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Journal of the European Ceramic Society 24 (2004) 2241–2246

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Synthesis and sintering of chemically derived BaO–ZrO_2 solid solutions

Stefano Maschio[a,*], Alessandro Bachiorrini[a], Elio Lucchini[b], Sergio Brückner[a]

[a]*Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, Via Cotonificio 108-33100, Udine, Italy*
[b]*Dipartimento di Ingegneria dei Materiali e Chimica Applicata, Università di Trieste, via A. Valerio 2, 34127 Trieste, Italy*

Received 18 January 2003; received in revised form 10 June 2003; accepted 6 July 2003

Abstract

Several zirconia–baria solid solutions were obtained by sintering powders produced by coprecipitation from solutions of zirconyl chloride hydrate and barium nitrate. The fired materials had monoclinic, cubic or tetragonal structure depending of composition which ranged from 4 to 16 mol% BaO. The pure cubic phase could be retained at room temperature for compositions from 10 to 12 whereas materials containing 16 mol% BaO were tetragonal; for lower baria content a mixture of monoclinic and cubic phase was detected. The double phased materials can be fully transformed into the monoclinic form by grinding while for pure cubic or tetragonal samples the transformation is not full. Samples fired at 1450 °C had coarse microstructures and the grains dimension is of several microns just after 1 h of sintering, but materials containing 10, 12 and 16 mol% BaO remain cubic or tetragonal, their transformability being the same as that of materials sintered at lower temperature. The grains growth kinetic during the sintering process is similar to that of the $BaZrO_3$, and the resulting microstructures showed coarser grains than those observed in sintered tetragonal zirconia materials stabilized with other oxides. The crystal structures of cubic or tetragonal BaO stabilized zirconias seem to be isostructural to $BaZrO_3$ as they have similar cell parameters.

Keywords: Alkaline earth oxides; BaO–ZrO_2; Powders solid state reaction; Sintering; X-ray methods; ZrO_2

1. Introduction

Zirconia (ZrO_2) exhibits phase transformation as follows:

$$\text{Monoclinic} \leftarrow 1170^\circ \rightarrow \text{tetragonal} \leftarrow 2370^\circ \rightarrow \text{cubic} \leftarrow 2760 \rightarrow \text{melt}$$

The monoclinic to tetragonal phase transformation is likely martensitic in nature. This transformation has generated great interest among scientists and technologists because it contributes to the toughening of ceramics.

Many oxides can be added to pure zirconia to improve the mechanical properties of partially stabilized zirconia (PSZ) materials though transformation toughening.[1,2] This is achieved by retaining the tetragonal structure of zirconia at room temperature so that the transformation from the tetragonal to the monoclinic phase may occur under an applied stress field rather than spontaneously on cooling after sintering. Yttrium oxide has been perhaps the most studied stabilizing additive[3–5] together with cerium oxide,[6,7] calcium oxide,[8] magnesium oxide[9] although oxides of other elements have been used too.

The system zirconia–baria has not been yet deeply studied and only a limited number of papers can be found in literature which deal with its phase diagram in the zirconia-rich region.[10–12] Moreover studies of this binary system refer to equilibrium conditions so that the presence of metastable structures at room temperature is not discussed. In our opinion further investigation on the zirconia–baria system is therefore required.

According to literature data[13] the ionic radius of barium (1.34 Å) is almost twice that of zirconium (0.79 Å). Ionic radii of other elements used as stabilizing oxides such as Y^{+3} (0.893 Å), Ce^{+4} (0.92 Å), Mg^{+2} (0.66 Å) and Ca^{+2} (0.99 Å)[13] are closer to that of zirconium than

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* Corresponding author.
E-mail addresses: stef.maschio@dstc.uniud.it (S. Maschio), bachiorrini@dstc.uniud.it (A. Bachiorrini), lucchini@univ.trieste.it (E. Lucchini), bruckner@dstc.uniud.it (S. Brückner).

