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Synthesis of bulk tetragonal zirconia without stabilizer: The role of precursor nanopowders

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Abstract

The densification of undoped zirconia nanopowder was performed using the High-Pressure Field Assisted Sintering technique, with the aim of preparing bulk size-stabilized tetragonal zirconia. The role played by the structural and microstructural properties of the starting powders on the characteristics of the sintered materials was investigated by exploring several different synthetic routes. Nanopowders prepared by solvothermal methods were proven to give the most satisfactory results thanks to their microstructure, particularly characterized by uniform spherical microaggregates. Using solvothermally synthesized powder as a starting material, nearly fully dense (97% relative density) samples of undoped size-stabilized tetragonal zirconia were obtained with a sintering cycle of 5 min under a uniaxial pressure of 700 MPa, at sintering temperatures as low as 900 °C.
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1. Introduction

The stabilization of high temperature zirconia polymorphs has been investigated for decades, as they play a crucial role in several relevant technological applications in fields as different as combustion technology, energy conversion, thermal protection and structural materials. Traditionally the tetragonal and cubic polymorphs are stabilized at room temperature through the addition of a proper amount of aliovalent cations, following an approach introduced by Nernst over a century ago.[1] The physical properties of these chemically stabilized zirconias have been investigated thoroughly, considering all possible involved parameters. Recently, however, it has been demonstrated that the stabilization of high temperature polymorphs of zirconia can be achieved also without the addition of a chemical stabilizer, but simply reducing the grain size of the material into the nano range [Ref. 2 and references therein]. This so-called *size-induced stabilization* has been shown to occur when the particle size is reduced below a critical value. Although the exact nature of the stabilizing mechanism is still debated, it is now generally recognized that the size-induced stabilized tetragonal zirconia is thermodynamically more stable than the monoclinic form at room temperature, as long as grain growth is prevented.[3,4] Several different explanations have been presented in order to justify this stability inversion. The difference in surface free energy between the polymorphs, predicting an increase in stability of the tetragonal phase as grain size is reduced, has received great attention.[2] However, the influence of other factors, such as the presence of anionic impurities, lattice strain, structural similarities between the precursor materials and tetragonal zirconia, the influence of lattice defects and/or water vapor[3] have likewise been considered and debated as well.

Due to the extremely small grain size required for the stabilization of the tetragonal polymorph, the preparation of this material in bulk form and with high relative densities has proven particularly challenging. Sintering and densification of refractory materials are, in fact, usually associated with a significant increase in grain size. For this reason the literature pertaining to the size stabilization of zirconia refers only to materials in form of powders[2] and thin films,[5] whereas the bulk properties of this material are still virtually unknown. Recently, however, we have presented a possible route for the synthesis of undoped

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tetragonal zirconia in bulk form, based on the use of the High-Pressure Field Assisted Sintering (HP-FARS).[6] This technique has achieved good levels of densification whilst keeping the grain size small enough to preserve the size stabilization effect in the sintered material. In our previous report[7] we used zirconia nanometric powders obtained by the Pechini method[8] as a starting material. We thereby achieved relative densities of ~95% using sintering cycles of only 5 min at the remarkably low temperatures of 850–900 °C, with pressure of ~800 MPa. The final product, however, presented a quite significant amount of the monoclinic phase, up to 27%, due in part to the presence of a relevant amount of monoclinic zirconia in the starting powder. In order to improve the quality of the final sintered samples, in particular for what concerns phase purity, we explored several different synthetic methods for the preparation of zirconia nanopowder. In the present work we discuss the results obtained employing several different synthetic routes having thereby a double aim: obtaining a final product with higher phase purity and investigating the role that the characteristics of the starting powders play in stabilizing the tetragonal phase in the bulk material.

2. Materials and methods

All the reagents and solvents were purchased from Sigma–Aldrich and used as received. The solvothermal treatments were conducted in a 125 ml Parr reactor (model 4748, Parr Instruments, Molin, IL, USA).

2.1. Synthesis of zirconia nanopowders: state of the art

The best approaches towards the solution synthesis of zirconia nanopowders have been demonstrated recently based on the hydrolysis of alkoxides or on several solvothermal syntheses. These two methodologies have been reported as particularly promising in terms of grain size, degree of agglomeration and amount of organic residuals.[9–11] Whilst the synthesis of ceramic oxide particles from alkoxidic precursors has been studied extensively respective titania,[12–14] some investigations are available also in the case of zirconia [Ref. 15 and references therein]. In such a synthesis the formation of a stable colloid plays a crucial role in avoiding the coarsening of the particles during the synthesis.[13,16] The morphology of the products formed by hydrolytic condensation of alkoxides can be modified whilst taking into account several reaction parameters, such as nature of alkyl group in the alkoxide, water/alkoxide ratio, molecular separation of species, and reaction temperature.[17] The order of addition (metal to acid or acid to metal) could also play an important role for mass effects and reactive environment.[13,14] Moreover, peptization in acidic environment, conducted at elevated temperature, can be used to break up the agglomerates into very small aggregates (<20 nm) and primary particles.[18]

