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# Aluminum doped zirconia nanopowders: Wet-chemical synthesis and structural analysis by Rietveld refinement

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#### Abstract

Alumina/zirconia nanopowders, with up to 20 mol%  $Al_2O_3$ , were prepared by wet-chemical synthesis technique, using controlled hydrolysis of alkoxides. The as-synthesized powders are amorphous, have very high specific surface area and the corresponding particle size smaller than 4 nm. Amorphous powders with 0, 10 and 20 mol%  $Al_2O_3$  crystallize at 460, 692 and 749 °C, respectively, as a single-phase tetragonal zirconia, without any traces of alumina phases. Rietvled refinement of X-ray diffraction data, used for the detailed structural analysis of annealed nanopowders, showed that the high-temperature zirconia phase is stabilized due to the formation of  $ZrO_2/Al_2O_3$  solid solutions. High solubility of alumina in the tetragonal zirconia (up to 28.6 at%  $Al^{3+}$ ) and stabilization of tetragonal zirconia solid solution up to high temperature (as high as 1150 °C) were also confirmed. () 2007 Elsevier Ltd. All rights reserved.

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# 1. Introduction

Zirconia ( $ZrO_2$ ) is widely used in various applications (as catalysts, electrolyte for solid oxide fuel cell, oxygen sensor, thermal barriers, biomaterials, tough ceramics, etc.) because of its good mechanical properties, high oxygen ionic conductivity and high chemical stability. Pure zirconia exists in three different crystal structures, i.e. monoclinic, tetragonal and cubic. At room temperature, only the monoclinic form is stable. The high-temperature modifications of zirconia (tetragonal and cubic) can be stabilized at room temperature with different dopants [1–4]. Cations used for the stabilization typically have a lower charge state, a larger ionic size and a higher ionicity than  $Zr^{4+}$  [5]. The stabilization with trivalent dopants is achieved by their incorporation in the fluorite-type structure by substituting  $Zr^{4+}$  cations and creating oxygen vacancies to maintain local charge balance [1,3]. Oxygen vacancies associated with  $Zr^{4+}$  ions can provide stability for tetragonal and cubic zirconia as strong covalent nature of the Zr–O bond favors seven-fold coordination of  $Zr^{4+}$ . It is suggested [5] that dopant ionic size determines the preferred location of oxygen vacancies. Thus, oversized trivalent cations (such as  $Y^{3+}$ ,  $Gd^{3+}$  and  $Yb^{3+}$ ) tend to form eight-fold coordination with oxygen, leaving oxygen vacancies to the  $Zr^{4+}$  ions. On the other hand, undersized trivalent cations (such as Fe<sup>3+</sup> and Cr<sup>3+</sup>) are in six-fold coordination and thus in competition with  $Zr^{4+}$  ions for oxygen vacancies. These are the reasons why the

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stability of the high-temperature modifications of zirconia (tetragonal and cubic) with undersized dopants is much lower than with oversized dopants.

Al<sup>3+</sup> belongs to the group of undersized trivalent dopants, but is apparently too small (0.52 Å) to substitute extensively for  $Zr^{4+}$  (0.84 Å), resulting in rather limited equilibrium solubility [6,7]. However, recent developments of different nano-processing techniques in which precursors are mixed on the molecular level, have enabled the formation of different structures with many zirconium and aluminum ions connected through metal–oxygen–metal linkages [8–15]. Crystallization in these conditions allows the synthesis of phases with various forms of metastability, including extended mutual solubility. Thus, different alumina/zirconia solid solutions were prepared by wet-chemical (simultaneous hydrolysis of aluminum and zirconium alkoxide [8] or chloride [9], spray pyrolysis of aqueous solutions of zirconium acetate and aluminum nitrate [12]) as well as *gas phase synthesis methods* (condensation of aluminum and zirconium alkoxide vapors [15]). In these samples stabilization of the high-temperature zirconia phases was obtained and structures were characterized with a single-phase solid solution having stoichiometry  $Zr_{(1-x)}Al_xO_{(2-x/2)}$  [12,13].

