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Structural properties of ultra-fine zirconia powders obtained by precipitation methods

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We have investigated various aspects of the stabilization of the tetragonal (t) and cubic (c) forms (metastable at room temperature) with respect to the monoclinic (m) form in ultrafine zirconia powders obtained by calcining amorphous hydrated zirconium oxides at various temperatures. They were prepared by precipitation from $ZrOCl_2$ at different pH, using either NaOH or NH_4OH solutions. We have clarified the importance of the role of Na^+ ions in the initial zirconia gel as stabilizers of the cubic form. On the contrary, almost pure tetragonal phase was obtained at moderately low temperatures starting from precursors with a low content of sodium ($\leqslant 0.5$ wt%). By means of an X-ray diffraction (XRD) study and a suitable peak profile fitting procedure (convolutive method for the pattern decomposition followed by a straightforward Fourier analysis) the amounts of the different crystallographic forms as well their microstructural properties such as crystallite size and lattice disorder (when present) were obtained. The thermal evolution of the systems were followed by both differential thermal analysis (DTA) and XRD, and we studied the martensitic t → m transformation obtained by pressing a zirconia powder containing a prevailing content of t form at room temperature. To obtain further microstructural and morphological information on the c → m transition, transmission electron microscopy and small angle X-ray scattering techniques were used.

1. Introduction

The use of fine powders of zirconium oxide as a catalyst or as a support for metal catalysts has lately become increasingly popular [1–3]. It is therefore important to determine the factors that stabilize the metastable phases (tetragonal and cubic zirconia) against the stable one (monoclinic) at relatively low temperatures, especially when preparation methods of precipitation are employed for the precursor material.

The role of the pH (and time to attain the final pH) in the precipitation of the amorphous hydrated zirconium oxide has recently been reported [4–6], whereas it has been shown [7] that the presence of sodium (3 wt %) inside the gel precipitated at pH 13.5, using a solution of NaOH as alkali, causes the formation of the cubic zirconia phase after a suitable calcination treatment. On the contrary, the same initial gel which was thoroughly washed until the washing water proved neutral (the final content of sodium decreased to 0.5 wt %) did not give rise, after the calcination step, to a cubic zirconia, but to a mixture of tetragonal and monoclinic forms.

The aim of the present work is to analyse in more detail the microstructural features of the zirconia powders obtained as previously described and calcined at different temperatures by means of X-ray diffraction (XRD) methods and electron transmission microscopy (TEM). We have also used differential thermal analysis (DTA) to follow the thermal evolution of the initial gels, particularly in order to establish the temperature range of stabilization for the cubic form in the presence of sodium ions, also in comparison with the different route of reversion to monoclinic zirconia presented by the tetragonal crystalline form. At the same time we have investigated the possible role played by lattice distortions (microstrain) in the stabilization of the metastable zirconia crystalline forms.

2. Experimental details and methods

A gel of zirconia (amorphous hydrated zirconium) was precipitated from $ZrOCl_2$ using a NaOH solution at pH 13.5 (samples A and B). Sample A was washed three or four times and sample B thoroughly, until the washing water proved neutral. As a result, sample A and sample B contained 4 and 0.5 wt % of sodium, respectively, as measured by atomic absorption analysis. Another gel (sample C) was precipitated by using a solution of NH_4OH at pH 8.

In order to investigate the thermal evolution of these three gel specimens a differential thermal analysis (DTA) was performed using a Netzsch apparatus with calcined alumina as the reference material. The following experimental conditions were set: heating rate of $5^\circ C\,min^{-1}$; sensitivity of 0.2 mV for a full scale expansion; sample weight of 250 mg. On the basis of the DTA traces, different calcination temperatures

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TABLE I Samples preparation features

Initial gel	pH of precipitation	Sodium content (wt %)	Zirconia samples with the relevant calcination temperature (° C)
A	13.5 (with NaOH)	4.0	A_1 (435); A_2 (545); A_3 (580) A_4 (620); A_5 (695); A_6 (900)
B	13.5 (with NaOH)	0.5	B_1 (380); B_2 (435)
C	8 (with NH_4OH)	0.0	C_1 (390)

were selected for a prefixed time of 24 h, as recorded in Table I.