Solvothermal treatment of amorphous gels prepared starting from zirconyl nitrate or chloride represents one of the most popular routes for the synthesis of nanometric zirconia.[19–21] In this method the solvent plays a crucial role for what concerns both phase composition and morphology. In general, alcohols, like MeOH (methanol) and *i*-PrOH (isopropanol), possess a weaker ability to dissolve the ZrO_2 precipitates, preventing the occurrence of the dissolution-precipitation process, during the solvothermal treatment, which is responsible for the transition towards the monoclinic phase. As an example, Li et al.[22] prepared 100% tetragonal zirconia by solvothermal processing of a solution of zirconyl precursor and urea in MeOH. The same reaction, conducted in water solvent, leads to a 100% monoclinic phase. If water is present at trace levels, some traces of the monoclinic phase result in the product. Urea plays an important role in removing water by hydrolysis and its conversion to ammonia: when urea is not present in a sufficient amount (usually urea to Zr molar ratio greater than 2), the residual water promotes the transition to the monoclinic phase.[22] The solvent has also a strong effect on the product morphology as shown by Hua et al.[23], who prepared tetragonal zirconia by forced hydrolysis of zirconyl salts under solvothermal conditions varying the solvent medium from water, to MeOH, to various *i*-PrOH/MeOH ratios. Concerning the properties of the solvent, dielectric constant and steric hindrance of organic groups most influence the shape and the hardness of the agglomerates. Thus, when MeOH is used as the reaction media, the product particles are uniform spherical hard agglomerates of around 1 μm, in contrast with the irregular large shaped aggregates formed in a water environment. Moreover, a MeOH medium produces hard aggregates, whilst *i*-PrOH/MeOH mixtures produce soft agglomerates.[23]

2.2. Synthesis via hydrolysis of alkoxides

As general guideline, it should be pointed out that we followed the procedure described by Scolan and Sanchez[24] for the synthesis of titania from Ti-isopropoxide. Zr-isopropoxide isopropanol complex is dissolved at reflux in *i*-PrOH (0.125 M). Under vigorous stirring an aqueous diluted solution of nitric acid is added dropwise, causing quantitative precipitation of a fluffy white solid. (The molar ratio between water, Zr and H^+ is $H_2O{:}Zr{:}H^+ = 10{:}1{:}0.2$.) After holding the suspension under reflux and stirring for 12 h, the white solid is finally collected by centrifugation. In addition to the original procedure, some modifications were also tested, including: the use of a different organic alkoxide with different steric organic precursor (Zr-propoxide), freeze-drying and peptization of the final product, and inverted order of addition (metal to acid or acid to metal).

2.3. Synthesis via solvothermal methods

In this case we adopted the general method described in Ref. 22, using MeOH or a mixture of *i*-PrOH/MeOH 90/10 as solvent. Proper amounts of $ZrO(NO_3)_2{\cdot}6H_2O$ and urea are dissolved in 40 mL of solvent to give solutions of various concentrations between 0.4 and 0.04 M. Urea is added with a molar ratio to Zr of 10. The solution is poured into the Teflon vessel of the hydrothermal reactor, sealed and heated at 160 °C for 20 h. The obtained suspension is filtered, washed with 2 × 20 mL of MeOH (or *i*-PrOH/MeOH 90/10 mixture, accordingly to the selected reaction media), 2 × 40 mL of deionized water to neutrality and dried in an oven at 110 °C for 4 h.

Table 1
Main synthetic routes explored: annealing temperature and characteristics of the obtained powder in terms of phase composition and grain size.

Synthetic route	Powder annealing temperature (°C)	Tetragonal phase (%)	Grain size tetragonal phase (nm)
Pechini	625	83	14.8
Alkoxide			
A – isopropoxide	600	90	22
B – propoxide	600	92	20
C – propoxide invert. addit.	600	89	23
Solvothermal			
D – MeOH 0.4 M	600	96	10
D – MeOH 0.2 M	600	97	8
D – MeOH 0.04 M	600	97	9
E – *i*-PrOH/MeOH (90/10) 0.2 M	600	94	15
E – *i*-PrOH/MeOH (90/10) 0.04 M	600	75	16

2.4. Densification of the nanopowders

The powders exhibiting most interesting characteristics were sintered in a home-made HP-FARS apparatus. In each experiment 0.15 g of powders were loaded in a double stage die. The low pressure section of the die was made out of high density graphite, whilst the high pressure section was made out of silicon carbide.[25] The die was loaded in the HP-FARS apparatus, which was evacuated to a pressure of 10 Pa. A moderate initial uniaxial pressure (150 MPa) was applied. The temperature was then increased with a heating rate of 200 °C min^{-1}. Once the sample reached the designated temperature, the pressure was rapidly increased to the final value (700 MPa). The sample (5 mm in diameter, ~1 mm thick) was held under these conditions for 5 min and then the pressure was quickly released and the power turned off. Temperatures were measured using a shielded K-type thermocouple inserted in the lateral wall of the die. Further details concerning the HP-FARS procedure can be found in Refs. 6,25.

2.5. Sample characterization

Microstructural characterization of the samples was made using a high-resolution scanning electron microscope (SEM, TESCAN Mira 3) operated at 25 kV. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images were acquired on a FEI Tecnai G2 F20, operated at 200 kV. X-ray diffraction data were acquired on a Bruker D8 Advance, with a step of 0.02° (2θ) and an acquisition time of 5 s per step.

