics was obtained by Archimede's method.

3. Results and discussion

After calcination, the BZ powder consists of practically single-phase $BaZrO_3$ with only traces of $BaCO_3$ and ZrO_2, as can be seen from Fig. 1. For BZY8 and BZY16, beside the main $BaY_xZr_{1-x}O_{3-x/2}$ phase, small amounts of unreacted $BaCO_3$ and ZrO_2 were observed. However, as will be seen later, the reaction becomes complete during sintering, resulting in single-phase ceramics. The particle size, as observed by SEM, is of the order of 100 nm for BZ and BZY8 and of the order of 200 nm for BZY16, Fig. 2. The specific surface areas of the powders (BET method) were 7.9 $m^2\ g^{-1}$ for BZ, 6.4 $m^2\ g^{-1}$ for BZY8, and 6.0 $m^2\ g^{-1}$ for BZY16. The equivalent BET diameters of the particles are 122, 152 and 166 nm, respectively. Single-phase $BaY_xZr_{1-x}O_{3-x/2}$ powders can be obtained by calcination at higher temperatures. However, this resulted in significant coarsening and agglomeration of the particles which negatively affects the sintering process.

In a recent paper[26] it was shown that $BaZrO_3$ grows as a layer at the surface of the ZrO_2 particles with progressive consumption of the parent particles. As a result, the size

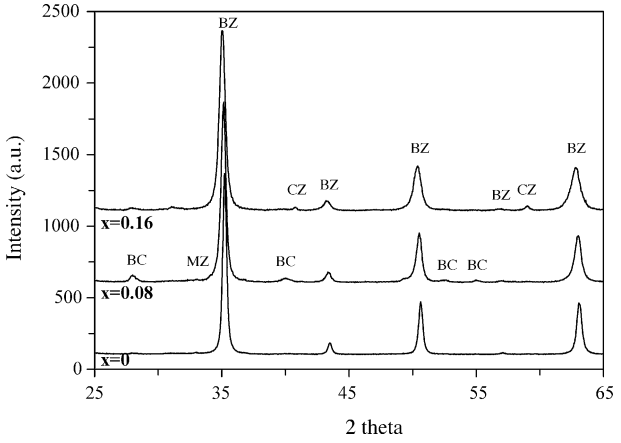

Fig. 1. XRD patterns (Co Kα radiation) of $BaY_xZr_{1-x}O_{3-x/2}$ powders calcined for 6 h at 1000 °C ($x = 0$ and 0.08) and 1050 °C ($x = 0.16$). BZ: $BaY_xZr_{1-x}O_{3-x/2}$; BC: $BaCO_3$ whiterite; MZ: monoclinic zirconia; CZ: cubic zirconia.

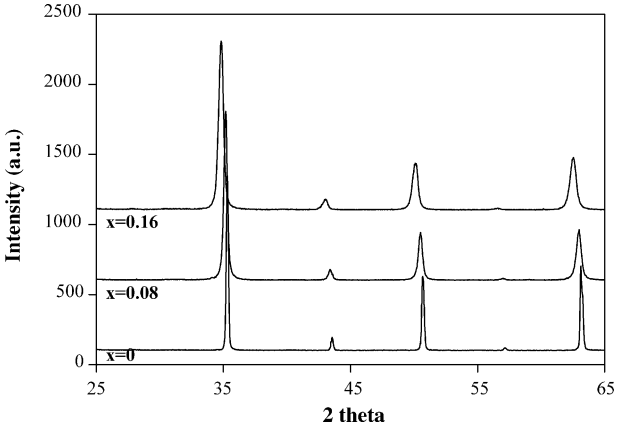

Fig. 3. XRD patterns (Co Kα radiation) of $BaY_xZr_{1-x}O_{3-x/2}$ ceramics obtained by spark plasma sintering at 1600 °C.