The different crystalline forms of the zirconia samples so obtained, their relative amounts and their microstructural features like crystallite and particle sizes as well as the microstrain (when present) were determined by using wide angle XRD procedures described in detail [7–9] elsewhere. These procedures are based on a peak profile "convolutive" refinement method which also takes into account the peak asymmetry in the instrumental broadening thus extracting only the structurally broadened best-fitted analytical profiles in the form of pseudo-Voigt functions, as referred to the $K\alpha_1$ contribution. When limited angular ranges in the XRD pattern were analysed, the optimization was carried out using a modified version of the Simplex method [10] with a program in Basic running on Olivetti Personal Computers M24. When it was necessary to perform a total-XRD-pattern decomposition, a version of the MINUIT/CERN program (in Fortran) was used and made to run on a Cray X-MP/48 computer.

By applying the Fourier analysis (see for example [8] where there is a description of the Warren–Averbach method as directly applied to the analytical best-fitted peak profiles) to the broadened (1 1 1)–(2 2 2) XRD peaks, we obtained the volume weighted crystallite size distributions from which the relevant average crystallite diameters $\langle D \rangle$ were derived. We also obtained the r.m.s. microstrain $\langle \varepsilon^2(L) \rangle^{1/2}$ function, which was computed by us at $\langle D \rangle/2$, with L distance in the direct space over which the microstrain is averaged.

We used a Philips vertical goniometer connected to a highly stabilized generator. Ni-filtered Cu$K\alpha$ radiation was employed and the diffracted X-ray beam was scanned using suitable step sizes in 2Θ (0.02° or 0.05°); 2×10^4 pulses per angular abscissa were accumulated using a proportional counter as detector.

The sizes of ZrO_2 particles were determined by means of small angle X-ray scattering (SAXS) and by transmission electron microscopy (TEM). An outline of SAXS equations employed by us is reported elsewhere [11, 12]. We used a Kratky camera with a Zr-filtered Mo$K\alpha$ radiation and a scintillation counter with fixed counting statistics of 10^5 pulses per point.

3. Results and discussion

3.1. Zirconia samples containing 4 wt% sodium

Figure 1 shows the DTA diagrams for the three zirconia gels A, B and C with the selected calcination temperatures. From an accurate fit of the XRD peaks in the angular region between 69.5° and 77.5° in 2Θ (see Fig. 1a and b of [7] as an example), which is well suited for the purpose of distinguishing the tetragonal lattice of zirconia from the presence of the (0 0 4)–(4 0 0) doublet, it was possible to conclude that samples A_1, A_2 and A_3 contain only the cubic form (a = 0.5113(2) nm for all the three samples). This value is intermediate between the unit cell edge found by Nishizawa *et al.* (0.5119 nm, see [13]) and that