The relative density (r.d.) of the sintered samples was measured using the Archimedes method and from geometric and gravimetric measurements. The powders resulting amorphous or characterized by the presence of organic residuals underwent a subsequent crystallization or calcination at the proper temperature. Thermal stability in terms of percentage of tetragonal phase and grain size was also evaluated. The molar fraction of the monoclinic and tetragonal phases, reported as percentage of tetragonal phase in the following, was evaluated from the peak areas of the most intense signals of tetragonal (1 0 1) and monoclinic (−1 1 1, 1 1 1) phases, at 30.2°, 28.2° and 31.5°, respectively, from Eq. (1) [26]:

$$\frac{M_m}{M_t} = 0.82 \times \frac{I_m(-1\ 1\ 1) + I_m(1\ 1\ 1)}{I_t(1\ 0\ 1)} \tag{1}$$

where M_m and M_t are the mol of monoclinic and tetragonal phases, I_m and I_t are the intensities (as areas) of the peaks of the monoclinic and tetragonal phases. The factor 0.82 is a correction that takes into account the different structure factors of the two phases. Grain size was calculated from peak broadening using the Scherrer equation.

3. Results

3.1. Precursor nanopowder

Table 1 summarizes the characteristics of all the precursor nanopowders obtained from the syntheses approaches we investigated, whilst Figs. 1–3 present their morphologies (left sides), together with those of the corresponding sintered samples (right sides).

In our previous work[7] we synthesized dense nanometric zirconia from nanopowders obtained by the Pechini method.[8] This method, however, presents two well known limitations: (i) the products are affected by severe agglomeration, presenting hard agglomerates often in the range of tenths or hundreds of micrometers (Fig. 1a), and (ii), the produced materials require annealing at high temperatures for long times in order to remove any organic residue. Since the final grain size and the amount of monoclinic polymorph increase with the calcinations temperature and time, we have been able to obtain carbon free powders in our previous work, but only in association with a grain size of 14.8 nm and a rather high amount of monoclinic phase (~17 wt.%).[7]

The products obtained in this work from both the alkoxide hydrolysis and the solvothermal methods are characterized by a much more limited amount of organic residuals. In both cases they are represented by the alkoxidic groups bounded to the particles surface,[27] that can be completely removed with a short calcination at 600 °C, as confirmed by preliminary thermogravimetric measurements (not shown).

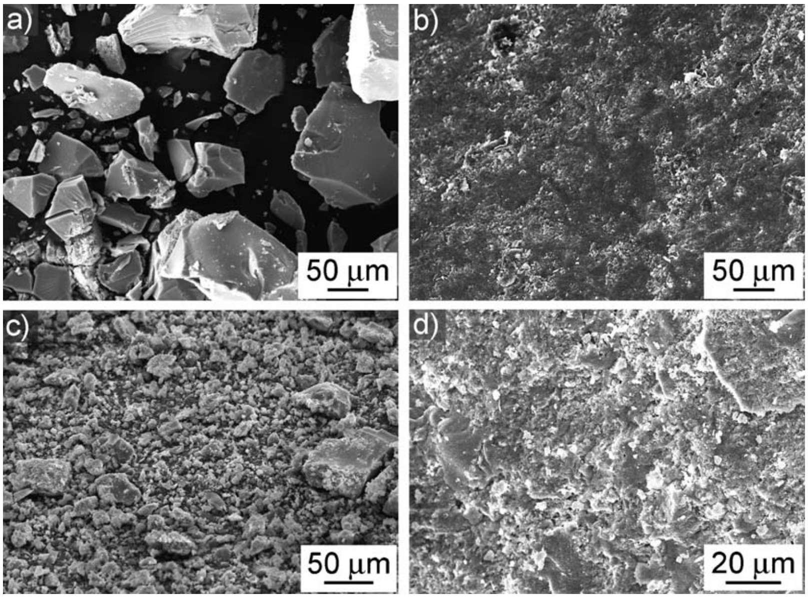

Fig. 1. SEM micrographs of (a) powder obtained from the Pechini route; (b) sintered sample from the Pechini route powder; (c) powder obtained from the alkoxide route (A – isopropoxide); (d) sintered sample from the alkoxide route powder (A – isopropoxide).

The results summarized in Table 1 show that the powders produced by the alkoxide hydrolysis (routes A–C) showed only marginal improvements over the Pechini method. If, on the one hand, the amount of monoclinic phase is reduced to around 10 wt.%, the grain size increases (∼20 nm). Only minimal effects, if any (Table 1) were produced even after all the modifications of this approach,[24] based on the use of different alkoxides and/or on variation in the order of addition of the reactants were taken into account. The microstructure is still characterized by the presence of large agglomerates with dimensions ranging between few microns and the tens of microns (Fig. 1c), although in all the microstructures appear to be much softer than those produced by the Pechini method. Limited improvements in the product morphology were obtained through peptization of the products. Freeze-drying was much more effective in terms of de-agglomeration of the powders, however the use of both methods was not considered any further, since they produced a considerable transition towards the monoclinic phase, with a 30% content of this phase for the peptized product and 60% for the freeze-dried, after heat-treatment at 600 °C.

