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Hydrothermal synthesis of ZrO_2–Y_2O_3 solid solutions at low temperature

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Abstract

Ultrafine powders of ZrO_2–Y_2O_3 solid solutions have been synthesized by hydrothermal treatment at 110°C. Zirconia gel, crystalline Y_2O_3 and various mineralizing solutions have been utilized as precursors for the hydrothermal synthesis. Yttria-stabilized zirconia (YSZ) with different Y_2O_3 content and characterized by different crystallite sizes have been produced by changing the hydrothermal treatment temperature, and the nature and concentration of the mineralizer solution. The role of mineralizer solutions on the crystallization-stabilization of zirconia gel at low temperature of hydrothermal treatment is discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Zr_2O_2–Y_2O_3; Powders-chemical preparation; Hydrothermal synthesis; Mineralizers

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1. Introduction

Wet-chemical methods represent a route procedure[1–7] which enables the production of reactive and chemically more homogeneous powders of ZrO_2 solid solutions. Nevertheless, in the densification process during compaction and sintering, weakly agglomerated powders must also result by applying adequate procedures.[8–12] Some preliminary treatments, in removing the water and non-bridging hydroxo groups of wet-chemically prepared powders, are necessary to reduce formation of hard agglomerates associated with condensation reactions involving non-bridging hydroxo groups during the calcination of powders. The reduced inter-crystallite and inter-agglomerates bonding strengths of conventionally co-precipitated powders favour the formation of uniform pore-size distribution compacts[13–15] and the production of zirconia ceramics with enhanced properties. Among such preliminary treatments, the hydrothermal treatment appears to be the more simple and less expensive method.

Y_2O_3-stabilized ZrO_2 (YSZ) with cubic or tetragonal structure can be synthesized at much lower temperatures than 1300°C as requested in powder processing. The formation of cubic phases, by heating at approximately 450°C fine particles of co-precipitates obtained from different precursors, is well known. Precipitation from aqueous solutions of inorganic precursors,[7] hydrolysis of alkoxides,[5,16] combustion process[17] represent alternative methods of synthesis at low temperatures. YSZ powders were also prepared by hydrolysis of conventional coprecipitates in the presence of an excess amount of ammonia at 190°C for 1 h.[18] The hydrothermal treatment was carried out in any case by using zirconia gel as a precursor.

Further studies showed that the crystallization of zirconia gel depends upon both mineralizer solution and on the conditions of thermal treatment.[19–21] Metastable tetragonal and cubic zirconia have been produced, in fact, with various mineralizers. In a recent paper, the synthesis of mouldable powders of CaO-stabilized zirconia by hydrothermal treatment at low temperature has been achieved by using an alkaline hydroxide as mineralizer solution.[22] The aim of this work concerns the possibility to produce, in a single step, mouldable YSZ powders by low-temperature hydrothermal treatment.

2. Experimental procedure

Zirconia gel, crystalline Y_2O_3, Na_2CO_3 and/or NaOH solutions were employed as precursors for the hydrothermal synthesis.

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A prepared batch of zirconia gel precursor was precipitated from GR grade $ZrCl_4$ (Merck, Germany) solution with ammonia, filtered and repeatedly washed with distilled water to remove the chloride ions. The ZrO_2 content of this precursor was determined by thermogravimetric analysis (TGA). The dopant of zirconia was crystalline and commercially available Y_2O_3 of GR grade (BDH, UK). Both NaOH and $Na_2CO_3.10H_2O$ of RPE grade (C. Erba, Italy) were utilized for the preparation of mineralizer solutions at concentration levels ranging from 0.01 to 3.0 M. Many different suspensions with the mol% Y_2O_3 content changing in a wide range of composition up to 25% were prepared.

The temperature of the hydrothermal treatment was 110°C and a solid/liquid ratio equal to 1/40 was adopted. The reaction time was on average 7 days, but in some cases shorter or longer durations were also adopted. The precursors were transferred to half-filled and sealed Teflon vessels (250 mm^3) held in an outer pressure vessel made of stainless steel. Such vessels were rotated in air-thermostated oven at about 25 rpm to mix the precursors during the hydrothermal treatment. After the selected reaction, the products were filtered and repeatedly washed with distilled water until to remove Na^+ ions, and dried on silica gel.

