

Synthesis of Fully Dense Nanostabilized Undoped Tetragonal Zirconia

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Zirconia-based materials, with very low or null doping contents (YO_{1.5} between 0% and 4% mol), were prepared in the form of bulk nanostructured materials through a two-step process. Nanometric powders of size-stabilized tetragonal zirconia were synthesized by the Pechini method and subsequently densified using the high-pressure field-assisted rapid sintering method at temperatures around 850°–900°C for 5 min under a pressure of ~800 MPa. By this method, theoretical densities of ~98% were achieved while retaining the grain size in the final product between 40 and 50 nm. The transition to the thermodynamically stable monoclinic phase was consequently prevented, allowing for the first time the synthesis of size-stabilized zirconia in a high-density bulk form.

I. Introduction

ZIRCONIA at ambient pressure exists in three different polymorphs: monoclinic (room temperature—1175°C), tetragonal (1175°–2370°C), and cubic (2370°–2680°C). Tetragonal and cubic polymorphs are those relevant for technological applications, based on their oxygen conductivity as in solid oxide fuel cells, sensors, and in catalysis. The tetragonal and cubic phases are traditionally stabilized at room temperature by doping with lower valence cations (e.g., Ca²⁺, Mg²⁺, Y³⁺).¹

Recently, the stabilization of metastable phases induced by the nanostructure has attracted considerable attention, not only in zirconia, but in several other oxides, including Al_2O_3 ,^{2,3} TiO₂,⁴ and perovskites.^{5–7} This effect is generally observed when the dimension of the crystalline domains is below some critical value. Since its discovery by Garvie,^{8,9} a large number of studies have been devoted to the nanoinduced stabilization of zirconia, especially in the form of nanopowder.^{10–18} Despite this, the mechanism responsible for the nanoinduced stabilization has not been completely clarified. While the differences in surface energy between the polymorphs is by far the most popular explanation, the influence of anionic impurities, lattice strain, structural similarities between the precursor materials and tetragonal zirconia, influence of lattice defects, and/or water vapor have also been proposed.¹⁰ On the other hand, it is generally agreed that nanocrystalline tetragonal zirconia is not just kinetically metastable, but can be truly thermodynamically more stable than the monoclinic form, as long as coarsening is precluded.10,13

As summarized by Li *et al.*,¹² several different values of critical size can be found in the literature, ranging between 3 and 30 nm, depending on the synthetic route and the size determination technique. Some authors also reported the possibility to stabilize the cubic polymorph at even smaller sizes than those required for the tetragonal phase,^{19–21} although some controversy exists on this point. The size-induced stabilization has been exclusively explored on nanopowders or in thin films.²² No attempt to retain such characteristics in high-density bulk materials has ever been reported. The possibility to obtain bulk tetragonal, or cubic, zirconia with no dopant content would open the possibility to investigate the functional and structural properties of zirconia in conditions never explored before. The difficulty encountered in the preparation of bulk nanocrystalline materials, especially when a very low level of porosity is required, so far prevented the possibility to obtain dense zirconia samples with a grain size below the critical value for size-stabilization of the tetragonal phase.

It has recently been shown that the high-pressure spark plasma sintering (HP-SPS) allowing rapid sintering cycles at high pressures (up to 1 GPa), can be used to prepare nearly fully dense nanocrystalline materials with minimal grain growth.^{23–25} Through this approach, the feasibility of consolidation of yttria fully stabilized zirconia (8% YSZ) and ceria samples to relative densities exceeding 98% and with a grain size below 20 nm has been demonstrated.

The aim of this work was the application of a technique similar to the HP-SPS, known as high-pressure field-assisted rapid sintering method (HP-FARS) to the densification of zirconia nanopowders with null or low dopant levels with the intent of obtaining bulk nanostabilized tetragonal ZrO₂ samples at dopant levels below the stabilization limit for the tetragonal phase at room temperature.