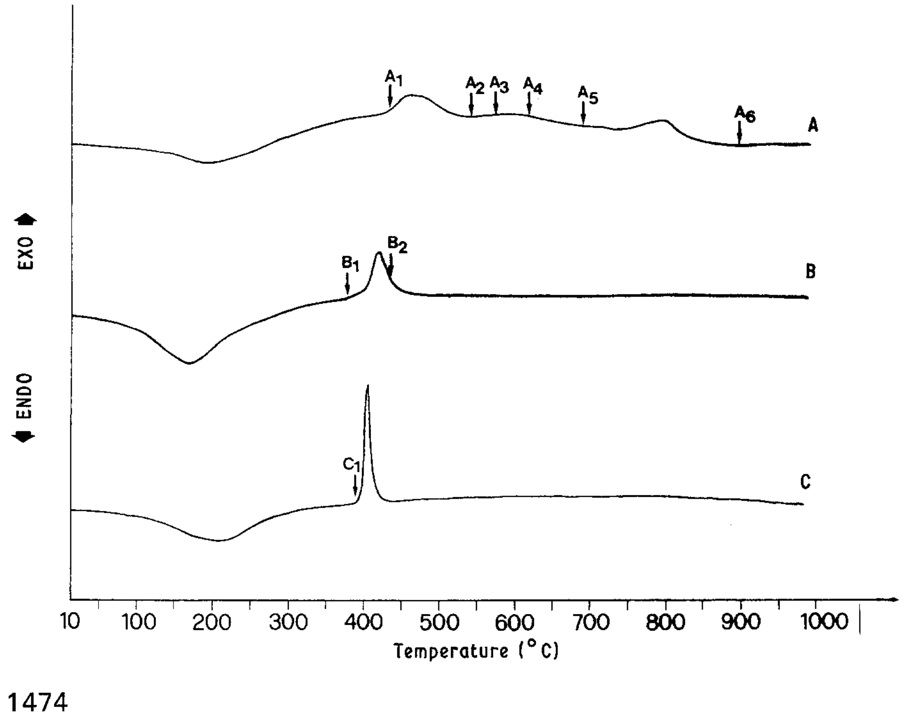

Figure 1 Materials thermal evolution. DTA traces of A, B and C gels where the temperatures of calcination are indicated by arrows.

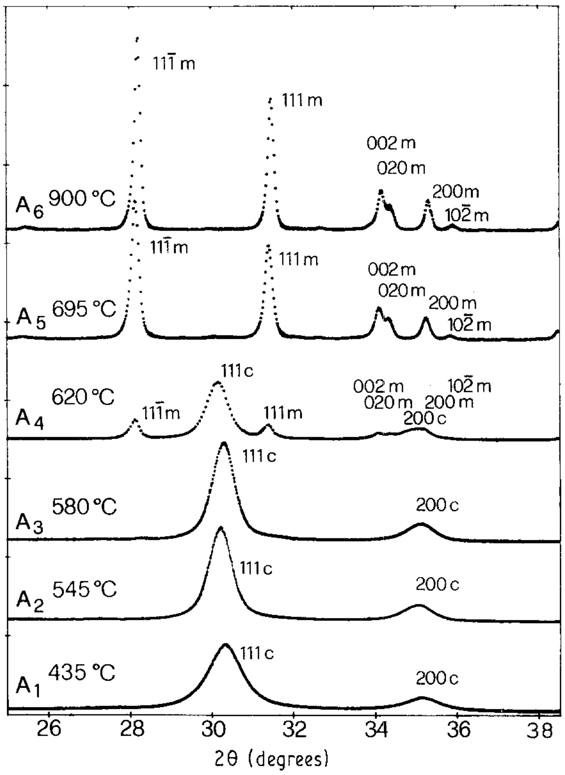

Figure 2 Phase transition from c to m zirconia for the samples of A-series, containing 4 wt % sodium, analysed by X-ray diffraction as function of the calcination temperature.

found by Katz (0.5090 nm, see [14]). It is worth noting that the above authors have also prepared the precursors of zirconia metastable cubic samples by means of NaOH solutions.

Therefore, the first pronounced exothermic peak in the A trace of Fig. 1, which follows the endothermic effect given by the dehydration of the gel, is certainly caused by the crystallization process of zirconia in the cubic metastable form. It is very interesting to note, in the same DTA trace, a second very weak and enlarged exothermic peak centred at about 580° C and another pronounced exothermic peak at about 800° C. The sample calcined at 620° C (A_4), immediately after the slight exothermic effect, turned out to be a mixture of cubic and monoclinic forms (see Fig. 2), whereas at 695° C zirconia has completely transformed into the stable monoclinic phase. It is therefore a logical conclusion to ascribe this very weak exothermic effect to the c → m phase transition for which not too much heat can evolve owing to the similar crystal structure of the two phases. This is the first case, to our knowledge, in which the c → m phase transition at low temperature has been described with combined DTA and XRD investigations. They have permitted the discovery of a slight but unequivocal exothermic effect, clearly distinct from the first crystallization peak. Quite differently, the t → m phase transition does not usually give a distinct exothermic effect either because it is concurrent with the crystallization process or because it is very broadly spread out on the temperature scale.