The products were characterized by X-ray powder diffractometry (XRD) using a X'PERT diffractometer of Philips and CuK_α radiation. The crystallite size of products were determined by the Scherrer formula by measuring the half width of XRD peak with a software for the correction of $\alpha1\alpha2$ overlap and by using polycrystalline silicon for the correction of instrumental broadening.

The powders were also characterized by simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) using a Netzsch thermoanalyzer mod. STA 409, α-Al_2O_3 as reference and a 10°C min^{-1} heating rate. The specific surface area of powders was determined by the BET method using a Gemini of Micromeritics and utilizing nitrogen as adsorbate after drying at 60°C. The morphology of powders was analyzed by scanning electron microscopy (SEM) using a Philips model XL30.

3. Results and discussion

3.1. Hydrothermal treatments of zirconia gel with Na_2CO_3 solutions

The batch of ZrO_2-based precursor resulted amorphous material according to XRD, showed in DTA a very sharp exothermic peak of crystallization into tetragonal zirconia at 420°C and gave in TGA a weight loss of 23%.

The employment of Na_2CO_3 in the mineralizer solutions during the crystallization-stabilization of zirconia gel, will be explained below.

The phases present in products of hydrothermal treatments performed on zirconia gel at 110°C for 7 days in the presence of increasing Na_2CO_3 concentrations are gathered in Table 1. The treatment in 0.01 M Na_2CO_3 resulted in an amorphous product, while a mixture of amorphous, monoclinic and tetragonal zirconia has been revealed in 0.05 M. The test carried out in 0.10 M resulted instead in a fully crystallized mixture of monoclinic and tetragonal zirconia. The typical exothermic peak in DTA at 420°C, due to the crystallization of zirconia gel resulted, in fact, absent indicating full crystallization of the gel precursor.

The treatments in 0.50, 1.0 and 3.0 M Na_2CO_3 solutions resulted in mixtures containing cubic zirconia whose content increased with increasing mineralizer concentration, while the content of the monoclinic form decreased. Traces of uncrystallized zirconia are present in products of treatments in 0.5 and 1.0 M Na_2CO_3, while a full crystallization resulted in 3.0 M Na_2CO_3. The effect of increasing mineralizer concentration favours the following sequence of zirconia phases:

$$\text{Amorphous} \rightarrow \text{Monoclinic} \rightarrow \text{Tetragonal} \rightarrow \text{Cubic}$$

Such a sequence can be explained in terms of surface-energy theory.[23] The products of hydrothermal treatments are characterized, in fact, by decreasing crystallite sizes as the concentration of the Na_2CO_3 mineralizer was increased (Table 1). According to Garvie,[23] the particle size for stabilizing the metastable tetragonal phase must be $\leqslant 30$ nm. The formation of metastable tetragonal ZrO_2 in the products obtained in 0.05 and 0.1 M agrees both with the values 8.6 and 9.3 nm of the crystallite sizes of phase precursors (monoclinic) and with those of tetragonal form. The presence of the metastable cubic phase in the products obtained in the

Table 1

Phases present, surface area, crystal size and % weight loss of products obtained by hydrothermal treatment of zirconia gel at 110°C for 7 days as a function of concentration of Na_2CO_3 mineralizer[a,b]

Na_2CO_3 molarity	Phases, crystal size (nm)	Surface area (m^2/g)[c]	Weight loss (%)[c]
0.01	A***	270	22.3
0.05	A**, M* (8.6)[b], T* (31.0)	186	22.1
0.10	M** (9.3), T** (18.3)	53	11.2
0.50	[A], M** (4.6), C* (2.5)	64	14.3
1.0	[A], M* (4.7), C** (2.3)	67	15.3
3.0[d]	M* (5.1), C*** (2.5)	79	21.7

[a] A, M, T and C are amorphous, monoclinic, tetragonal and cubic ZrO_2, respectively. Phase content: *** high, ** medium, * small.

[b] Square brackets indicate the presence of traces of a phase, round brackets indicate the crystal size of phases.