and shape of the final $BaZrO_3$ particles are expected to be primarily determined by the morphology of the starting zirconia. Taking into account the BET diameter of the monoclinic zirconia particles, ≈70 nm, a volume increase of a factor of ≈2 corresponding to the transformation of ZrO_2 to $BaZrO_3$ and neglecting any further coarsening process, the final diameter is expected to be ≈90 nm. This value compares well with the size of the BZ particles as observed by SEM (≈100 nm, Fig. 2). In the case of BZY16, the expected particle size is ≈200 nm, again a value that agrees with the particles observed by SEM (Fig. 2). However, if the reaction rate were uniquely controlled by the size of the ZrO_2 particles (as predicted by shrinking core models of solid-state reactions), one would expect only a minor influence of the particle size of $BaCO_3$. In contrast, it was found that the use of nanocrystalline $BaCO_3$ significantly increased the reaction rate in comparison to the use of standard, micrometric carbonate. This beneficial effect has to be ascribed to a more intimate contact between the two reactants and to a decrease of the mean distance for surface mass transport. Similar observations on the effect of the $BaCO_3$ particle size were made for the solid-state synthesis of $BaTiO_3$.[27] Therefore, the calcination temperature can be lowered to 1000 °C, resulting in relatively pure, nanocrystalline, and reasonably unagglomerated $BaZrO_3$ and $BaY_xZr_{1-x}O_{3-x/2}$ powders. The use of yttria-stabilized zirconia represents a convenient way to obtain good quality powders of $BaY_xZr_{1-x}O_{3-x/2}$ by solid-state reaction. The main advantage in comparison to conventional mixing and calcination of $BaCO_3$, ZrO_2 and Y_2O_3 is a more homogeneous distribution of yttrium in the final particles, avoiding local composition fluctuations related to imperfect mixing and the slow solid-state diffusion of yttrium in the perovskite lattice.

The SPS-consolidated dense ceramics consist of single phase $BaY_xZr_{1-x}O_{3-x/2}$ as shown by the XRD patterns reported in Fig. 3. The unit cell parameter of pure $BaZrO_3$ was 4.194 Å, which is in excellent agreement with the reference value of 4.193 Å (#6-0399, Powder Diffraction File, International Center for Diffraction Data, Newton Square, PA, 1994). The unit cell parameters (calculated by means of

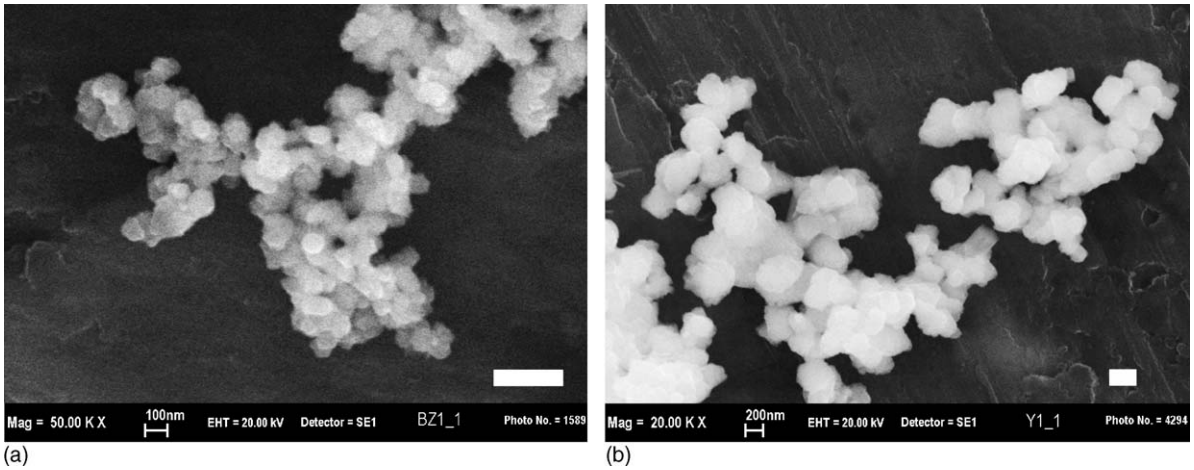

Fig. 2. Morphology (SEM) of calcined powders (a) $BaZrO_3$, 6 h at 1000 °C. (b) $BaY_{0.16}Zr_{0.84}O_{2.92}$, 6 h at 1050 °C. Bar: 300 nm.

the Rietveld refinement method) corresponding to $x = 0.08$ (4.204 Å) and $x = 0.16$ (4.216 Å) are in good agreement with the measurements reported by Schober and Bohn.[11] Thus it can be concluded that yttrium is fully incorporated at the Zr site and its negative effective charge is compensated by oxygen vacancies. The progressive shift of the XRD peaks towards lower 2θ values with increasing Y-content related to the expansion of the unit cell is well evident from Fig. 3. The theoretical density calculated from the unit cell parameter is 6.22 g cm^{-3} for $x = 0$, 6.135 g cm^{-3} for $x = 0.08$, and 6.033 g cm^{-3} for $x = 0.16$.