II. Experimental Procedure

 ZrO_2 nanopowders with a dopant (YO_{1.5}) content ranging between 0 and 4 at.% Y (i.e., from pure ZrO_2 to $Zr_{0.96}Y_{0.04}O_{2-x/2}$) were obtained using a modified Pechini method.²⁶ The stability range of the pure monoclinic phase at room temperature is covered by the composition interval considered. Zirconyl (IV) nitrate and citric acid were taken in a molar ratio of 1:1. To a proper amount of a commercial aqueous solution (35% weight in nitric acid) of Zirconyl (IV) nitrate, a saturated solution of citric acid was added (typically, to 30 mL of Zirconyl solution, 12 mL of saturated citric acid solution was added). The solution was then stirred on a hot plate at 80°C, to obtain a solution of increasing viscosity. After a time period that depends on the amount of solution used (3 h for the volumes reported above), the viscous mass turned into a colorless transparent glass. Further heating (typically 5 h for the reported amounts) provided a white solid, which was subsequently ground in a mortar and calcined in a furnace at 625°C for 2.5 h; the calcination temperature was selected as the lowest that leads to a complete removal of the carbonaceous residuals. The white powders were successively densified using a home-made HP-FARS apparatus. This apparatus presents the same general design of an HP-SPS, but uses low-voltage AC high-intensity current instead of the pulsed DC current generally used in the SPS. A similar apparatus has been used previously by Gauthier et al.²⁷ In each experiment, 0.15 g of powders were loaded in a double-stage die. The lowpressure section of the die was made of high-density graphite, while the high-pressure section was made of silicon carbide and

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tungsten carbide.²³ 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. Once the sample attained the designated temperature, the pressure was rapidly increased to the final value. 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 was turned off. Temperatures were measured using a shielded K-type thermocouple inserted in the lateral wall of the die.

Microstructural characterization of the samples was made on uncoated fracture surfaces, using a high-resolution SEM (HRSEM, Philips XL30s, Eindhoven, the Netherlands). The average grain size was determined measuring at least 100 grains on each HRSEM image using the software AnalySIS (Soft Imaging System Corp., Lakewood, CO). The density of the samples was measured using the Archimedes method and from geometric and gravimetric measurements.

The X-ray powder diffraction patterns were collected at the beamline ID31 of the synchrotron source European Synchrotron Radiation Facility (ESRF) in Grenoble, with a wavelength of 0.399946 (3) Å, calibrated against NIST 640c standard silicon at room temperature. The beam was monochromated by a cryogenically cooled Si 111 double-crystal monochromator and a bank of nine detectors was vertically scanned to measure the diffracted intensity as a function of 20. Each detector was preceded by a Si 111 analyzer crystal. The powders were contained in a boron glass capillary (0.6 mm diameter), while for densified samples, a fragment of the pellet was placed in a larger capillary (1.5 mm diameter) and fixed with wax to avoid moving the sample during spinning. The capillaries were spun for a better counting statistics.

The cell refinements and the quantitative analyses were performed using the Rietveld method, using the software GSAS+EXPGUI.^{28,29} The crystallite size and the root mean square (RMS) microstrains were evaluated using the software MAUD³⁰: the standard used for the evaluation of the instrumental broadening was LaB₆ (NBS 660). The model used was the isotropic one, in which the microstructural evaluation was made over the whole diffraction pattern, assuming that the diffracting domains were isotropic in shape. The crystallite size and the RMS microstrain were evaluated for both the zirconia polymorphs when they were present in adequate quantities. When the monoclinic phase was <10% wt., the whole peak broadening was assumed to be originating from small crystallite size only.

III. Results

XRD patterns of the $Zr_{1-x}Y_xO_{2-x/2}$ (0<x<0.04) powder samples after calcination at 625°C are shown in Fig 1; the



Fig. 1. XRD patterns of the $Zr_{1-x}Y_xO_{2-x/2}$ (0<*x*<0.04) powder samples after calcination at 625°C.

corresponding structural and microstructural characteristics, obtained by the refinement of the XRD data, are reported in Table I. The diffraction peaks are significantly broadened, indicating the formation of zirconia nanocrystals. The calculated grain size of the tetragonal phase is around 15 nm with variations among the different compositions within the uncertainty typical of the synthetic method (Table I). The grain size is mainly controlled by the calcination conditions and smaller grains could be obtained by lowering the calcinations temperature. Although full crystallization of the zirconia powder is achieved at temperatures close to 400°C, the elimination of the carbonaceous residuals requires temperature above 600°C. The thorough removal of all these impurities is essential in order to avoid their incorporation in the sintered samples.