[c] 285 m^2/g and 23.0% are surface area and weight loss of untreated zirconia gel, respectively.

[d] Solution prepared at 100°C.

presence of higher Na_2CO_3 concentration also agrees with the surface-energy theory. In this case, the crystal sizes of phases precursors on average are lower than 5 nm, while the crystal sizes of cubic ZrO_2 on average are of order of 2.4 nm.

The weight loss, determined by TGA, of the same products is reported in Fig. 1. The minimum in the curve corresponds to a fully crystallized product obtained in 0.1 M Na_2CO_3. The decrease in the weight loss from 22.3 to 11.2% of products, obtained with mineralizer concentrations ranging between 0.01 and 0.10 M Na_2CO_3, can be related to the increasing crystallization degree of gel the precursor. The successive weight loss increase of fully crystallized products obtained at increasing concentration up to 3.0 M, can be related to the corresponding crystallite size decrease of the products.

An analogous trend for the specific surface area of the same products at increasing Na_2CO_3 concentration has been observed and is given in Fig. 2. Also in this case the minimum in the surface area was measured for the product obtained in 0.1 M Na_2CO_3. The two minima of Figs. 1 and 2 correspond to the mineralizer concentration which separates the partial crystallization of zirconia gel from that of full crystallization. The minimum corresponds also to the minimum driving force in promoting the full crystallization of the gel. At concentration higher than that of the minimum, a higher driving force for the structural rearrangement of the gel is to be expected so determining the formation of products characterized by a progressive increase of the surface area according to the observed decrease in the crystal sizes.

These results are very similar to those found when NaOH solutions have been employed as mineralizer during the hydrothermal crystallization of zirconia gel.[22] In this last case the minimum is shifted to slightly lower NaOH concentration according to the strong basic character of the mineralizer.

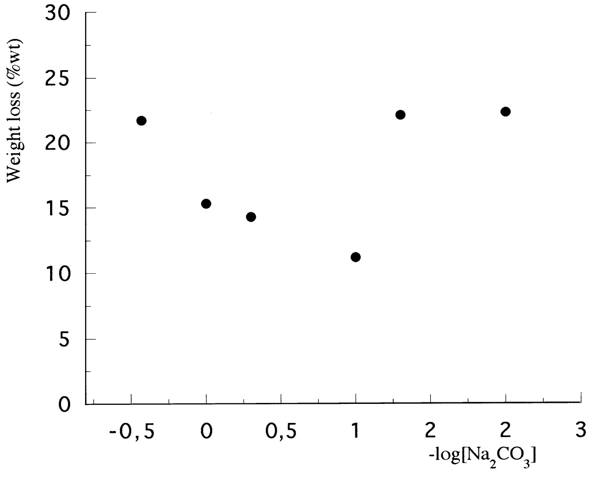

Fig. 1. Weight loss of products obtained from ZrO_2 gel hydrothermally treated for 7 days at 110°C and in the presence of increasing Na_2CO_3 concentrations.

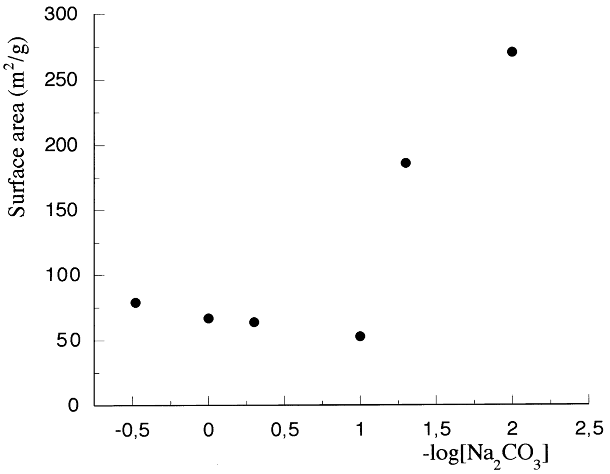

Fig. 2. Surface area of same products of Fig. 1.