The results obtained using the solvothermal method resulted to be considerably more satisfactory (Table 1, routes D and E). In this approach, however, both structural and microstructural properties of the nanopowder were strongly affected by the

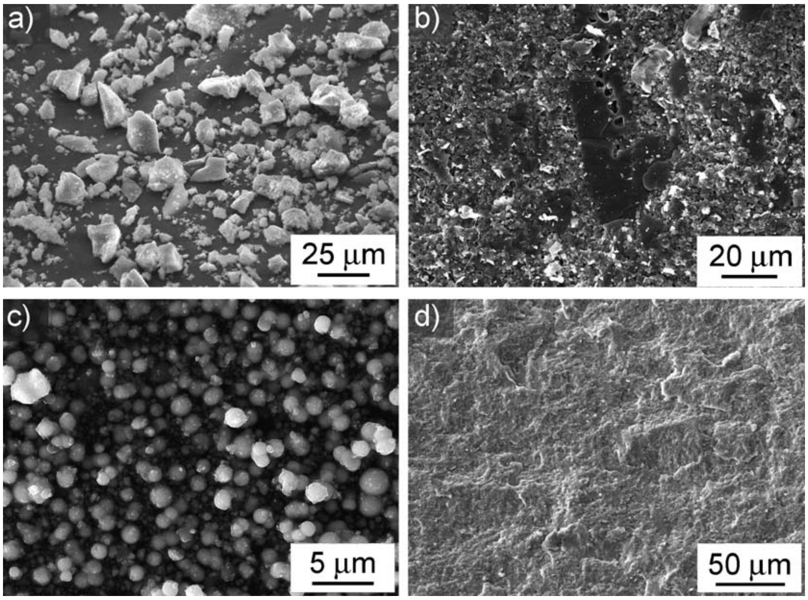

Fig. 2. SEM micrographs of the powders and sintered samples obtained from the MeOH route D: effect of concentration on the agglomeration. (a) Powder obtained from the 0.4 M solution and (b) sintered sample; (c) powder obtained from the 0.2 M solution and (d) sintered sample.

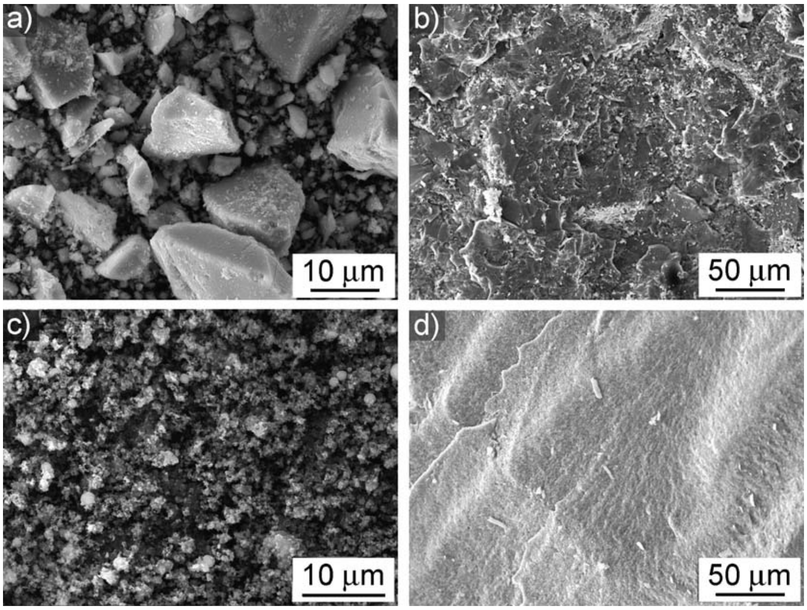

Fig. 3. SEM micrographs of the powders and sintered samples obtained from the *i*-PrOH/MeOH route E: effect of concentration on agglomeration. (a) Powder obtained from the 0.2 M solution and (b) sintered sample; (c) powder obtained from the 0.04 M solution and (d) sintered sample.

solvent. The use of MeOH produced undoped zirconia nanopowders characterized by a negligible amount of monoclinic phase and with grain size below 10 nm. This result was only marginally affected by any variations in the concentration of the Zr precursor (Table 1, route D) which, on the contrary, showed a dramatic effect on the powder morphology. At high concentrations (0.4 M), in fact, the product was affected by serious agglomeration, showing a morphology not dissimilar to that obtained by the Pechini method (Fig. 2a). Reducing the concentration by a factor of two (0.2 M) produced a considerable improvement in the product morphology (Fig. 2c), thereby showing in this case uniform spherical transparent aggregates, with a diameter ≤1 μm. The internal microstructure of these aggregates can be observed in Fig. 4, which reports the TEM micrographs of the powder annealed at 400 °C (a) and 600 °C (b), together with the relative SAED patterns. The TEM images clearly show the presence of uniformly sized crystalline domains, with a diameter of approx. 4 nm and 8–10 nm, respectively. Further reduction in the initial concentration (0.04 M) did not produce any significant change in the morphology.

In the attempt to further improve the powder characteristics we tried to obtain soft agglomerates by attaching larger alkoxidic groups to the powder surface.[23] *i*-PrOH/MeOH 90/10 solvent mixture was also employed (route E). Due to the lower solubility of $ZrO(NO_3)_2$ in *i*-PrOH, the maximum concentration considered was in this case equal to 0.2 M. At this concentration the product morphology was characterized by large irregular agglomerates (Fig. 3a). Lowering the concentration to 0.04 M resulted in a highly disagglomerated fluffy material (Fig. 3c). The use of *i*-PrOH/MeOH 90/10 as a solvent caused also an increase in the mean grains size (∼15 nm). In all cases, however, the formation of disagglomerated powder was accompanied by a relevant increase in the amount of the monoclinic phase (Table 1).