The third exothermic effect, present only in the DTA trace of A gel, can be ascribed to a sudden recrystallization process of the monoclinic phase (baddeleyte). As a matter of fact, the monoclinic lattice parameters decrease passing from sample A_5 to sample A_6 as follows:

Sample A_5:
$a = 0.5151(7)\,\mathrm{nm}$; $b = 0.5228(7)\,\mathrm{nm}$;
$c = 0.5318(8)\,\mathrm{nm}$; $\beta = 99.2°\ (2)$
Sample A_6:
$a = 0.5141(3)\,\mathrm{nm}$; $b = 0.5215(3)\,\mathrm{nm}$;
$c = 0.5308(5)\,\mathrm{nm}$; $\beta = 99.1°\ (1)$

Fig. 3 shows TEM micrographs relevant to A_1 and A_2 samples of zirconia whose approximate particle sizes are recorded in Table II.

The amounts (vol %) of the two crystalline forms (c and m) present in sample A_4 (see Table II) have been computed with the procedure by Toraya *et al.* [15], by fitting and separating the 1 1 1 reflection of the cubic form from the 1 1 $\bar{1}$ and 1 1 1 peaks of the monoclinic one. As an example, Fig. 4 shows the total-XRD pattern refinement of sample A_2 performed with the MINUIT/CERN program.

Table II records the average crystallite and particle sizes for three zirconia samples of the series originated from gel A, containing 4 wt % of sodium. The similarity of the sizes obtained with such different methods for samples A_1 and A_2 (XRD-Line Broadening, SAXS and TEM) indicates that the particles are essentially monodomains in the zirconia samples calcined at lower temperatures. No lattice disorder was detected, within the $\langle D \rangle$ range, by the peak profile Fourier analysis on all cubic zirconia powders here examined, in contrast with our previous results reported in [7].

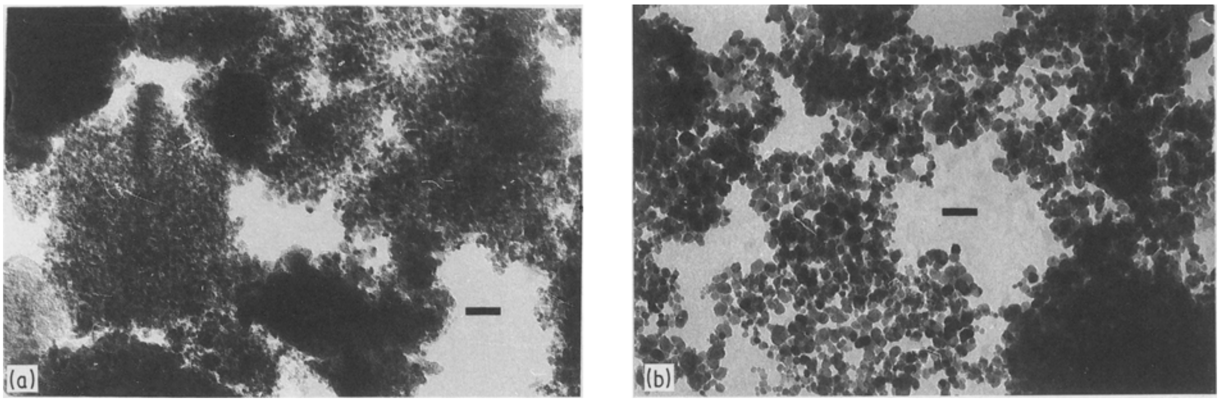

Figure 3 TEM micrographs of samples (a) A_1 and (b) A_2. The bar corresponds to 50 nm.

TABLE II Average crystallite and particle sizes and r.m.s. microstrain for zirconia samples A_1, A_2, A_4 and B_1

Zirconia samples	*Crystalline form (vol %)	†Average crystallite size $\langle D \rangle$ (nm)	Average particle size (nm) SAXS‡	TEM	Average microstrain $\langle \varepsilon^2 \rangle^{1/2}$ at $\langle D \rangle/2$
A_1 (435°C)	100c	6.4	7.1	~5	<0.0005
A_2 (545°C)	100c	10.7	15.1	~15	<0.0005
A_4 (620°C)	76c + 24m	11.4	n.d.	~20	<0.0005
B_1 (380°C)	91t + 9m	7.5	n.d.	n.d.	0.0034 (in t-phase)

(c = cubic; t = tetragonal; m = monoclinic)

*Obtained by the procedures of Toraya *et al.* [15, 18]. Error: ±2%.