Taking constant temperature and duration of hydrothermal treatment, the concentration of the mineralizer solution and, in particular, the basic value of pH influences the rate of structural rearrangement of gel during its crystallization by promoting the formation of oxo-bridgings between the non-bridging structural hydroxyl groups present in the gel. The rate of such a structural rearrangement is favoured by increasing pH values, while an insufficient driving force is forecast at relatively low pH. As the minimum in the curve of Fig. 1 or 2 corresponds to the minimum concentration of mineralizer solution able to promote the full rearrangement of gel, the corresponding nucleation rate must be relatively low in agreement with the measured and relatively high crystal sizes of the corresponding hydrothermal products. For pH values higher than that at the minimum in the curves of Fig. 1 or 2, the increasing driving force determines an increasing nucleation rate. In this circumstance the formation of products with decreasing crystallite sizes is favoured. These results agree with those of Nishizawa et al.[24] Cubic zirconia, in fact, was observed in NaOH solutions higher than 1 M and at 130–140°C and the crystallite size decreased as the concentration of the NaOH mineralizer was increased.

All the products of hydrothermal treatment obtained in different concentrations of mineralizer solution, when thermally treated at temperatures higher than 700°C, transform into monoclinic ZrO_2 so showing the metastable character of both crystallized tetragonal and cubic forms.

3.2. Hydrothermal treatments of ZrO_2 gel in the presence of Y_2O_3 and mineralizer solutions

Various attempts to synthesize YSZ failed when mixtures of zirconia gel and crystalline Y_2O_3 were hydrothermally treated both in the presence or absence of NaOH as a mineralizer solution. Fig. 3(b) shows the

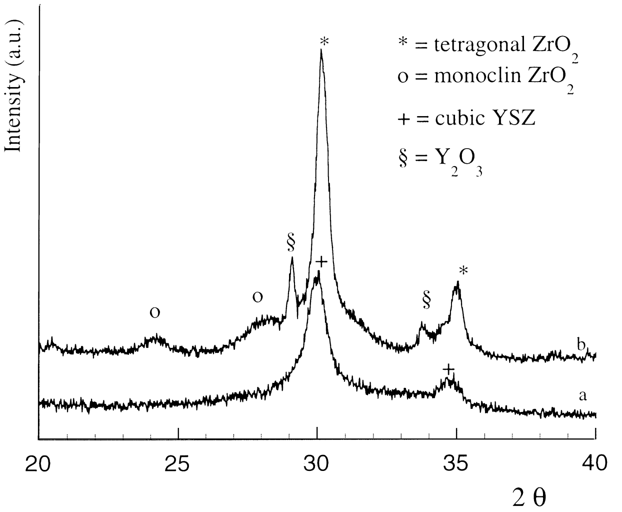

Fig. 3. XRD powder patterns of ZrO_2–7mol% Y_2O_3 hydrothermally treated for 7 days at 110°C in presence of NaOH 0.5M (b) and in presence of Na_2CO_3 0.5 M (a), respectively.

XRD pattern of ZrO_2–7 mol% Y_2O_3 hydrothermally treated for 7 days at 110°C in 0.5 M NaOH. The presence of both monoclinic and tetragonal zirconia, produced by the effect of NaOH mineralizer on zirconia gel, together with the dopant Y_2O_3 is apparent. When the same mixture was hydrothermally treated under the same experimental conditions, but now in the presence of 0.5 M Na_2CO_3 mineralizer, the formation of cubic zirconia solid solution was observed as can be seen in the corresponding XRD powder pattern of Fig. 3(a). Such a result allows the formulation that two conditions must contemporaneously occur in the formation of YSZ at low temperature of hydrothermal treatment:

a relatively high pH value of the mineralizer solution is required for the structural rearrangement of the zirconia gel;
b certain solubility of dopant in the suspension containing the gel precursor is required for the stabilization of zirconia.

3.2.1. *Effect of Y_2O_3 content*

The crystalline phases of products obtained by hydrothermal treatment of zirconia gel at 110°C for 7 days as a function of Y_2O_3 content and at constant Na_2CO_3/Y_2O_3 molar ratio (equal to 20), are shown in Table 2. Powders with Y_2O_3 content up to 5 mol% consist of mixtures containing solid-solutions of both monoclinic and tetragonal zirconia. The amount of the last form increases with increasing Y_2O_3 content. Cubic and traces of monoclinic zirconia formed with an Y_2O_3 content of 6 mol%. Single cubic phases have been detected for Y_2O_3 content higher than 6 mol% and up to 10%. Poorly crystallized products have been detected in the composition range between 13 and 25 mol% of Y_2O_3.