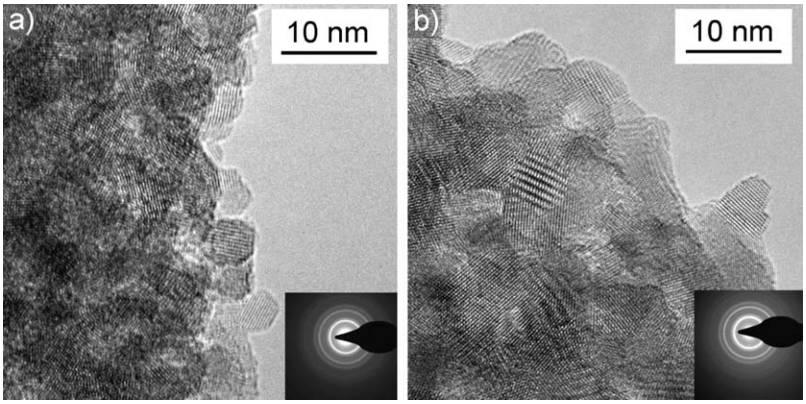

Fig. 4. TEM micrographs and SAED patterns (insets) of the powders obtained from the MeOH route (D – 0.2 M): (a) annealed at 400 °C and (b) annealed at 600 °C.

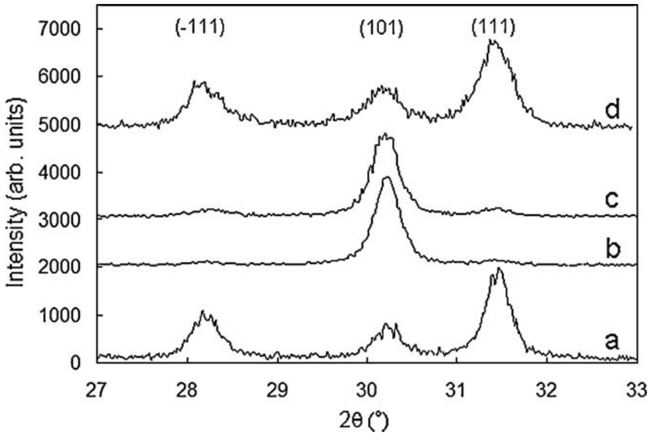

Fig. 5. XRD patterns of the most representative sintered samples, showing the 2θ range with the most intense signals of tetragonal (30.2°) and monoclinic (28.2°, 31.5°) phases. From bottom: (a) alkoxide (B – propoxide), (b) MeOH (D – 0.2 M), (c) *i*-PrOH (E – 0.2 M), (d) *i*-PrOH (E – 0.04 M).

3.2. Densified samples

All the densification experiments have been performed under a uniaxial pressure of 700 MPa in order to achieve the densification at the lowest possible temperatures.[6] On the basis of preliminary tests, we reached the conclusion that the sintering temperature should not exceed 900 °C, otherwise a rapid transition to a monoclinic phase occurs. On the other hand, the use of temperatures below 900 °C produced low levels of densification. Although small differences exist between the various powders, we decided to sinter all the samples at 900 °C, facilitating in this way an even more direct comparison between samples obtained by different nanopowders.

The densified samples resulted to be white coloured and their main characteristics are summarized in Table 2. The grain size of the tetragonal phase is very similar in almost all cases, despite the marked differences in the grain size of the starting powders. With the sole exception of the sample prepared using diluted (0.04 M) *i*-PrOH/MeOH 90/10 all the sintered materials have a grain size falling in a narrow range, between 25 and 31 nm. Despite the similarity in the grain size, large differences were found in sample relative densities and in the amount of monoclinic phase. The phase purity seems to be dramatically dependent on the route followed for the synthesis of the precursor powder. Nanopowder prepared by solvothermal method in MeOH (route D) almost completely retains the tetragonal structure. The use of *i*-PrOH/MeOH 90/10 as a solvent (route E), on the other hand, promotes the transition to the monoclinic phase, in particular when low concentrations are used. Finally the use of precursor powder prepared by the hydrolysis of an alkoxide (routes A–C) seems to be totally inadequate, since the corresponding sintered samples retain a weight percentage of tetragonal phase of approx. 30% (Table 2). Fig. 5 summarizes the XRD results for the most interesting sintered samples and provides evidence that our best products have been obtained using MeOH (b) and *i*-PrOH (0.2 M, c). It is evident from these results that no simple relationship between grain size and stabilization effect exists in the sintered undoped zirconias.

Furthermore, the microstructure of these samples appears also to be largely controlled by the characteristics of the starting powders. The images on the right side of Figs. 1–3 show a comparison between the fracture surfaces of sintered samples prepared using different precursor powders. The detrimental effect played by the irregular agglomeration of the powders prepared by Pechini and alkoxide methods (Fig. 1) and by solvothermal methods using high concentration of $ZrO(NO_3)_2$ is evident (Fig. 2a and b). The relative density of these materials is lower than 90%, mainly due to the presence of intergranular porosity. Larger fully dense areas, corresponding to the original agglomerates, are clearly visible (e.g. in Figs. 1d and 2b). On the contrary, the starting powders characterized by the small uniformly round aggregates obtained by the solvothermal synthesis in MeOH at low $ZrO(NO_3)_2$ concentration (Fig. 2c) and the finely grained powders obtained by solvothermal synthesis in *i*-PrOH/MeOH at low $ZrO(NO_3)_2$ concentration (Fig. 3c), produced high density samples (r.d. ∼ 98%) with a very homogeneous microstructure (Figs. 2d and 3d).

