

Neutron Diffraction Study of the Size-Induced Tetragonal to Monoclinic Phase Transition in Zirconia Nanocrystals

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Accurate neutron powder diffraction experiments at several temperatures allow one to monitor the reconstructive tetragonal to monoclinic phase transition as a function of the size of zirconia nanoparticles. The structure of the tetragonal phase observed in the nanocrystals is identical to that observed in micrometric zirconia above 1400 K. A uniaxial strain depending on grain size is observed. The phase transition occurs above a threshold crystal size. These results are analyzed within the Landau theory and can be understood as a mechanism of size-dependent phase transition where the primary order parameter is altered by the nanoparticle size.

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In the last 30 years, the soft mode model has been successful for describing displacive phase transitions in solids [1]. Within the framework of the Landau theory, the amplitude of the soft mode corresponds to the primary order parameter for these phase transitions. The existence of secondary order parameters (e.g., strain field, ...) generally induces only little changes in this kind of phase transition. For instance, in martensitic transformations, occurring in many alloys, the onset of an important strain field suggests a strong coupling between the primary and the secondary order parameters. ZrO_2 can be considered as a textbook example [2] for such a coupling: this compound is stoichiometric and homogeneous (no Ginzburg terms in the Landau free energy expansion). Moreover, in this compound, it is possible to generate a uniform strain field controlling the particle size.

Micrometric grains of zirconia, monoclinic at room temperature and normal pressure, undergo a reversible but disruptive first order phase transition at about 1200 K towards a tetragonal phase [3] that cannot be quenched at room temperature [4,5]. Nevertheless, it is also well known that this tetragonal phase can be observed at room temperature in zirconia nanoparticles [6] of less than 30 nm diameter. Several authors [7,8] confirm these observations and others report observations of metastable phases in various materials such as alumina [9] and graphite [10]. The observation of stabilized phases in very fine powders is generally understood in terms of a surface free energy in the nanocrystalline tetragonal phase lower than in the normal phase [11]. Nevertheless, this explanation is not generally accepted [12] and some authors report either the appearance of 6 nm diameter monoclinic zirconia nanoparticles [13] or they do not relate the decreasing of the tetragonal phase to the increase in the grain size of zirconia nanoparticles [7]. The main reasons for these controversial opinions seem related to extrinsic factors such as the presence of impuri-

ties [14,15] and to the existence of residual stresses in the nanoparticle agglomerates [16].

To clarify this complex picture, it is of paramount importance to perform accurate studies on very pure samples where the effect of particle size, the pertinent parameter, can be clearly identified. In this Letter, we will show that the accurate study of the transformation kinetics in zirconia nanocrystals allows a straightforward interpretation of the experimental results and to formulate a model for the mechanism of the tetragonal to monoclinic phase transition observed in pure samples. To this purpose, we have simultaneously studied the structure and the microstructure of nanocrystalline pure ZrO_2 using high resolution neutron powder diffraction at different annealing temperatures. Rietveld refinements allow one to extract the behavior of the structural [17,18] and microstructural parameters and to describe their evolution versus the grain size at several temperatures. By this analysis, it is then possible to establish a detailed description of the evolution of the tetragonal phase versus the size of zirconia nanoparticles. These results are analyzed within the Landau theory and they can be understood by the mechanism of a size-induced phase transition where long-range interactions are altered by particle size.

Among the various methods synthesizing nanocrystalline ZrO_2 , the freeze-drying process [19] can produce very disperse single crystals with a narrow size distribution. $ZrCl_4$ was used as raw material to prepare very diluted aqueous solutions (4–8 g of $ZrCl_4$ /liter) that were evaporated to dryness at 360 K. In this work, nanocrystals of zirconia were synthesized decomposing an anhydrous sponge of $ZrOCl_2$ at temperatures ranging between 650 and 750 K during 600 s. X-ray diffraction, Raman scattering, and NMR were performed at room temperature to assess the tetragonal crystallographic structure and the absence of surface adsorbed OH. No

Raman signature of a cubic phase was observed. The transmission electron microscopy (TEM) also allowed us to show that each individual grain is a tetragonal single crystal (Fig. 1) and that the population has indeed a very narrow size distribution. To study the particle size effect on the phase transition kinetics, the as-prepared powders were put in a vanadium sample holder and several high resolution neutron diffraction patterns (about 400) were collected on the D20 high flux diffractometer at ILL Grenoble. Each diffraction pattern was collected in 180 s which seemed the best compromise between counting statistics and time resolution. These diffraction patterns were collected at fixed temperatures between 300 and 963 K to monitor simultaneously the change of the tetragonal and monoclinic volume fractions in the sample. Rietveld refinements on diffraction patterns allow to measure accurately ($R_{wp} \leq 5\%$) the intrinsic integral breadths of Bragg peaks of nanocrystals. The evolution of breadths versus the Bragg angles gives an estimation of nanoparticles sizes (Hall Williamson plots) at each temperature.