It must be pointed out that all the hydrothermally crystallized powders revealed a broad endothermic peak in DTA curve at temperatures ranging between 130 and 150°C due to the loss of water followed by a further weight loss due to residual hydroxyl groups which extends up to 500°C. The average value of such weight loss, determined by TGA, was of the order of 9% for fully crystallized products. Also in this case, the typical exothermic peak in DTA at 420°C, due to the presence of uncrystallized zirconia, resulted absent confirming the full crystallization-stabilization of gel precursor. The powders obtained in the 13–25 mol% of Y_2O_3 revealed instead the exothermic peak at 420°C indicating the poor crystallization-stabilization of zirconia.

3.2.2. *Effect of Na_2CO_3 concentration*

Taking as constant the conditions of hydrothermal treatment and the Y_2O_3 content in the mixture with zirconia gel, the effect of Na_2CO_3 concentration on the crystallization-stabilization of ZrO_2-based phases has been investigated also. Phases obtained by hydrothermal treatment of zirconia gel doped with 9% mol of Y_2O_3 at 110°C for 7 days as a function of concentration of Na_2CO_3 solution, are reported in Table 3. An incomplete crystallization-stabilization of the zirconia gel is evident at low mineralizer concentration up to 0.1 M Na_2CO_3. Fully crystallized-stabilized samples of cubic zirconia have been detected in the concentration range between 0.5 and 3.0 M Na_2CO_3. The decreasing values of the crystallite sizes of cubic forms, obtained at increasing Na_2CO_3 concentration, confirm the effect of mineralizer concentration on the nucleation rate during the crystallization-stabilization of zirconia gel.

Table 2
Phases present of products obtained by hydrothermal treatment of zirconia gel at 110°C for 7 days at $Na_2CO_3/Y_2O_3 = 20$ as a function of Y_2O_3 content[a]

Y_2O_3 content (mol%)	1	2	3	4	5	6	7	8	9	10	13	15	20	25
Phases	T* M**	T** M**	T** M*	T*** (M)[b]	T*** (M)	C*** (M)	C***	C***	C***	C***	U	U	U	U

[a] M, T and C are monoclinic, tetragonal and cubic ZrO_2, respectively. U corresponds to poor crystallized product. Phase content: *** high, ** medium, * small.

[b] Parentheses indicate the presence of traces of a phase.

Table 3
Phases present and crystallite size of cubic zirconia of products obtained by hydrothermal treatment of zirconia gel doped with 9% mol of Y_2O_3 at 110°C for 7 days as a function of concentration of Na_2CO_3 mineralizer[a]

Na_2CO_3 molarity	Phases	Crystallite size of cubic ZrO_2 (nm)
0.05	A**, M*, C*	19
0.10	A**, C**	9
0.50	C***	8
1.0	C***	8
3.0	C***	5

[a] A, M and C are amorphous, monoclinic and cubic ZrO_2, respectively. Phase content: *** high, ** medium, * small.

3.2.3. *Effect of both temperature and time of hydrothermal treatment*

The temperature of the hydrothermal treatment also influences the crystallization-stabilization of zirconia. In particular, the crystallization degree increases with the increase of the temperature of hydrothermal treatment especially when the temperature was changed from 80 to 110°C (Fig. 4).

A further parameter that has been investigated concerns the minimum duration of hydrothermal treatment to achieve the full crystallization-stabilization of ZrO_2. It has been revealed that such reaction time is also affected by the Y_2O_3 content of starting composition. The higher the Y_2O_3 content, the longer is the reaction time for YSZ formation. For the crystallization-stabilization of ZrO_2–25 mol% Y_2O_3 in the presence of 3.0 M Na_2CO_3 solution, a reaction time longer than 20 days was required. In the same mineralizer solution, for ZrO_2–9 mol% Y_2O_3, the formation of YSZ was completed after only 7 days of hydrothermal treatment. Taking both the Y_2O_3 content of starting composition and the experimental conditions of hydrothermal treatment constant longer reaction times are required at lower concentration of the mineralizer solution.