All the X-ray reflections of Fig. 1 can be indexed by the tetragonal and monoclinic polymorphs. In agreement with the literature,^{8–18} the high-temperature tetragonal phase is the major component of the product thanks to the stabilizing effect of the nanometric particle size. As expected, there is a synergic stabilizing effect played by both the reduced crystallite dimension and the doping amount; consequently, the fraction of the monoclinic phase decreases as the amount of the stabilizing Y^{3+} is increased. The amount of monoclinic phase, calculated by Rietveld refinement of the XRD data, decreases from 17.1% wt. in the pure ZrO₂ sample to below the detection limit in the Zr_{0.96}Y_{0.04}O_{2-x/2} one (Table I). The concomitant presence of the monoclinic and tetragonal phases in pure (or low dopant content) zirconia was reported by most previous works and their

Table I.	Structural and	Microstructural	Characteristics	of the	Starting	Powder
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Tetragonal						
Y at.%	<i>a</i> (Å)	<i>c</i> (Å)	$V(\text{\AA}^3)^{\dagger}$	c/a	< D > (Å)	RMS strain (×10 ⁻³)
0	5.0878 (1)	5.1791 (3)	67.03	1.0179	148 (1)	3.21(3)
0.3 2 4	5.08841 (9) 5.09110 (9) 5.09989 (9)	5.1792 (3) 5.1802 (2) 5.1672 (4)	67.13 67.20	1.0178 1.0174 1.0132	131(1) 161(1) 125(1)	3.42 (2) 5.31 (5)
Monoclinic						
Y at.%		< D > (Å)				RMS strain (× 10^{-3})
0 0.5 2 4		198 (4) 164 (3) 120 (4) ND			2.31 (5) 1.78 (8) 2.3 (4) ND	

[†]Please note that the volume was calculated using the original primitive cell used in the refinements, and not with the centered cell usually used in the literature, which is reported for an easier comparison with the literature data (e.g., Garvie and colleagues^{8–18}). RMS, root mean square.

Table II.	Sintering	Conditions	and	Product	Density
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Y at.%	Heating rate (°C/min)	Temperature (°C)	Pressure (MPa)
0	200	850	790
0.5	200	875	800
2	200	875	825
4	200	900	825

relative amount appears to depend not only on the particle size but also on the synthetic route used.^{8–18} Zhang *et al.*¹⁸ observed the coexistence of both monoclinic and tetragonal polymorphs when the average particle size was between 14 and 31 nm, while only the tetragonal phase was observed below 14 nm, and only the monoclinic one above 31 nm. The coexistence of the two polymorphs in the intermediate grain size range is suggested to result from the size distribution; because there is a certain grain size distribution in one batch of samples, this implies that the grain sizes of the monoclinic phase are larger than those of the tetragonal one. Our results are not in agreement with this conclusion because, with the exception of the dopant-free sample that shows a slightly higher value (19.8 nm) of the grain size of monoclinic phase, we did not detect a significant difference between the crystallite size of two polymorphs (Table I).

The calcined precursor nanopowders were densified by the HP-FARS method. As already mentioned, the main aim was to produce a high-density material with minimal grain growth to prevent, as much as possible, the tetragonal to monoclinic transition. Different sintering conditions were explored for this purpose, with particular focus on the maximum sintering temperature and uniaxial applied pressure. Table II summarizes the experimental parameters that produced the best results in terms of density and crystallite size. A very short hold time (5 min) was used in all experiments as this parameter was shown to have a limited influence on sample density, because the major portion of the overall densification occurs before reaching the final temperature.³¹ In a study on the densification via SPS of a commercial nanometric powder of fully stabilized zirconia (Tosoh, 16 at.% Y), we showed that the temperature required to achieve the 95% of the theoretical density decreases linearly with the logarithm of the applied pressure.³¹ As a consequence, it was possible to obtain a more than exponential decrease in the final grain size by increasing the applied pressure. In agreement with the above, in the present study also, the minimum grain growth and highest density were obtained by using the maximum pressure allowed by the instrument, which is around 800 MPa.