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doi:10.1016/S0955-2219(03)00642-3

that of barium. In all of those binary solid solutions the tetragonal phase can be retained in metastable or stable form at room temperature as a function of composition. The same phenomena are not observed upon baria addition.[10–12] On the other hand, if an eventual metastable phase can be retained at room temperature, it should be influenced by an element having such a large ionic radius and an extremely deformed structure should take place giving rise to a possible autocatalytic effect during transfomation.[14,15]

Several methods are presently available in literature that deal with the production of most PSZ powders having particles of nanometer dimension[16,17] and consequently sintered materials can be fired to selected grain sizes just optimizing the sintering cycle. Coprecipitation is, among the numerous methods of preparation of powders, simple and enable the preparation of large amounts of powders having high purity and nanometer particles dimensions.

We have studied the zirconia–baria binary system, in the zirconia-rich region, starting from the composition with 4 mol% BaO content up to 16 mol% BaO. Zirconia–baria materials were obtained by sintering, at various temperatures for different times, nanometer-sized powders initially produced by coprecipitation from solutions of zirconyl chloride hydrate and barium nitrate. Sintered samples were characterized by measuring their density, crystallographic constants and grain size distributions.

2. Experimental

Preparation of 4, 6, 8, 10, 12, and 16 mol% ZrO_2/BaO powders was achieved by coprecipitation followed by calcination. Mixtures of $ZrOCl_2 \cdot 8H_2O$ (99.0% Aldrich Chem.) and $Ba(NO_3)_2$ (99% Aldrich Chem.) were dissolved into aqueous 0.5 mol solution. The solutions were poured while stirring into concentrated ammonia (28 wt.%) at room temperature. The product was washed with deionized water and with acetone–toluene–acetone. The powders were then heated at 80 °C in an oven and sieved through a 63-μm sieve. Such products were attrition milled for 1 h in a plastic container with zirconia/yttria (3 mol%) spheres at 300 cycle/min using isopropanol as dispersing medium and then calcined.

Simultaneous thermal analysis (STA) diagrams were obtained on a Netzsch STA equipement at a heating rate of 10 °C/min up to a temperature of 1250 °C. According to such results, coprecipitated, milled and dried powders were fired at 700 °C for 2 h. After calcination, all the powders were again attrition milled for 6 h using the same milling parameters reported above. Attrition milling causes wear of the milling balls which determines contamination of zirconia/baria powders by yttria. In order to minimize the contamination 30 g of powders were processed each time and consequently the released amount of yttria was calculated below 1 mol%; this value can be considered neglible since the starting zirconia precursor have a similar purity. After this second milling, powders were again dried and sieved as already done after coprecipitation.

Powders were uniaxially pressed at 30 MPa to form cylindric specimens (8 Φ mm×25), which were then cold isostatically pressed at 200 MPa. Sintering was done in air at 1250, 1350 or 1450 °C for 1, 2 or 4 h. The density of the green samples as well as that of the sintered bodies was evaluated by the ratio between weight and volume which was determined by a geometrical method.

X-ray diffraction data were recorded on an XRG 300 INEL powder diffractometer equipped with CPS 120 detector. Monochromatic Co$K\alpha_1$ was obtained by setting 35 kV and 20 mA as operating conditions. Calibration of the 2θ scale, based on a diffractogram from an Al_2O_3 (corundum) sample, was carried out with the aid of a software package (PULWIN) written by one of the authors of the present note,[18] the same software allowed for refinement of peaks positions, for peak indexing and for the refinement of the cell parameters as well as of a zero-shift on the 2θ scale. The monoclinic intensity fractions both on powders and on sintered specimens were accessed by X-ray intensity measurements following the same procedure described by Garvie and Nicholson for the determination of the tetragonal/monoclinic fraction in zirconia containing materials.[19] In our investigations the same procedure was used also in samples containing cubic and monoclinic stuctures. After the sintering, the resulting microstructures were examined with the SEM.