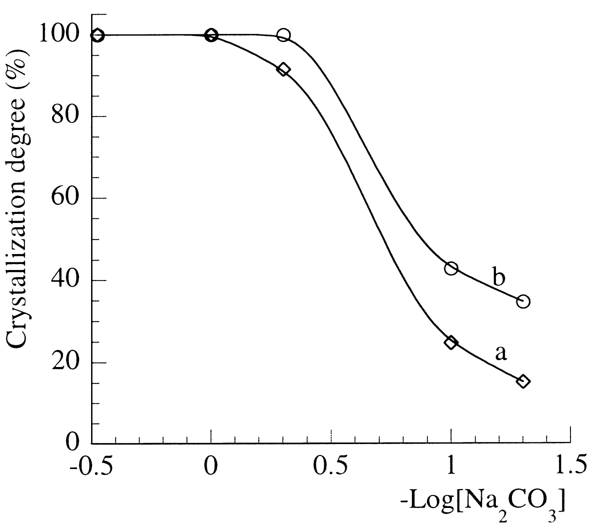

Fig. 4. Crystallization degree of ZrO_2–9 mol% Y_2O_3 samples obtained after 7 days of hydrothermal treatment at 80°C (a) and 110°C (b), respectively and in presence of increasing Na_2CO_3 concentrations.

3.2.4. *Effect of simultaneous presence of NaOH and Na_2CO_3 in the mineralizer solution*

In order to reduce the reaction time for the formation of YSZ, the hydrothermal treatment has been performed with mineralizer solutions containing both NaOH and Na_2CO_3. In this case ZrO_2–13 mol% Y_2O_3 was selected as starting composition. Taking the molar ratio Na_2CO_3/NaOH constant and equal to 3, two total molarities (Na_2CO_3 + NaOH) of mineralizer solution were used, 0.3 and 1.0 M, respectively. The full crystallization-stabilization of zirconia was detected after 3 days of hydrothermal treatment at 110°C in 1.0 M solution as appears in the XRD powder patterns of products obtained for increasing reaction times (Fig. 5). By adopting the same starting composition and a 0.3 M total molarity, 7 days were necessary for the formation of YSZ. When the hydrothermal treatment was carried out on ZrO_2–3 mol% Y_2O_3 and in presence of 1.0 M mineralizer solution, only 2 days were required for the formation of YSZ.

3.2.5. *Effective stabilization of hydrothermally synthesized ZrO_2–Y_2O_3 solid solutions*

The small crystal sizes of doped powders, their high surface area and as a consequent an excess surface energy might determine the formation of metastable phases of undoped zirconia.[25] On the other hand, the possibility has been considered that the products might

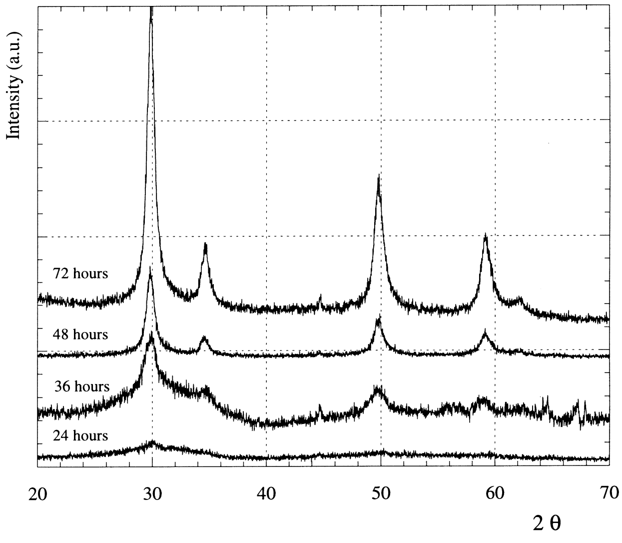

Fig. 5. XRD powder patterns of products of hydrothermal treatment performed on ZrO_2–9 mol% Y_2O_3, with molar ratio Na_2CO_3/NaOH = 3 and [Na_2CO_3 + NaOH] = 1 M solution, at 110°C and at different reaction times.