The densification under the maximum applied pressure required slightly higher sintering temperatures for the composition richer in yttrium in order to achieve a theoretical density similar to the one obtained for lower contents (~95%-96%). As a consequence, a small but consistent increase in the grain size was observed as the doping content is increased (Table III). The temperature range is anyway narrow as it varies between 850°C for pure ZrO₂ and 900°C for 4 at.% Y. It must be stressed that the conditions reported in Table II are quite strict and the quality of the samples decreases dramatically either by reducing the pressure and/or the temperature (insufficient density) or increasing them (grain size exponentially increases with temperature). The temperatures used in this study are considerably lower than those required for the sintering of zirconia by traditional methods.¹ At such low temperatures and short sintering times, the sintering mechanism is most probably based on mechanisms different from the thermal-activated diffusion of the atomic species. The only fast-diffusing species in zirconia at low temperatures is oxygen, but sintering and densification of these materials require the diffusion of cations, which at these temperatures is very limited.³² Furthermore, the rapid application of pressure produces very high strain rates. Under these conditions, plastic (or superplastic) deformation may play a very important role in supporting a densification mechanism based on grain-boundary sliding and grain rotation.

Figure 2 shows the fracture surface of a sample with 2 at.% Y sintered under the experimental conditions reported in Table II. The fracture surface allows to appreciate the small grain size, the good grain size homogeneity, and the absence of appreciable residual porosity. Similar to what was observed on other materials such as fully stabilized YSZ,^{24,31} pure²³ and Sm-doped ceria,²⁵ LSGM³³ etc., the HP-FARS technique allowed the production of high-density materials with a limited (typically two to three times the initial value) grain growth even starting, as in this case, from the badly agglomerated powder, which generally produces sintered samples characterized by large mesoporosity.

Figure 3 shows the XRD patterns collected on the densified samples. The most important result is indeed represented by the phase composition, which is summarized in Fig. 4 (upper part) as a function of the Yttrium content for both the starting powder and the sintered samples. Although the amount of the monoclinic phase is higher in the densified samples, due to Ostwald ripening during the sintering process, the tetragonal phase remains in all cases the major component; even in the pure bulk ZrO_2 sample, the amount of the monoclinic phase is only around 25% in weight in the sintered sample. Figure 4 (lower part) shows the variation of the grain size and stress content determined by the MAUD program for both powder and dense samples as a function of Y³⁺ content. It should be observed that the crystallite size of Fig. 4 is in good agreement with the particle

Tetragonal							
Y at.%	<i>a</i> (Å)	<i>c</i> (Å)	$V(\text{\AA}^3)^{\dagger}$	c/a	< D > (Å)	RMS strain ($\times 10^{-3}$)	
0	5.08381 (8)	5.1869 (2)	67.02	1.0203	412 (3)	1.56 (3)	
0.5	5.08449 (7)	5.1860 (1)	67.04	1.0199	452 (5)	1.39 (2)	
2	5.08738 (7)	5.1836 (2)	67.08	1.0189	473 (6)	1.31 (3)	
4	5.09336 (9)	5.1769 (4)	67.15	1.0164	472 (9)	1.35 (6)	
Monoclinic							
Y at.%			< D > (Å)			RMS strain ($\times 10^{-3}$)	
0			491 (12)			3.3 (2)	
0.5			643 (23)			4.3 (2)	
2			805 (13)			2.9 (4)	
4			NĎ			ND	

Table III. Structural and Microstructural Characteristics of the Sintered Samples

[†]Please note that the volume was calculated using the original primitive cell used in the refinements, and not with the centered cell usually used in the literature, which is reported for an easier comparison with the literature data (e.g., Garvie and colleagues^{8–18}). RMS, root mean square.