3. Results

STA analysis of the powders containing different amounts of baria did not show any appreciable dependence on composition. The STA patterns were characterized by an endothermic peak at 195 °C and two exothermic at 390 and 570 °C, respectively; the endothermic peak is due to water evaporation and decomposition of hydroxil compounds, whereas exothermic occurred at alcohol combustion and powders crystallization respectively. The weight loss ceased at 640 °C for all preparations. On the basis of such results powders were calcined at 700 °C for 2 h as reported in the Section 2.

After the thermal treatment at 700 °C, all powders showed the presence of two phases: one was identified as monoclinic, the other being probably cubic. Diffraction patterns of the powders showed rather broad peaks: in particular peaks 002 and 200, which can be used to identify the tetragonal structure, were not resolved and only one broad peak was detectable at the required 2θ angle. For these reasons we cannot assert the presence of a cubic or tetragonal phase in calcined powders. This will be clarified later on. Attrition milling partly transformed this second phase into a monoclinic one. Fig. 1 shows the monoclinic fraction (%) as a function of composition of powders calcined for 2 h at 700 °C and after attrition milling for 6 h. Both series of powders show that the amount of monoclinic phase decreases as the quantity of BaO increases, deviations from the linear trend may be not significant since they can be the result of the procedure followed. Nevertheless, it emerges quite clearly that the monoclinic fraction is sensibly lower before attrition milling than after, and this is true for all compositions. The cubic (or tetragonal) phase is clearly metastable.

The relative density of the green samples, reported in Table 1, ranges from 53 to 60%. Spreading of data, as a function of the composition, may be due to density measurements adopted (geometrical) as well as the calculation of the density theoretical values which is not particularly accurate for powders having low cristallinity.

The sintering of the green samples at the different temperature for different times did not led to fully dense materials and the density of fired samples ranged from 70 to 85% of the theoretical value.

After firing at 1250 °C for 1 h, samples containing 4, 6, and 8 mol% BaO had mainly (>50%) monoclinic phase whereas in those containing 10, 12 and 16 mol% BaO such phase was detected in a very low percentage (<5). Longer soaking time at that temperature did not change the crystal structure. The relative density of specimens, at all compositions, did not change with the sintering soaking time and remained very low (<75% T. D.). Sintering at 1350 °C 1 h or for longer times did not produce any significant enhancement of the relative density, nor a reduction of the monoclinic phase at all compositions.

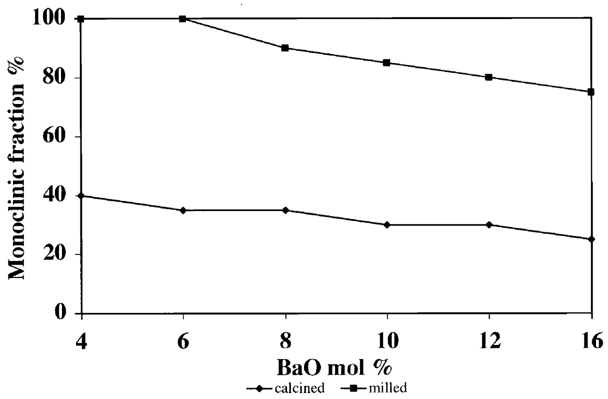

Fig. 1. Monoclinic fraction of powders as a function of composition after calcination for 2 h at 700 °C and then after attrition milling.

Table 1
Relative density of the green samples isostatically pressed at 200 MPa

BaO mol%	4	6	8	10	12	16
Rel. Dens. (%)	56	53	58	55	60	58

Sintering at 1450 °C for 1, 2 and 4 h led to specimens having relative density higher than those fired at lower temperatures at any soaking time, but low in absolute values: data were around 85% T. D. The monoclinic phase completely disappeared, after any thermal treatment, in samples containing 10, 12, and 16 mol% BaO and such samples appear as fully monophasic materials. On the other hand, materials containing 4, 6 and 8 mol% BaO showed the presence of two phases at all soaking times.