Only the tetragonal ($P4_2/nm c$) and the monoclinic ($P2_1/c$) phases are needed to fully explain the neutron diffraction patterns. The scale factor variations of these two phases do not suggest any significant disorder, additional short range order modulations, or the existence of other phases. A clear decrease of the tetragonal phase fraction is observed when the grain size increases. This result is consistent with Garvie's observations [6].

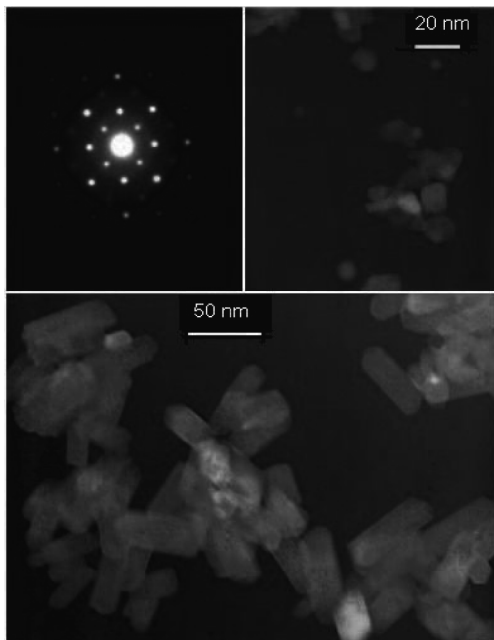


FIG. 1. TEM images of ZrO_2 nanocrystals for decomposed (top right) and annealed (bottom) samples. The electron diffraction inset (top left) obtained on a single particle shows that the sample is actually composed by single crystal particles. The growth occurs preferentially along one direction, explaining the needlelike shape of the annealed crystals.

Since grain boundaries are a source of excess energy, there is a thermodynamics driven force for the reduction of the overall grain surface which can be successfully achieved only increasing the average nanocrystal size φ_g . Only the width of 00l reflections decreases witnessing an increase of the grain size along the c_t axis. This evolution of the profile function enables us to compute accurate values of the grain size, φ_g . Figure 2 presents the time dependence of φ_g at different temperatures. The kinetics of the crystalline size show a classical parabolic evolution versus time and a stabilization of the grain size after 10 h. This parabolic law can be written as [20]:

$$\varphi_g^2 = \varphi_c^2 + 8m(T)\gamma t \quad (\varphi_g \geq \varphi_c), \quad (1)$$

where $m(T)$ is the grain boundary mobility, t is the annealing time, γ the surface free energy associated to the initial configuration of the grain, and φ_c the initial grain size (13.7 nm).

The temperature enters in the growth rate through the boundary mobility which can be written as [20]

$$m(T) = \frac{m_0}{T} e^{-(E_a/kT)}, \quad (2)$$

where m_0 is a constant and E_a is an effective activation energy for boundary migration. Figure 3 presents the dependence of $Tm(T)$ versus the annealing temperature T . A weighted least square fit yields an effective activation energy of about 0.4 eV. From this analysis of the increase of grain size, it seems that the grain size follows a classical law of grain boundary diffusion [16,20].

Because the grain size is the physical variable controlling the stability of the tetragonal phase of zirconia, all structural parameters are described as a function of the grain size instead of the annealing time.

Figure 4 clearly shows that the a_t parameter does not change whereas the c_t parameter increases when the grain size increases. TEM photographs (Fig. 1) of zirconia

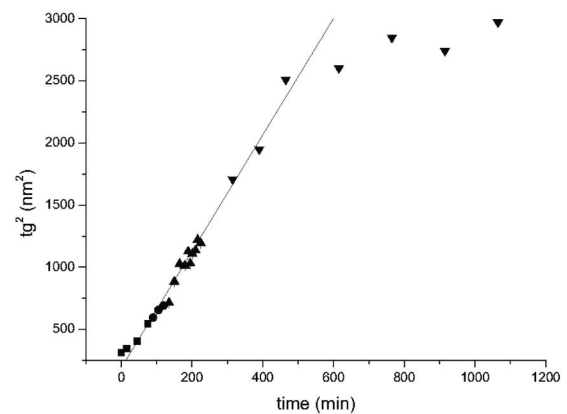


FIG. 2. Grain size of zirconia nanoparticles versus annealing time for annealing temperatures equal to 843 K (squares), 893 K (circles), 923 K (up triangles), and 963 K (down triangles). The fit clearly displays a parabolic evolution of the grain size with time for small times.