†Volume-weighted average size obtained by the line-broadening Fourier analysis: Warren–Averbach method applied to the pair of (1 1 1)–(2 2 2) XRD reflections pertinent to c or t-phase. Error: ±10%.

‡Volume-weighted average size obtained by small-angle X-ray scattering using the Schmidt–Fedorova [12] approach. Error: ±15%.

On the other hand, by means of an analysis using the equation developed by Halder and Wagner [16], which in our case took into account the integral breadths of the (1 1 1)–(2 2 2) pair of $K\alpha_1$ reflections (corrected by instrumental broadening), we have detected a lattice microstrain of about 0.001. In any case, as shown by Crist and Cohen [17], a Gaussian component to the "true" structurally broadened peak profile can be caused also by sample inhomogeneity (fluctuation of lattice parameter from crystal to crystal within the polycrystalline sample). Therefore, it is not possible to state that the cubic metastable zirconia samples investigated by us contain lattice distortions; if they are present, however, they must be very low.

3.2. Zirconia samples containing 0.5 wt% sodium

The two samples B_1 and B_2, the first obtained at the foot of the exothermic peak (see the DTA diagram B) and the second after the peak maximum, are a mixture (see Fig. 5) of tetragonal and monoclinic forms (91 t–9 m vol % and 50 t–50 m vol %, respectively) as seen by an XRD analysis based on a procedure by Toraya *et al.* [18]. The computed lattice parameters for the t phase in the B_1 sample are:

$$a = 0.5090(4)\,\text{nm}; \qquad c = 0.5183(4)\,\text{nm}.$$

It is worth noticing that a halo due to an incompletely crystallized amorphous phase is shown in the diffractogram of B_1, at low 2Θ angles (see Fig. 5a). In this sample a lattice disorder analysis was carried out using the Warren–Averbach method on the (1 1 1)–(2 2 2) pair of reflections, after separating them from partially overlapped neighbouring peaks by means of the cited peak profile refinement procedure. A value of 0.0034 was determined for the microstrain $\langle \varepsilon^2(L) \rangle^{1/2}$