Fig. 6 shows the nanostructure of the best sintered samples prepared in MeOH (a) and *i*-PrOH (b). Uniform rounded shaped nanograins with grain size ranging between 20 and 30 nm can be observed, confirming the XRD analyses.

The excellent results obtained using the solvothermal approach based on a low concentration (0.2 M) solution of $ZrO(NO_3)_2$ in MeOH can be largely ascribed to the peculiar microstructure of the resulting powders, characterized by the presence of small, hard and round shaped aggregates. It must be noted that the presence of hard agglomerates represents generally a major problem for the preparation of microstructurally uniform sintered bodies. Moreover, in our case the presence of large and inhomogeneous agglomerates resulted in poor densities. Yet, the powders obtained by the solvothermal approach in MeOH and characterized by small and regular agglomerates produced very high relative densities, with no retention of aggregates microstructure in the final densified material (Fig. 2d). The homogeneous microstructure is also the result of the elevated uniaxial pressures used during the FARS densification. Fig. 7 shows the microstructure of a sample produced in the same conditions prescribed for the sample of Fig. 2d, but using an applied pressure reduced to 350 MPa. At this particular pressure the round agglomerates present in the starting powder are still visible, as the relative intergranular porosity. Fig. 7b highlights the remarkable inner nanostructure of these aggregates, characterized by the total absence of any internal porosity.

3.3. Thermal stability

The undoped tetragonal zirconia, either in nanometric bulk materials form or nanopowder form, undergoes a transition towards the monoclinic form upon heating. This is a well documented behaviour for nano-stabilized zirconia [Ref. 2 and references therein]. Despite this however, the details of this transition and the number and nature of the parameters controlling it are still not well understood. In particular, the relationship between the characteristics of the nanopowders and the

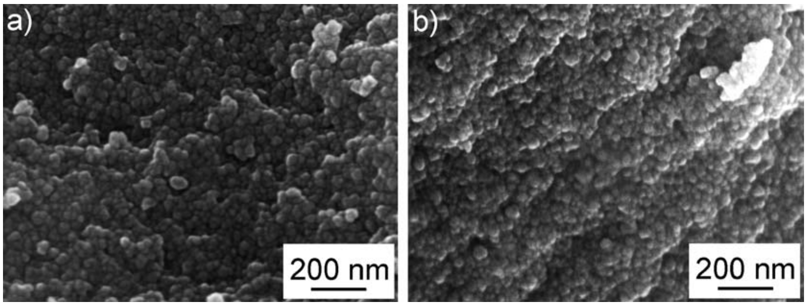

Fig. 6. SEM micrographs showing the nanostructure of the sintered samples of the routes: (a) MeOH (D – 0.2 M), (b) *i*-PrOH (E – 0.04 M).

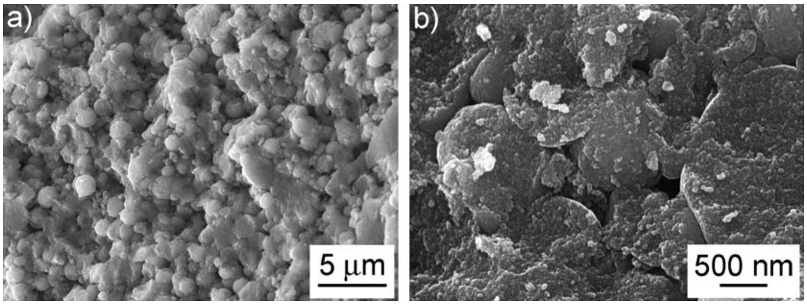

Fig. 7. SEM micrographs of a sintered sample of the MeOH route (D – 0.2 M) obtained at a halved pressure (350 MPa). (a) At 20k× magnification the original rounded shapes of the aggregates can be observed; (b) at 70k× magnification the inner totally dense nanostructure of the single aggregates are highlighted.

temperature at which the transition is observed is not at all sufficiently defined. Since in our case we have been able to produce the nano-stabilized zirconia in two different forms, aggregated nanometric powders and fully dense bulk material, it was possible to make a direct comparison between the thermal stability of these two materials. This has been accomplished by annealing powders and sintered samples coming from the same batch at temperatures ranging between 500 and 1000 °C for 1 h. For these tests, we used our best products, represented by powders and sintered samples obtained though the solvothermal route in MeOH. The results, in terms of grain size and fraction of monoclinic phase, are documented in Fig. 8. Quite surprisingly the bulk material seems to show an even better thermal stability than the powders (Fig. 8a). No significant increase in the amount of the monoclinic phase is observed up to 900 °C for this material, whilst a more relevant increase is observed in the powders starting from 700 °C. Fig. 8b shows how the grain size of the tetragonal phase changes in the two materials during the same temperature interval. In Fig. 8b the value relative to the powder at 1000 °C could not be assigned, since the percentage of tetragonal phase was too low to estimate a correct grain size. Obviously the starting value for the powders and the sintered samples are quite different, as the sintering process, usually achieved at 900 °C, produces a significant grain growth. However, the grain size of the densified samples appears to be quite stable, showing only a limited change with temperature. On the other hand, the grain size of the powders grows rapidly, starting with temperatures of 500 °C. It must be noted that the grain sizes of the powder and of the sintered material appear to converge for temperature values between 900 and 1000 °C. Notably, this is the same temperature interval where the rapid transition to the monoclinic form is observed.

Table 2
Characteristic of the sintered samples obtained from the synthetic routes explored: relative density, phase composition and grain size.