Fig. 2. Fracture surface of a sample with 2 at.% Y sintered under the experimental conditions of Table II.

size observed for the HRSEM images of the fracture surfaces (Fig. 2).

Figure 5 shows the comparison of the weight percentage of the monoclinic phase as a function of the crystallite size of the tetragonal phase for both the powders and the densified samples. The amount of zirconia that is transformed into the monoclinic polymorph during sintering is much larger as the dopant is reduced. As expected, there is a combined effect of the grain size reduction and the amount of doping in the stabilization of the tetragonal phase. It is reasonable to suggest, in agreement with the data of Fig. 4, that the effect of introducing Y^{3+} in the nanostructured tetragonal zirconia shifts the critical value for the transition to the monoclinic phase towards larger grain sizes.

Under the sintering condition adopted in this study, the grain size increases from around 15 nm in the starting powder to 43–50 nm in the densified samples. It could appear surprising that such a low monoclinic content is present in the sintered samples, especially for the lowest doping content. When compared with the available literature data, concerning pure zirconia in the powder form, the grain size exhibited by our sintered samples would, in fact, appear hardly compatible with the presence of large amounts of size-stabilized tetragonal phase. This point has been recently discussed by Li *et al.*¹² In their theoretical work, the authors suggested the possibility of a larger critical grain size (37 nm) in nanostructured bulk materials than in powders (10 nm) at room temperature. This result is justified by a considerably larger energy cost in the transition from the tetragonal to monoclinic phase when the free surface contribution ($\Delta \gamma = 0.18$ J/m) is replaced by the grain-boundary contribution



Fig. 3. XRD patterns of the densified samples with a nominal composition $Zr_{1-x}Y_xO_{2-x/2}$ (0 < *x* < 0.04).



Fig. 4. Upper part: variation of the amount of tetragonal phase as a function of the Y content (black symbols: powder; white symbols: sintered samples). Lower part: variation of the amount of crystallite size of the tetragonal phase as a function of the Y content (black symbols: powder; white symbols: sintered samples).

 $(\Delta \sigma = 1.24 \text{ J/m})$. Further increase in the critical grain size, possibly above 40 nm, can occur, according to the same authors, thanks to other factors such as the existence of internal strain and in particular the presence of a surrounding rigid matrix (as in our bulk samples) that prevents the volume expansion accompanying the tetragonal to monoclinic transition.

In our densified samples, the stabilization of the tetragonal phase could be also due to some structural alteration introduced by the fast sintering cycle that may create a quenched-in metastable state inside the material. The structural parameters of the tetragonal phase in the powder and in the sintered material were, therefore, analyzed and compared. Figure 6 shows the variations of cell volume (upper part) and of the individual cell parameters (lower part) with YO_{1.5} content. As expected, due to the larger ionic size of the Y³⁺ ion, cell volume linearly increases with an increasing Y³⁺ content even though an opposite trend can be observed for the individual cell parameters (lower part of Fig. 6). The c/a ratio (Fig. 7) is generally used as the parameter accounting for the "tetragonality" degree of the structure, intended as a deviation from the ideal cubic one (c/a = 1). As expected, the tetragonality decreases as the amount of yttrium is



Fig. 5. Variation of the amount of monoclinic phase as a function of the crystallite size of the tetragonal phase for the 2 at.% Y composition (circles), 0.5 at.% Y (squares), and pure zirconia (triangles). Black symbols, powder; open symbols, sintered samples.

increased as, according to the phase diagram, the structure should turn to the cubic polymorph at Y at.% = 16.