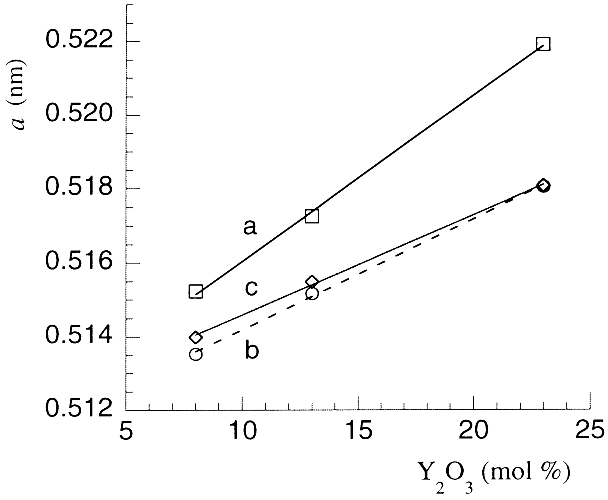

Fig. 6. Lattice parameters *a* of cubic zirconia as a function of Y_2O_3 mol% of hydrothermally synthesized samples (a), of literature data (b) and of hydrothermally synthesized samples after thermal treatment at 900°C for 2 h (c).

be coated with $YOCO_3$ during the hydrothermal treatment in the presence of Na_2CO_3 mineralizer as reported by Aiken et al.[26] In order to ascertain the true stabilization, the lattice parameters of products with increasing Y_2O_3 content and characterized by the cubic form have been measured. The linear increase of *a* parameter with increasing Y_2O_3 content, reported in Fig. 6(a), indicates the effective stabilization of zirconia. However, a higher value of *a* parameter in our results is observed for hydrothermally synthetized samples with respect to the corresponding anydrous phases of several authors[27] (Fig. 6(b)). Such a discrepancy can mainly be attributed to the presence of hydroxo groups in the hydrothermally synthesized phases. A thermal treatment at 900°C for 2 h, resulted in the lattice parameters of our samples (Fig. 6(c)) in agreement with the literature data.

4. Conclusions

The hydrothermal treatment performed on the ZrO_2–Y_2O_3–Na_2CO_3 and ZrO_2–Y_2O_3–Na_2CO_3–NaOH systems allows to synthesize ZrO_2–Y_2O_3 solid solutions with a wide range of compositions and different crystallinity. Taking the composition of zirconia-based phase constant, the crystallite sizes, can be changed widely by the hydrothermal process temperature as well as by the nature and concentration of the mineralizer solution.

The presence of Na_2CO_3 mineralizer in the starting mixtures of precursors appears fundamental to the synthesis of Y_2O_3–ZrO_2 solid solutions at very low process temperature. Two simultaneous roles can be attributed to Na_2CO_3. The first one is related to the relatively high pH value due to basic hydrolysis of the Na_2CO_3 mineralizer, a necessary condition for the structural rearrangement of zirconia gel during the crystallization; the other one is related to a certain solubility of Y_2O_3 in the Na_2CO_3 solution. Hydrothermal treatments performed in the presence of only NaOH as a mineralizer promote the crystallization of the gel, but without formation of solid solutions. Such behaviour can be explained taking into account the insolubility of Y_2O_3 in a NaOH solution.

As the rate of hydrothermal reaction increases with pH and consequently with the concentration of Na_2CO_3 mineralizer, the decreasing crystal sizes of products obtained at increasing concentration of mineralizer allow to formulate a nucleation and crystal growth process during the crystallization-stabilization of zirconia gel. In more concentrated solutions of mineralizer, a higher nucleation rate coupled with smaller crystal sizes of products are to be expected.

The addition of a strong base as NaOH to the Na_2CO_3 mineralizer solution influences both the reaction time for the full crystallization-stabilization of YSZ and its crystallinity. Under these circumstances a noticeable reduction of the reaction times of hydrothermal treatment are observed. Such behaviour can be related to a faster rate of structural rearrangement of zirconia gel in the presence of NaOH.

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