Synthetic route	Relative density (%)	Tetragonal phase (%)	Grain size tetragonal phase (nm)
Pechini	95	73	41
Alkoxide			
A – isopropoxide	87	31	27
B – propoxide	80	34	25
C – propoxide invert. addit.	82	34	26
Solvothermal			
D – MeOH 0.4 M	88	90	27
D – MeOH 0.2 M	97	94	31
E – *i*-PrOH/MeOH (90/10) 0.2 M	89	89	30
E – *i*-PrOH/MeOH (90/10) 0.04 M	98	39	18

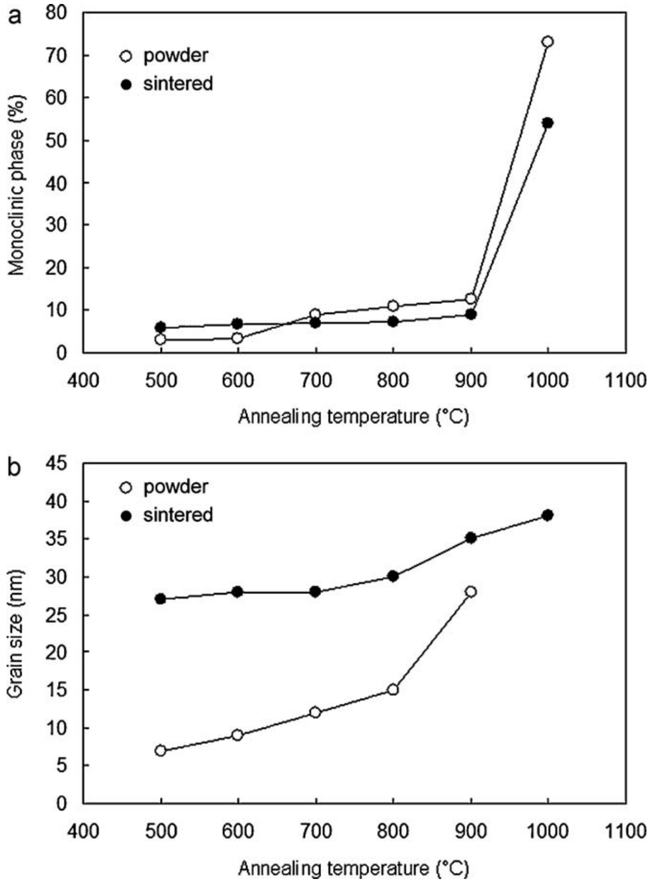

Fig. 8. Thermal stability of the powder and sintered samples obtained from the MeOH route (D – 0.2 M). (a) Percentage of monoclinic phase as a function of annealing temperature (white circles: powder, black circles: sintered). (b) Grain size as a function of annealing temperature (white circles: powder, black circles: sintered).

4. Discussion

The main conclusion based on the results reported in this paper clearly identifies that the synthesis of an almost pure, fully dense, bulk tetragonal zirconia is actually possible and can be produced by means of a careful selection of the densification conditions and careful control of the characteristics of the powders employed. This result, however, relies on the unique characteristics of the sintering method employed, as well as on the complex energy balance between the tetragonal and monoclinic polymorphs. It must be clear that grain size considerations alone cannot justify for the results we obtained. Even under the mildest sintering conditions, as those typical of the HP-FARS densification method, a 2–3 fold increase in grain size is unavoidable and the final grain size would be above the typical values reported in the literature for the size stabilization of the tetragonal phase. However, as was clearly discussed by Shukla and Seal in their recent review,[2] the scenario is much more complex and a number of other internal and external parameters must be taken into account. In other terms, although it is true that an extremely small grain size is an essential requirement for the stabilization of the tetragonal phase, the equilibrium between monoclinic and tetragonal forms cannot be discussed reliably on the basis of this sole parameter. This complexity is documented in an analysis of the literature: in Table 3 we summarized the values of critical dimension required to obtain the stabilization of the tetragonal phase in powders, as reported from the different authors. The values are scattered on an interval that spans over two orders of magnitude.

Table 3
Values of critical dimension required to obtain the stabilization of the tetragonal phase in powders, as reported from different authors.

Authors – year	Critical grain size (nm)	Agglomeration
Garvie[28] – 1965	30	Not discussed
Mitsuhashi et al.[29] – 1974	>30	Aggregate
Garvie et al.[30] – 1975	100	Aggregate with rigid matrix
Nitsche et al.[31] – 1996	6	Not discussed
Djurado et al.[32] – 2000	23	Aggregate
Chraska et al.[33] – 2000	18	Not aggregated
Valmalette et al.[34] – 2002	3	Not discussed
Shukla et al.[35] – 2002	45	Aggregate
Shukla et al.[36] – 2004	10	Single crystal
Shukla et al.[36] – 2004	33	Aggregate
Shukla et al.[36] – 2004	40–45	Aggregate with rigid matrix