A marked difference could, on the other hand, be found in the structural parameters of the powder and sintered samples of equal composition. The sintered samples always show a smaller $\langle a \rangle$, a larger $\langle c \rangle$, and a larger c/a ratio for all the explored compositions. This variation of the unit cell parameters, that ultimately leads to a smaller cell volume in the sintered samples, can in principle be explained on the basis of the following hypotheses: (1) a permanent deformation of the unit cell due to the stress applied during the densification, (2) the loss of larger Y^{3+} ions from the tetragonal structure, or (3) the creation of excess oxygen vacancies. The first hypothesis does not appear realistic, because the applied pressure is not sufficient to introduce such permanent modifications in the crystal structure. The absence of any trace of Y_2O_3 appears to exclude the second hypothesis also. The third hypothesis, i.e. the formation of non equilibrium oxygen vacancy distribution, appears on the other hand more realistic, due to the relatively fast heating/cooling cycle used and the reducing environment (due to the graphite dies) typical of the FARS technique. Even though the white color displayed by the sintered samples appears to exclude the presence of a large oxygen substoichiometry in these samples, a small variation of their number and distribution cannot be a priori excluded.

Another obvious alteration introduced by sintering is an increase in the grain size that on average is tripled in the densified samples. The cell parameter could therefore vary as an effect of the change in grain size. A comparison with the literature data concerning this point was possible only for the pure zirconia (Fig. 8). The variation of the lattice parameters and of the c/aratio observed in our samples is in good agreement with the trend observed by Lamas et al.³⁴ who evaluated these parameters in powders of particle size between 5 and 11 nm prepared by different synthetic routes. The strong decrease in the c/a ratio is taken by the authors as a possible indication of a transition toward a cubic structure (c/a = 1) at even smaller grain sizes, while the increase in the c/a parameters as the grain size increases is expected to lead to the formation of the monoclinic polymorph. Even though a similar trend was observed by other authors also,¹¹ a clear explanation on this point is not at hand.

The data shown in Fig. 8 indicate anyway as the sintered samples prepared by HP-FARS well fit within the trend exhibited by zirconia nanopowder and no alteration due to the high



Fig. 6. Upper part: Variation of the cell volume of the tetragonal phase as a function of the Y content for the starting powder and the sintered samples. Lower part: Variation of the unit cell parameters of the tetragonal phase as a function of the Y content for the starting powder and the sintered samples.



Fig. 7. Variation of the c/a ratio of tetragonal phase as a function of the Y content. Black symbols, powders; open symbols, densified samples.



Fig. 8. Upper part: variation of the $\langle a \rangle$ (open symbols) and $\langle c \rangle$ (black symbols) for the tetragonal phase as a function of grain size; circles, this study; squares, from Maglia et al.³³ Lower part: variation of the c/a ratio for the tetragonal phase as a function of grain size; circles, this study; square, from Lamas *et al.*³⁴

pressure used or the reducing condition are likely to have occurred.

IV. Conclusions

In the present work, we have carried out the synthesis of pure and low doping (<4 at.% $YO_{1.5}$) zirconia in the form of bulk nanostructured samples. The starting powder, prepared by the Pechini method, was densified using the High-Pressure Field-Activated Rapid Sintering method. High relative density (>98%) samples could be obtained at temperatures as low as 850°-900°C and for sintering times of only 5 min. As a consequence of the mild sintering conditions, a limited grain growth was observed; the sintered samples showed grain sizes around 45–50 nm for all the compositions investigated.

Thanks to the reduced dimension of the grain size, it was possible, for the first time, to retain the nanostabilization of the tetragonal phase even in bulk high-density samples. Only a very limited, or null, transition toward the thermodynamically stable monoclinic phase was detected during the sintering procedure.

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References

¹R. Stevens, An Introduction to Zirconia, pp. 1-22. Magnesium Elektron Ltd., Twickenham, U.K., 1983.

²J. M. McHale, A. Auroux, A. J. Perrota, and A. Navrotsky, "Surface Energies and Thermodynamic Phase Stability in Nanocrystalline Aluminas," Science, 277, 788-91 (1997).

³J. M. McHale, A. Navrotsky, and A. J. Perrota, "Effects of Increased Surface Area and Chemisorbed H₂O on the Relative Stability of Nanocrystalline γ-Al₂O₃ and α-Al₂O₃," J. Phys. Chem. B, 101, 603-13 (1997).