The influence of sintering temperature and hold time has been briefly investigated and some representative results are reported in Table 1. For pure $BaZrO_3$, a relative density (RD) of 96.1% without significant grain growth is obtained after only 1 min at 1500 °C. Use of longer sintering times (5 min) resulted in a minor improvement in density. At 1600 °C near full density is attained after 1 min with a grain growth factor of ≈2 (Fig. 4a). Longer dwell time generated further grain growth. For comparison, conventional sintering of BZ for 60 min at 1600 °C (heating rate 3 °C min^{-1}) resulted in

Table 1
Density and grain size of $BaY_xZr_{1-x}O_{3-x/2}$ ceramics obtained by spark plasma sintering

x	Temperature (°C)	Dwell time (min)	Relative density (%)	Grain size (nm)
0.0				
	1400	1	91.3	70–150
	1500	1	96.1	140
	1600	1	98.5	200
Conventional sintering[a]	1600	60	93	1200
Fast sintering[b]	1600	0	88	260
0.08				
	1400	5	93.7	–
	1600	1	94.4	170
	1600	4	95.0	190
0.16				
	1400	5	94.5	–
	1600	1	96.1	180
	1600	5	97.9	280

[a] Conventional sintering: 3 °C min^{-1}, 60 min at 1600 °C.
[b] Non-isothermal fast sintering: 20 °C min^{-1} to 900 °C, 5 °C min^{-1} to 1000 °C, 12 °C min^{-1} to 1600 °C, 0 min at 1600 °C, cooling at 12 °C min^{-1}.