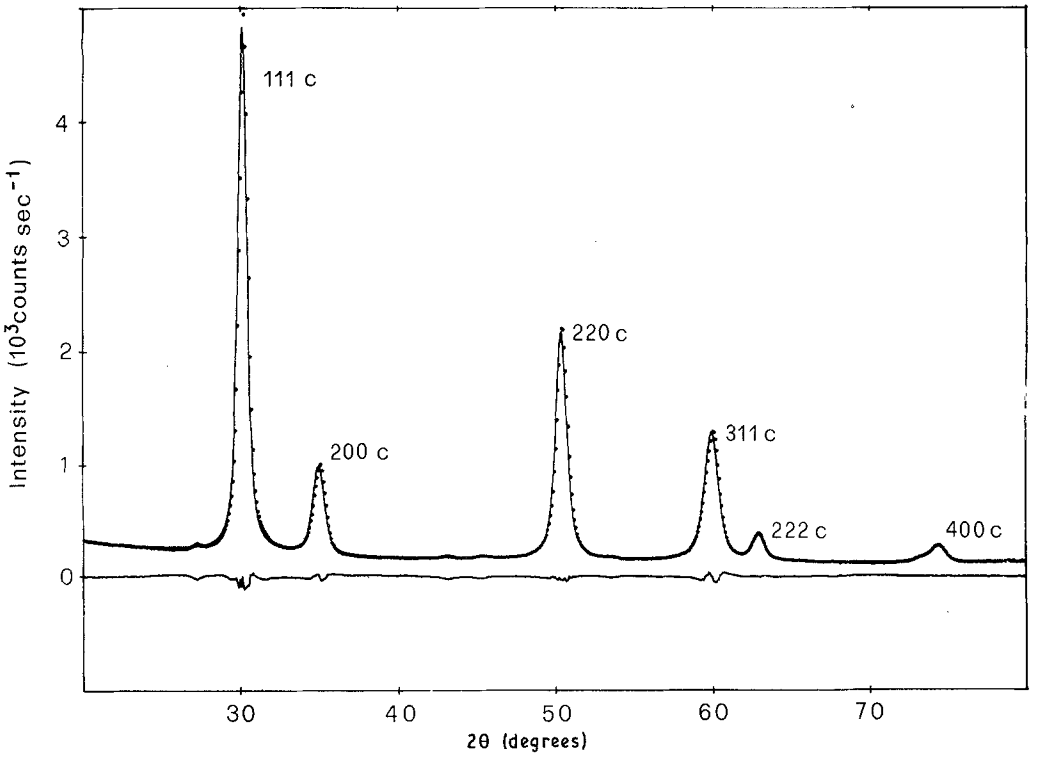

Figure 4 Total XRD-pattern refinement of sample A_2 (cubic metastable zirconia). The reliability index [8]:

$$R_p = \left\{ \frac{\sum_{i=1}^{N} [I_{\text{fit}}(2\theta_i) - I_{\text{obs}}(2\theta_i)]^2}{\sum_{i=1}^{N} [I^2_{\text{obs}}(2\theta_i)]} \right\}^{1/2}$$

results equal to 0.019. $I_{\text{fit}}(2\theta_i)$ and $I_{\text{obs}}(2\theta_i)$ are the computed and the observed intensities, respectively as defined at the corresponding $2\theta_i$ Bragg angles.

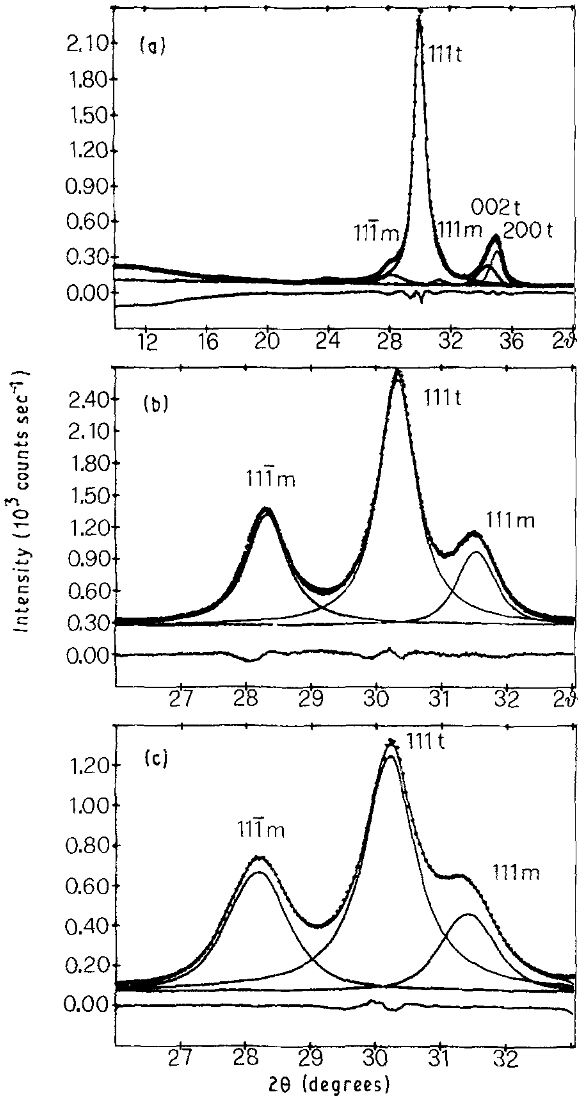

Figure 5 XRD peak profile fitting for (a) B_1 and (b) B_2 samples as well as for (c) B_1 sample pressed at 0.2 GPa for 2 h.

(computed at $L = \langle D \rangle /2$). The third diffractogram shown in Fig. 5c refers to the same B_1 powder after having pressed it at 0.2 GPa for 2 h. The monoclinic form content has considerably increased (from 9 to 53 vol %) due to the occurrence of the martensitic t → m phase transition.