⁴M. R. Ranade, A. Navrotsky, H. Z. Zhang, J. F. Banfield, S. H. Elder, A. Zaban, P. H. Borse, S. K. Kulkarni, G. S. Doran, and H. J. Whitfield, "Energetics of Nanocrystalline TiO2," Proc. Natl. Acad. Sci., 99 [2] 6476-81 (2002).

S. Tsunekawa, S. Ito, T. Mori, K. Ishikawa, Z. Q. Li, and Y. Kawazoe, "Critical Size and Anomalous Lattice Expansion in Nanocrystalline BaTiO3 Particles," Phys. Rev. B, 62, 3065-70 (2000).

⁶D. Fu, H. Suzuki, and K. Ishikawa, "Size-Induced Phase Transition in PbTiO₃ Nanocrystals: Raman Scattering Study," *Phys. Rev. B*, **62**, 3125–9 (2000).

⁷D. McCauley, R. E. Newnham, and C. A. Randall, "Intrinsic Size Effects in a Barium Titanate Glass-Ceramic," J. Am. Ceram. Soc., 81, 979-87 (1998).

⁸R. C. Garvie, "The Occurrence of Metastable Tetragonal Zirconia as a Crys-¹ Statistics of the determine of Metastatic retragonal Encona as a Crystallite Size Effect, 7 J. Phys. Chem., 69, 1238-43 (1965).
 ⁹ R. C. Garvie, "Stabilization of the Tetragonal Structure in Zirconia Micro-

crystals," *J. Phys. Chem.*, **82** [2] 218–24 (1978). ¹⁰M. W. Pitcher, S. V. Ushakov, A. Navrotskyz, B. F. Woodfield, G. Li, J. Boerio-Goates, and B. M. Tissue, "Energy Crossovers in Nanocrystalline Zirconia," J. Am. Ceram. Soc., 88 [1] 160-7 (2005).

¹¹E. Djurado, P. Bouvier, and G. Lucazeau, "Crystallite Size Effect on the Tetragonal-Monoclinic Transition of Undoped Nanocrystalline Zirconia Studied

VXRD and Raman Spectrometry," J. Solid State Chem., 149, 399–407 (2000).
¹²S. Li, W. T. Zheng, and Q. Jiang, "Size and Pressure Effects on Solid Tran-sition Temperatures of ZrO₂," Scr. Mater., 54, 2091–4 (2006).

¹³N. L. Wu, T. F. Wu, and I. A. Rusakova, "Thermodynamic Stability of Tetragonal Zirconia Nanocrystallites," *J. Mater. Res.*, **16** [3] 666–9 (2001).

T. Schmidt, M. Mennig, and H. Schmidt, "New Method for the Preparation and Stabilization of Nanoparticulate t-ZrO₂ by a Combined Sol–Gel and Solvothermal Process," J. Am. Ceram. Soc., 90 [5] 1401-5 (2007).

¹⁵S. Shukla, S. Seal, R. Vij, S. Bandyopadhyay, and Z. Rahman, "Effect of Nanocrystallite Morphology on the Metastable Tetragonal Phase Stabilization in Zirconia," Nano Lett., 2 [9] 989-93 (2002).

¹⁶S. Shukla and S. Seal, "Thermodynamic Tetragonal Phase Stability in Sol–Gel Derived Nanodomains of Pure Zirconia," *J. Phys. Chem. B*, **108**, 3395–9 (2004). ¹⁷J. Ch. Valmalette and M. Isa, "Size Effects on the Stabilization of Ultrafine

Zirconia Nanoparticles," Chem. Mater., 14, 5098-102 (2002). 18Y. L. Zhang, X. J. Jin, Y. H. Ronga, T. Y. Hsu (Xu Zuyao), D. Y. Jiang, and

J. L. Shi, "The Size Dependence of Structural Stability in Nano-Sized ZrO2 Particles," Mater. Sci. Eng. A, 438-40, 399-402 (2006).

¹⁹S. Tsunekawa, S. Ito, and Y. Kawazoe, "Critical Size of the Phase Transition from Cubic to Tetragonal in Pure Zirconia Nanoparticles," Nano Lett., 3 [7] 871-5 (2003).