Sintering soaking time appears not to play a significant role on crystal structure since this remained practically unchanged relative to those fired 1 h for all the tested temperatures and at any composition. At the same time, also sintering temperature seems to be little influent on crystal structure and samples fired at 1250 °C are similar as those fired at higher temperatures.

Samples fired 2 h at 1450 °C were analysed by recording their powder diffraction data. Peaks for each sample were precisely located through a peak-fitting routine.[18] Subsequently a peak indexing routine was run that is substantially derived from TREOR99;[20] and finally cell parameters were refined with the aid of a least-squares minimization routine that allows for the refinement of a zero-correction on the 2θ scale.

In Table 2 we report the refined cell parameters for the three samples containing 10, 12 and 16 mol% BaO together with the cell volumes. An overall volume increase is observed at increasing contents of BaO. Materials containing 16 mol% BaO has a tetragonal cell, at variance with those containing 10 and 12 mol% BaO, which are cubic. The presence of a tetragonal geometry in the sample having 16 mol% BaO cell is detectable through the splitting of a number of peaks into couples of highly overlapped but clearly distinguishable peaks.

In Fig. 2 we report the powder profile of the sample containing 12 mol% BaO, and in Fig. 3 we report, in greater detail, two examples of how peaks change with BaO content.

Table 3 reports the phases detected at the different temperature of the materials produced in the present research.

Table 2
Refined cell parameters for the three samples analysed

BaO mol%	Phase	*a*-axis (Å)	*c*-axis (Å)	Volume (Å^3)
10	Cubic	4.193(1)	–	73.72
12	Cubic	4.200(1)	–	74.08
16	Tetragonal	4.197(3) a = b	4.217(3)	74.28

One surface of the samples fired 2 h at 1450 °C was ground with a coarse emery paper, whereupon the monoclinic fraction was determined by X-ray diffraction and data are reported in Fig. 4. It is possible to see that samples containing 4, 6, and 8 mol% BaO completely transform into monoclinic, while those having 10, 12 and 16 mol%, only partly transform. it is also important to observe that there are not differences, after the grinding, between sample containing 12 and 16 mol% BaO, being the first cubic and the second tetragonal. In this binary system, the transformation is quasi quantitative in all the samples and just a very limited amount of the starting metastable phase is present after surface grinding. A similar transformation ratio was observed in samples fired at lower temperatures and at different times. It is also of great interest to note that fully cubic materials transform as the tetragonal do. This fact is, of course, unespected, since cubic stabilized zirconias are not known as metastable materials and transformation should not occur.

Fig. 5a and b show the microstructures of samples containing 16 mol% BaO fired 1 and 4 h at 1450 °C. Grains are coarse and exceed 5 μm in both cases. It can also be observed that grains slowly grow with the sintering time, but change their morphology since, after 1 h, their shape is more regular than after 4 h. A similar

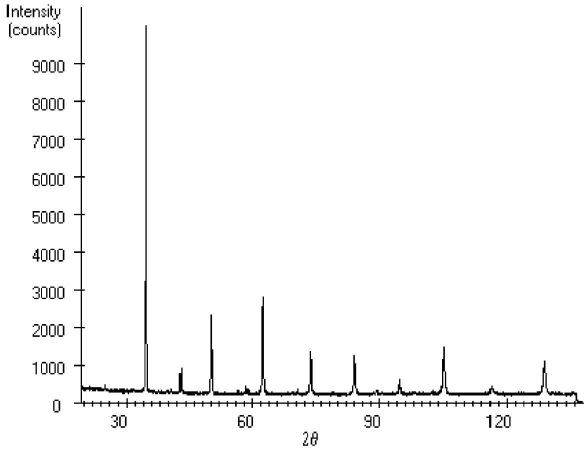

Fig. 2. The powder diffraction pattern obtained from the sample with 12 mol% BaO after sintering for 2 h at 1450 °C.