Among the parameters that, in addition to the grain size, have been considered to play a role in the stabilization of the tetragonal phase, there are some parameters of paramount importance for the present study, in both the powder synthesis and densification stage. The most important factor is surely the level of agglomeration of the nanopowders. Agglomeration, normally considered as a negative factor in the sintering technology, plays in this specific context a complex role. On the one hand, the presence of large and irregularly shaped aggregates leads to the formation of poorly dense and morphologically inhomogeneous bodies characterized by residual intergranular porosity. On the other hand, aggregation modifies the interfacial energies of the nanopowder, increasing considerably the stability of the tetragonal polymorph with respect to the monoclinic polymorph.[2] Apart from small differences in the interfacial energy related to the coherency of the intergranular interface within the agglomerates, an increase of a factor 3 in the critical size (from 10 to 33 nm) was predicted for agglomerated powders.[2] However, large and irregular agglomerates tend to produce poor microstructures, whilst smaller, spherical and homogeneous aggregates can result in a homogeneous material, provided that a sufficiently high pressure is applied. The extent of the interaction between the particles inside each agglomerate is, on the other hand, the aspect that has probably a major control over the phase composition. Strongly bonded, hard agglomerates are extremely effective in inhibiting the transition towards the monoclinic phase, both during the synthesis and the sintering stage, whilst loosely bonded soft agglomerates, regardless of their size, are characterized by higher amounts of the monoclinic phase and also produce higher amounts of the monoclinic phase upon sintering. The hard aggregates obtained via solvothermal synthesis in methanol ($ZrO(NO_3)_2$ conc. 0.2, 0.04 M) appear to be highly transparent by optical microscopy observation; an indication of either extremely high relative density or extremely uniform nanoporosity. The sintering of this material is therefore represented by the removal of the voids between the spherical agglomerates, as depicted in Figs. 2d and 7.

The efficiency of these hard aggregates in maintaining the tetragonal form can be interpreted taking into account the following points: (i) the surface energy in these compact aggregates can be entirely substituted by the grain boundary energy (except for the grains on the external surface of the agglomerate) and (ii) their high mechanical strength introduces an extra energy requirement for the transition from the tetragonal to the monoclinic form. It is well known, in fact, that the transition to the monoclinic phase occurs with a volume expansion of around 5%. The presence of a rigid matrix, as in the case of these hard aggregates, determines the build up of a hydrostatic stress that inhibits the phase transition.[2] As a result of this, even at room temperature the tetragonal polymorph has been reported in grains larger than 50–100 nm.[2] In soft agglomerates, on the other hand, the individual grains are only loosely bonded and the conditions for the retention of the tetragonal phase are less favourable. The importance of the presence of a rigid matrix for the prevention of the phase transition can also be appreciated observing the results of Fig. 8. The transition towards the monoclinic phase is very slow, or almost absent, in the temperature interval between r.t. and 900 °C, when annealing is performed on the sintered samples.

There are finally two other factors that might influence the phase stability in our samples and that are specifically related to the sintering stage: (i) the presence of an external uniaxial stress caused by the applied load and (ii) the reducing conditions under which the HP-FARS operates.

Due to the different density of the polymorphs, the stability range of the tetragonal phase is, in fact, extended as a result of an external load. The application of an external pressure similar to that employed in our case (700 MPa) was shown to determine an increase of the room temperature critical size from 10 nm (in non agglomerated powder) to approximately 20 nm.[2] Although the extent of the pressure effect is different at different temperatures and grain sizes, it could indeed play a positive role in the preservation of the tetragonal phase. Under an applied pressure of 700 MPa and at a temperature of 900 °C in fact, the tetragonal phase is the thermodynamically stable form even at grain sizes well above those studied here.[2] Densification of the nanopowders could therefore be achieved under largely favourable conditions for the tetragonal phase; the subsequent transition towards the monoclinic phase, once the temperature and pressure are returned to the ambient values, can then be limited or prevented by the matrix effect as previously discussed.

The reducing conditions of the FARS method, generated by the graphite dies that contain the samples, should also favour the retention of the tetragonal phase. The formation of oxygen vacancies, either as an effect of doping with lower valence cations or due to the reducing environmental conditions, is the primary method for stabilizing at room temperature the tetragonal and cubic (at higher vacancy concentrations) zirconia polymorphs. In this case however, the amount of oxygen removal is most probably not sufficient to play any relevant role in the preservation of the tetragonal polymorph, due to the mild temperature conditions employed.

5. Conclusions

In the present work we investigated the possibility of preparing high density size stabilized zirconia samples by means of the HP-FARS technique. Particular attention was paid to the role played by the properties of the precursor powder in determining the phase composition and the microstructural characteristics of the sintered materials. For this purpose, different popular synthetic routes, recently reported in the literature for the synthesis of oxide nanopowder, were used for the synthesis of the starting powder. Grain size, agglomeration degree and amount of tetragonal phase in the starting product largely determine the quality of the sintered materials. Agglomeration in particular strongly affects not only the final density but also the possibility of retaining the tetragonal phase during sintering. Disagglomerated fluffy powders, although ideal for the production of high dense uniform sintered samples, showed a marked tendency towards the transition to the monoclinic phase as the grain size increases during the sintering cycle. On the contrary, aggregated powders showed a noteworthy retention of the tetragonal phase. Optimal results were therefore obtained by using peculiar synthetic conditions leading to the formation of nanopowder with a microstructure characterized by uniform spherical microaggregates of around 1 μm in diameter. Using such powders as a starting material, almost fully dense samples of undoped size-stabilized zirconia were obtained with a sintering cycle of 5 min under a uniaxial pressure of 700 MPa, at sintering temperatures as low as 900 °C. These results produced for the first time a fully dense (r.d. 97%) sintered sample of undoped zirconia, characterized by a grain size of 31 nm and noteworthy purity in tetragonal phase (94%). The sintered sample furthermore resulted in a thermally stabile product, up to 900 °C.

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