²⁰S. Roy and J. Ghose, "Synthesis of Stable Nanocrystalline Cubic Zirconia," *Mater. Res. Bull.*, **35**, 1195–203 (2000). ²¹U. Martin, H. Boysen, and F. Frey, "Neutron Powder Investigation of

Tetragonal and Cubic Stabilized Zirconia, TZP and CSZ, at Temperatures up to 1400 K," Acta Cryst., Sect. B, 49, 403–13 (1993).

²²M. A. Schofield, C. R. Aita, P. M. Rice, and M. G. Josifovska, "Transmission Electron Microscopy Study of Zirconia-Alumina Nanolaminates Grown by Reactive Sputter Deposition. Part I: Zirconia Nanocrystallite Growth Morphology,' Thin Solid Films, **326**, 106–16 (1998). ²³U. Anselmi-Tamburini, J. E. Garay, and Z. A. Munir, "Fast Low-Temper-

ature Consolidation of Bulk Nanometric Ceramic Materials," Scr. Mater., 54, 823-8 (2006). ²⁴U. Anselmi-Tamburini, F. Maglia, G. Chiodelli, P. Riello, S. Bucella, and

Z. A. Munir, "Enhanced Low-Temperature Protonic Conductivity in Fully Dense Nanometric Cubic Zirconia," Appl. Phys. Lett., 89, 163116, 3pp (2006).

²⁵U. Anselmi-Tamburini, F. Maglia, G. Chiodelli, A. Tacca, G. Spinolo, P. Riello, S. Bucella, and Z. A. Munir, "Nanoscale Effects on the Ionic Conductivity of Highly Doped Bulk Nanometric Cerium Oxide," *Adv. Funct. Mater.*, 16, 2363–8 (2006).

²⁶M. P. Pechini, "Method of Preparing Lead and Alkaline-Earth Titanates and Niobates and Coating Method Using the Same to Form a Capacitor"; U.S. Patent

No. 3 330 697, 1967. ²⁷V. Gauthier, F. Bernard, E. Gaffet, Z. A. Munir, and J. P. Larpin, "Synthesis of Nanocrystalline NbAl3 by Mechanical and Field Activation," Intermetallics, 9, 571-58 (2001).

²⁸C. Larson and R. B. Von Dreele, *General Structure Analysis System (GSAS)*,

pp. 86–748. Los Alamos National Laboratory, Los Alamos, NM, 1994. ²⁹B. H. J. Toby, "EXPGUI, a Graphical User Interface for GS," *Appl. Crys*tallogr., 34, 210-3 (2001).

³⁰L. Lutterotti and S. Gialanella, "X-Ray Diffraction Characterization of Heav-ily Deformed Metallic Specimens," *Acta Mater.*, **46**, 101–10 (1998).
³¹U. Anselmi-Tamburini, J. E. Garay, A. Munir, Z. A. Tacca, F. Maglia, and G.

Spinolo, "Spark Plasma Sintering and Characterization of Bulk Nanostructured Fully Stabilized Zirconia: Part I. Densification Studies," J. Mater. Res., 19 [11] 3255-62 (2004).

³²S. C. Liao, W. E. Mayo, and K. D. Pae, "Theory of High Pressure/Low Temperature Sintering of Bulk Nanocrystalline TiO2," Acta Mater., 45, 4027-40 (1997).

³³F. Maglia, U. Anselmi-Tamburini, G. Chiodelli, H. E. Çamurlu, M. Dapiaggi, and Z. A. Munir, "Electrical, Structural, and Microstructural Characterization of Nanometric $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) Prepared by High-Pressure Spark Plasma Sintering," Solid State Ionics, 180, 36-40 (2009).

⁴D. G. Lamas, A. M. Rosso, M. Suarez Anzorena, A. Fernàndez, M. G. Bellino, M. D. Cabezas, N. E. Walsoe de Reca, and A. F. Craievich, "Crystal Structure of Pure ZrO₂ Nanopowders," *Scr. Mater.*, **55**, 553–6 (2006).