In the case of zirconia samples rich in monoclinic phase like the pressed B_1 sample we simply applied the Scherrer equation by using the FWHM of the tetragonal (1 1 1) and monoclinic (1 1 $\bar{1}$) $K\alpha_1$ fitted profiles in order to compute the volume-weighted crystallite size. In effect, the separation of the different contributions to line broadening is not reliable when too large a peak overlapping is present in the diffractograms, even if refinement procedures are used. As a result, a value of 10.5 nm was determined for the tetragonal phase, while a value of 8.5 nm was calculated for the monoclinic phase martensitically transformed from the tetragonal phase by pressure. This "unexpected" result is similar to those reported by various authors [5, 6, 19, 20] in the case of polymorphism induced by thermal treatments and it was tentatively attributed by the above cited authors to twinning and/or strain fracture of baddeleyte crystals. It is worth noticing that, using the most precise Warren–Averbach method (see Table II) on the tetragonal (1 1 1)–(2 2 2) pair of reflections, an average crystallite size of 7.5 nm was found for the non-pressed sample B_1 (for which the Warren–Averbach method can be applied). It is therefore likely that a more precise value for the average crystallite size for the monoclinic form present in the pressed sample should be smaller than the value of 8.5 nm previously indicated. Therefore, in the framework of the Garvie's [21, 22] size effect stabilization hypothesis for the metastable tetragonal form of zirconia, it is possible to conclude that the critical radius above which the baddeleyte phase becomes stable cannot be larger than about 3.5–4.0 nm.

4. Conclusions

From all the evidence concerning the cubic zirconia polymorph (samples A_1–A_2–A_3) we have confirmed the role of Na^+ ions present in the initial gel in stabilizing this crystalline phase. Very likely Na^+ ions in the cubic zirconia structure are associated with oxygen vacancies required to maintain charge balance. This result is in agreement with that of Nishizawa *et al.* [13, 23] who succeeded in stabilizing, at room temperature, the cubic form of zirconia by inserting Na^+ (or Ca^{2+}) ions into the initial gel by means of suitable hydrothermal reactions. Also Clearfield [24] has reported obtaining cubic zirconia by heating amorphous hydrous zirconia in the presence of aqueous NaOH or KOH solutions. For the high pH (13.5) here used, which can be reached only by employing NaOH or KOH as alkali in the precipitation process, the role of the pH itself does not appear to be as important as hypothesized by Davies [4] and Srinivasan *et al.* [5, 6]. As a matter of fact, while the precursors A and B derive from the same gel precipitated at pH 13.5, only samples A_1, A_2 and A_3, which contain 4 wt % of sodium, have, after the calcination step, shown a cubic structure that is stable up to about 600° C.

Srinivasan *et al.* [5, 6] attribute to the tetragonal polymorph the XRD patterns of zirconia samples obtained from a precursor precipitated at a pH of about 13.5, using either NaOH or KOH as alkali, after a calcination at 500° C, but we think that their samples too could be cubic and not tetragonal, as already discussed by us elsewhere [7]. As a matter of fact, because of the broadness of the peaks, only a fitting procedure similar to that used in the present paper can clearly distinguish, at the appropriate angular 2Θ interval (see for example Figs 1a and b of [7]), between a cubic or a tetragonal (pseudo-cubic) zirconia phase.

The sample C_1, which does not contain sodium since it originated from a precursor prepared using NH_4OH at pH 8, is a mixture of tetragonal (54 vol %) and monoclinic forms (46 vol %) in agreement with the present hypothesis on the role of sodium (and/or of the associated oxygen vacancies) in stabilizing the cubic zirconia, but also in agreement with a possible role that pH could play in the calcined samples with respect to the tetragonal/monoclinic phase content ratio, when an alkali like NH_4OH is used in the precipitation of the precursor [4].

Finally, from the present results we can infer that lattice distortions could be another cause in stabilizing the tetragonal metastable form as already suggested by Mitsuhashi *et al.* [25] and by Fagherazzi *et al.* [26]. On the other hand, the lattice disorder can also arise in the course of the t → m martensitic transformation and therefore the presence of microstrains in sample B_1 could also be attributed to this process.

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