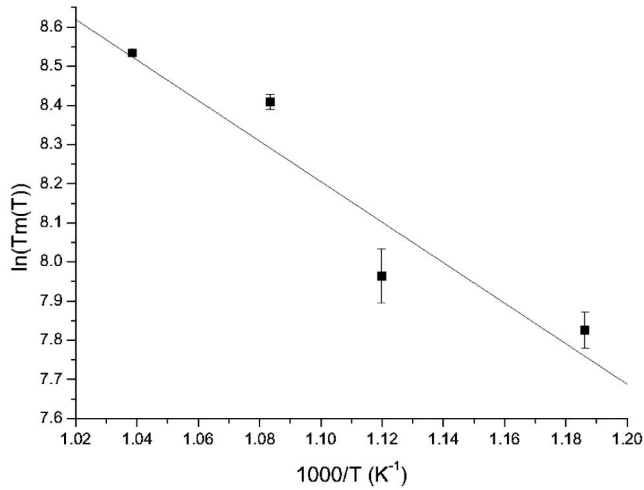


FIG. 3. $T_m(T)$ versus the annealing temperature. $T_m(T)$ follows a classical Arrhenius law (full line).

nanocrystals for different annealing temperatures exhibit an anisotropic growth along [001]. This supports a larger γ value for $(hk0)_t$ planes [6] and it explains the different behavior observed for the lattice parameters.

The evolution of the unit cells parameters of the tetragonal phase versus the grain size allows one to compute e_3 (using Voigt notation), the only pertinent component of the volume strain tensor within the grain, using a modified Laplace's law

$$e_3 \propto \frac{\gamma}{\varphi_g - \varphi_c}. \quad (3)$$

The estimated critical grain size φ_c is 13.6 nm in very good agreement with the previous estimation.

To analyze the mechanism responsible for the phase transition, the evolution of the tetragonal phase versus average grain size was studied. Neutron diffraction pat-

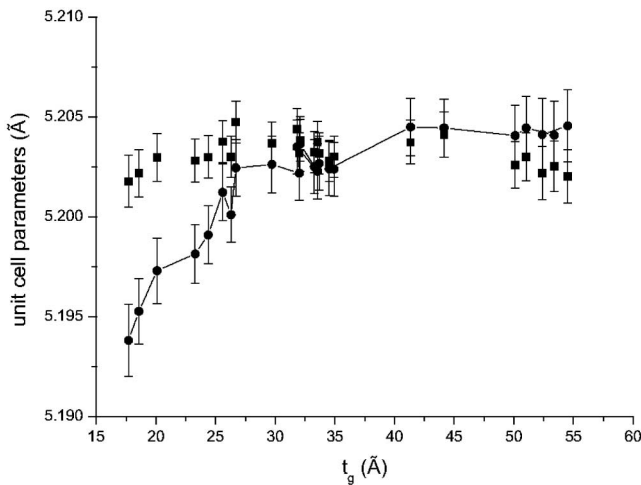


FIG. 4. Tetragonal unit cells parameters a_t (multiplied by 1.022, filled squares) and c_t (filled circles) as a function of the grain size. The parameter c_t decreases with the grain size, whereas a_t remains unchanged.

terns show that this transformation occurs continuously over the whole range of annealing temperatures and that the monoclinic and tetragonal phase still coexist in the sample. On the other hand, TEM observations show that the grain sizes in nanocrystalline zirconia follow a log-normal distribution. The observed change in the tetragonal volume fraction can be reproduced if we admit that any nanocrystal exceeding a given threshold size φ_t , independent on the annealing temperature, suddenly transforms into the monoclinic phase. This condition leads to the following relation, valid for all the annealing temperatures, between the average grain size in the sample and the volume fraction of the tetragonal phase

$$x_t(\bar{\varphi}_g) = \frac{1}{\sigma\sqrt{2\pi}} \int_0^{\varphi_t} \frac{1}{\varphi_g} e^{-\{[\ln(\varphi_g) - \bar{\varphi}_g]^2 / 2\sigma^2\}} d\varphi_g, \quad (4)$$

where x_t is the volume fraction of the tetragonal phase, $\bar{\varphi}_g$ is the average grain size, and σ^2 is the distribution variance. The best fit of these experimental data gives $\varphi_t = 54$ nm and $\sigma = 2$ nm. The small value of σ corresponds to a very sharp nanocrystal size distribution confirmed by the TEM observations. Figure 5 presents the comparison between the observed and calculated tetragonal volume fraction with the average grain size.