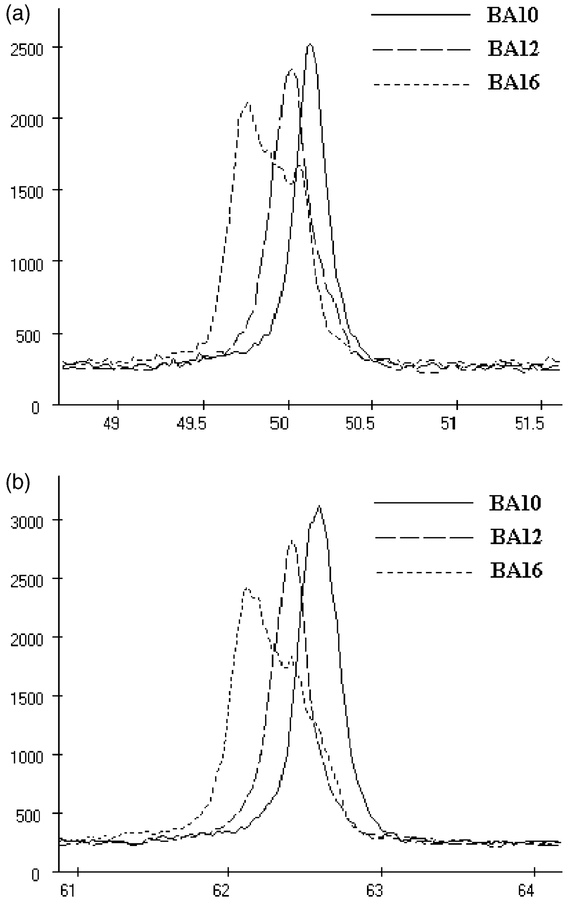

Fig. 3. Two details of the powder diffraction patterns showing the peak splitting occurring in the sample containing 16 mol% BaO sample after sintering for 2 h at 1450 °C. (a) the 200 region; (b) the 211 region.

Table 3
Crystal phases detected in the "as sintered" materials as function of composition and sintering temperature

BaO mol%	1250 °C	1350 °C	1450 °C
4	m + c	m + c	m + c
6	m + c	m + c	m + c
8	m + c	m + c	m + c
10	c + m(*)	c + m(*)	C
12	c + m(*)	c + m(*)	C
16	t + m(*)	t + m(*)	T

m = monoclinic, c = cubic, t = tetragonal. (*) monoclinic phase fraction below 5 vol%.

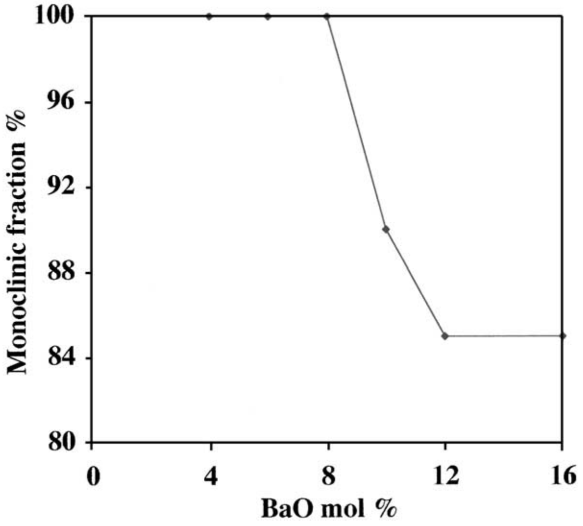

Fig. 4. Monoclinic fraction on ground surface as function of composition for samples sintered 2 h at 1450 °C.

behaviour was observed in the samples containing 10 and 12 mol% BaO.