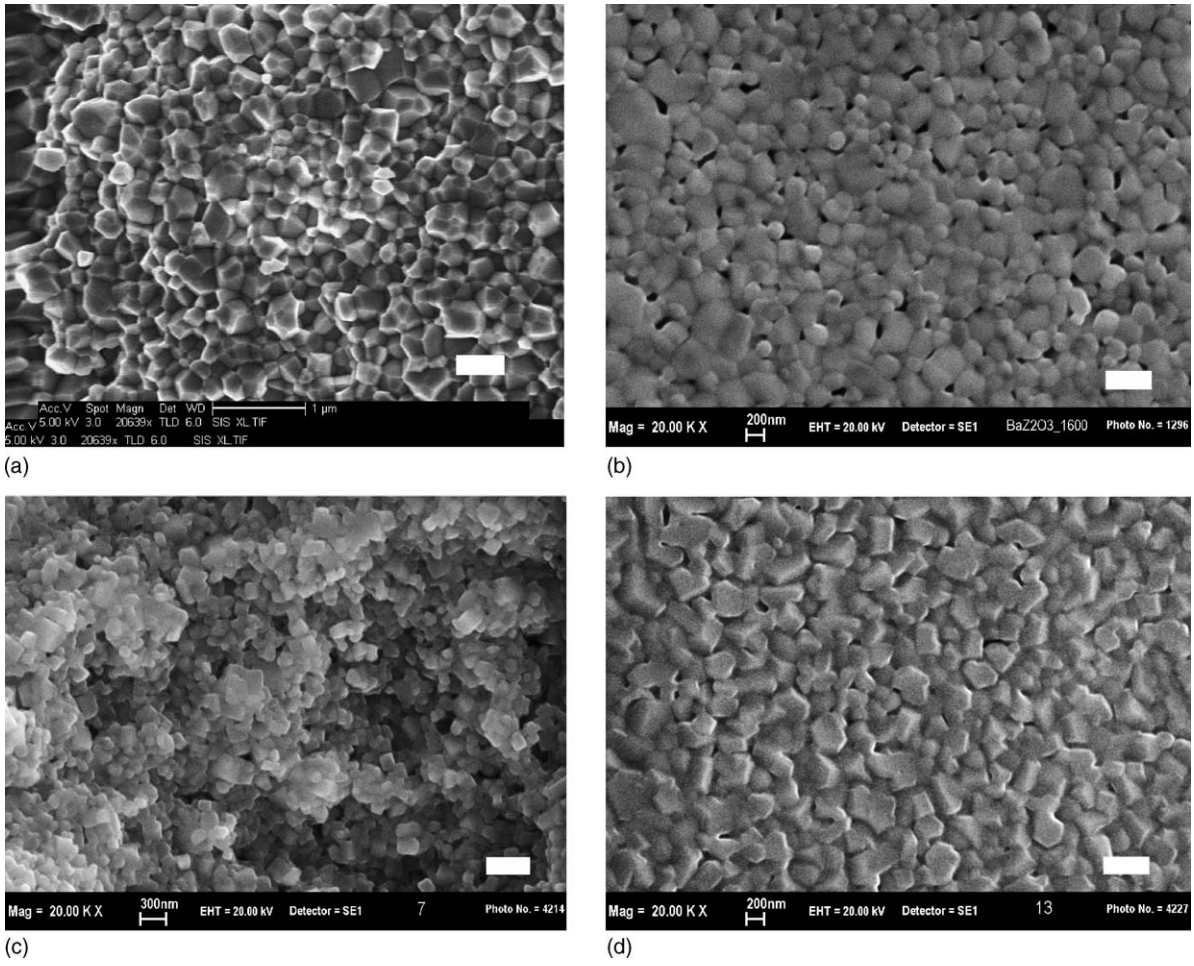

Fig. 4. Microstructure (SEM) of $BaY_xZr_{1-x}O_{3-x/2}$ ceramics obtained by spark plasma sintering at 1600 °C. (a) $x = 0$, 1 min. (b) $BaZrO_3$ ceramic obtained by non isothermal fast sintering in a conventional furnace. (c) $x = 0.08$, 4 min. (d) $x = 0.16$, 5 min. (a, c): Fracture surface. (b, d): After thermal etching. Bar: 500 nm.

a ceramic with 93% RD and grain size of 1.2 μm. Non-isothermal fast sintering up to 1600 °C produced a ceramic with an average grain size of 260 nm but higher porosity (12%), as shown in Fig. 4b. This means that the high heating rates and the high pressure applied during the SPS treatment have a beneficial effect on densification and on minimizing grain growth, in agreement with recent results reported for spark plasma sintering of alumina and cubic zirconia.[28,29]

Densification of yttrium-doped ceramics was more difficult. Relative densities equal or greater than 95% could be attained only after sintering at 1600 °C (Table 1). For BZY16 samples an appreciable density improvement (from 96.1 to 97.8%) was obtained by increasing the hold time up to 5 min, while the grain size remains <300 nm. It appears that the powder with $x = 0.16$, although coarser, can be more easily densified than the powder with $x = 0.08$. This is possibly related to the use of yttria-stabilized zirconia as precursor in the case $x = 0.16$. Examples of the microstructure of the ceramics sintered at 1600 °C are reported in Fig. 4c–d. Non-isothermal sintering in a conventional furnace as for BZ leads to fine grained ceramics (≈300 nm) with RD below 90%. Thus, the use SPS has a significant effect even on the densification of Y-doped ceramics.

4. Summary and conclusions

$BaY_xZr_{1-x}O_{3-x/2}$ powders ($x = 0$, 0.08 and 0.16) were prepared by a solid-state reaction between $BaCO_3$ and ZrO_2. The use of nanocrystalline raw materials resulted in a relatively low (1000 °C) calcination temperature and, consequently, in very fine (particle size 100–200 nm) and weakly agglomerated powders. Solid-state preparation using nanocrystalline raw materials is therefore a promising alternative to chemical routes for the preparation of fine powders suitable for the fabrication of dense submicron ceramics.

The calcined powders were densified by means of spark plasma sintering. Nearly fully dense ceramics with grains size < 300 nm can be obtained after 1–5 min sintering at 1600 °C. For pure $BaZrO_3$, good densification (96%) is already obtained at 1500 °C. These results represent a significant improvement in comparison to conventional sintering and previous results reported in the literature. The sintering temperature required to obtain nearly full densification can be lowered by 100–200 °C with a grain growth factor ≤2. Once again it is demonstrated that SPS is a unique opportunity to obtain densification with limited grain growth.

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