Moreover, the structural refinements allow us to study simultaneously the structure of the nanocrystalline tetragonal phase. No significant change of the position $z_t(O)$ of the O atom is observed in this phase at the different annealing temperatures. The tetragonal structures of micrometric and nanometric ZrO_2 are the same. Therefore, the structural instabilities in nanometric ZrO_2 can be described using the same Landau free energy expansion already used in micrometric ZrO_2 [21,22]. The primary order parameters (Zr and O displacements) and the corresponding choice of basis set invariants are the same in micrometric and nanometric zirconia. On the other hand, in nanometric zirconia the existence of a large surface

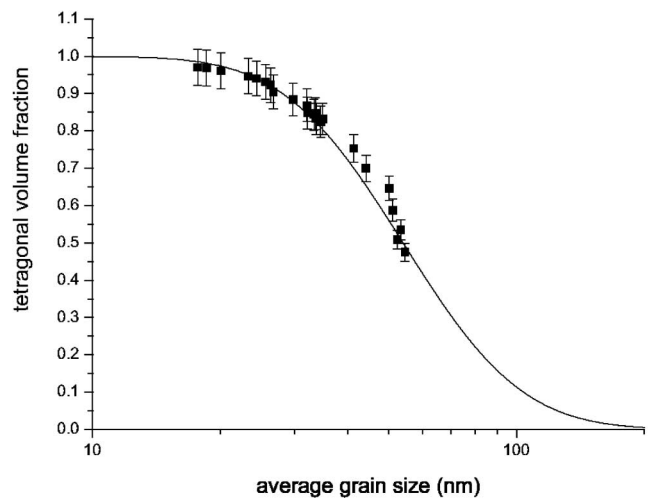


FIG. 5. Calculated (full line) and experimental (squares) tetragonal volume fraction of zirconia versus average grain size.

free energy constrains the secondary order parameters (strain field) to a fixed value which depends only on the observed grain size [Eq. (3)]. The existence of a coupling between secondary and primary order parameters leads to a pinning at a fixed value of the primary order parameters. This coupling is then responsible for the stability of the tetragonal phase in nanocrystals. The Landau free energy, F , computed to describe all possible couplings between order parameters [23] associated to the tetragonal to monoclinic phase transition in micrometric zirconia [21], can be successfully used to formulate the mechanism of this phase transition in zirconia nanocrystals as a function of the nanoparticle's size. To this purpose, it is still necessary to use two invariants, $I_1 = \eta^2 + \phi^2$ and $I_2 = \eta^2 \phi^2$, associated to Zr and O displacements, as a basis for the Landau free energy expressed in the tetragonal phase :

$$F(I_1, I_2) = \frac{(a + 2fe_3)}{2} I_1 + \frac{b}{4} (I_1^2 - 2I_2) + \frac{c}{2} I_2 + \frac{d}{6} (I_1^3 - 3I_2 I_1) + \frac{C_{33}}{2} e_3^2, \quad (5)$$

where a, b, c, d, f are phenomenological coefficients and C_{33} is the isothermal elastic constant [24]. The existence of two phases for different grain sizes dictates a positive value of the phenomenological coefficient f .

This equation shows that for different grain sizes, the strain tensor component e_3 changes the relative stability of the monoclinic and tetragonal phases by modifying the coefficient of the linear term of I_1 . The critical temperature, controlling the evolution of this leading term in F , exhibits a grain size dependence. This critical temperature is negative for $\varphi_g < \varphi_t$, quenching the tetragonal phase at all temperatures. On the other hand, when $\varphi_g > \varphi_t$, this critical temperature becomes positive and the phase transition may occur.

Thus, the behavior of the tetragonal to monoclinic phase transition in nanometric ZrO_2 can be effectively predicted within the same framework already developed for the more common micrometric phase. No additional primary order parameters are necessary to explain the experimental observations. The grain size, responsible for the observed uniaxial strain related to the surface tension, simply induces a shift of the frontier between the stability domains of the monoclinic and tetragonal phases in the (I_1, I_2) phase diagram [21].

Therefore, the key parameter controlling this phase transformation is not the annealing time but the crystal size. This mechanism of primary order parameter being altered by the particle size can possibly be extended to other technologically relevant oxide [25] based systems where a structural change is expected when the particle size is reduced.

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