Grains dimension is more similar to that of $BaZrO_3$ materials[21,22] than to other metastable tetragonal zirconias where they remain below such size when similar sintering conditions are followed. Furthermore the crystal structures of BaO stabilized zirconias seem to be isostructural to $BaZrO_3$ as they have similar cell parameters. For sake of clarity it is possible to compare data reported in Table 2 with Refs. 23 and 24 We cannot exclude, however, that a volume heterogeneity of a sample takes place and a superficial enriched by barium layer which is close on structure to $BaZrO_3$ is formed.

Assuming the structure of $BaZrO_3$ as a model for our materials, we can estimate the theoretical densities of samples containing 10, 12 and 16 mol% BaO; they are respectively 5.70, 5.70 and 5.74 g/cm^3.

If we consider that coarse microstructures and crystal structures are similar to those of $BaZrO_3$ we might hypothesize that BaO stabilized zirconias can be obtained by a first reaction of BaO with ZrO_2 to form $BaZrO_3$ and only in a second time a precipitation of metastable zirconia grains from the supersaturated solution. Unfortunately this hypothesis is not supported by STA measurements performed on sintered sample since no reaction were detected up to the temperature of 1250 °C.

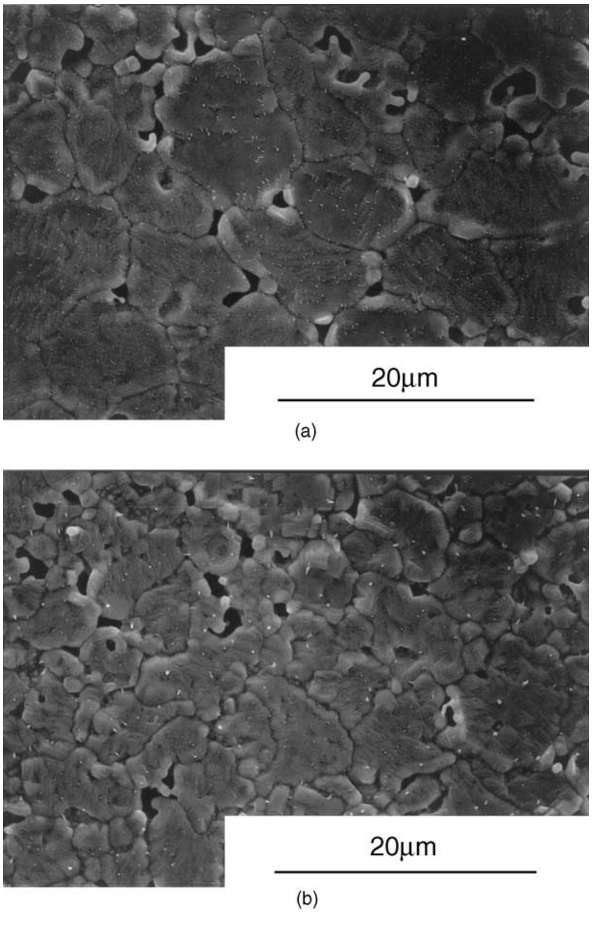

Fig. 5. SEM micrographs of samples containing 16 mol% BaO sintered 1 h (a) and 4 h (b) at 1450 °C.

4. Conclusions

Nanometer-sized powders produced by coprecipitation, calcination and attrition milling can form cubic or tetragonal solid solution in the zirconia–baria system at low baria contents. The pressed powders do not lead to high density samples after sintering and grains size of sintered samples are surprisingly coarse. The crystal structure of fired specimens is function of composition and pure monophasic samples can be obtained only for composition ranging from 10 to 16 mol% BaO, for lower baria content the monoclinic phase has also been detected. The cubic or tetragonal phases can be transformed into monoclinic by grinding the samples surface by emery paper revealing that cubic and tetragonal structures are present as metastable forms. This fact has been widely documented in several zirconia tetragonal materials, but represents an important results in the case of a cubic form.

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