The aim of the presented work is to investigate effects of alumina on the characteristics of zirconia nanoparticles prepared by wet-chemical synthesis, starting from alkoxides. Results will provide further insight into nature of the metastable solid solutions formed in ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> system.

## 2. Experimental

## 2.1. Sample preparation

Pure  $ZrO_2$  and  $ZrO_2/Al_2O_3$  nanopowders were prepared by wet-chemical synthesis technique, i.e. controlled hydrolysis of alkoxides. Zirconium alkoxide ( $Zr(OC_3H_7)_4$ , Fluka, Switzerland) and aluminum-alkoxide ( $Al(OC_4H_9)_4$ , Fluka, Switzerland) were mixed in appropriate ratio under inert atmosphere, dissolved in anhydrous ethanol and hydrolyzed with distilled water under acidic condition (pH ~ 2) and at room temperature (alkoxide, water and hydrochloric acid molar ratio was 1:4:0.8). Aqueous sols were obtained by continuous evaporation (at ~80 °C) and replacing the ethanol with distilled water without changing the concentration and pH. The hydroxides were precipitated by slowly adding the aqueous sols to a well-stirred ammonium hydroxide solution (pH > 11). The precipitated powders were washed with distilled water until there was no indication of residual Cl<sup>-</sup> (qualitatively determined by adding a few drops of the wash effluent to a AgNO<sub>3</sub> solution), and than three times with absolute ethanol to remove free water and replace the particle surface hydroxyl with ethoxy groups. After washing, the gel nanopowders were filtered, dried at 120 °C for 1 day and annealed in air at different temperature up to 1150 °C for 1 h, and finally dry milled with zirconia balls (TOSOH).

#### 2.2. Characterization

The specific surface area of the as-synthesized and annealed alumina/zirconia nanopowders was measured by low-temperature nitrogen adsorption according to the BET method using a Quantachrom Autosorb-3B instrument. The particle size was calculated assuming spherically shaped particles by  $d_{\text{BET}} = 6/(\dot{\rho}S_v)$ , where  $\rho$  is the density and  $S_v$  the specific surface area of the sample.

Thermal analysis of as-synthesized nanopowders was performed with Bähr STA 503 instrument in temperature interval 20–800 °C and heating rate of 10 °C/min in stationary atmosphere.

The X-ray diffraction measurements were performed with a Siemens D5000 instrument using Ni-filtered Cu K<sub> $\alpha$ </sub> radiation, produced at 40 kV and 30 mA. The XRD data were recorded with a collection mode of 30 s/step and a step size of 0.05° 2 $\theta$  over the angular range from 20 to 110° 2 $\theta$ . Complete analysis of the X-ray data, i.e. refinement of structural parameters (such as atomic coordinates, occupancies and lattice parameters) and microstructural parameters (such as particle size and lattice strain) were obtained using Rietveld's powder structure refinement analysis with computer program "FullProf 2003" [16]. The program "FullProf 2003" is able to refine simultaneously both structural and microstructural parameters through a last squares minimization technique. The background was defined by a six-parameter polynomial and refined simultaneously with the zero-point and scale. Both, the instrumental and sample intrinsic profiles were described by a convolution of Lorentzian and Gaussian components, and the TCH-pseudo Voigt profile function was used. Parameters characterizing the instrumental resolution function were obtained

Table 1 Notation and characteristics of as-synthesized nanopowders

Sample notation	Composition			Surface area (m <sup>2</sup> /g)	
	(at% Al <sup>3+</sup> )	(at% Zr <sup>4+</sup> )			
0-A/Z	0	100	Amorphous	293.7	
10-A/Z	20	80	Amorphous	354.0	
20-A/Z	35	65	Amorphous	397.9	

from a LaB<sub>6</sub> standard powder sample by the appropriate Rietveld analysis and kept constant during refinements. Refinements were undertaken in space group  $P2_1/c$  for monoclinic ZrO<sub>2</sub> with all atoms in general positions, in space group  $P4_2/nmc$  for tetragonal ZrO<sub>2</sub> with Zr and O atoms in the special positions 2(a) and 4(d), respectively, and in space group Fm3m for cubic ZrO<sub>2</sub> with Zr and O atoms in the special positions 4(a) and 8(c), respectively. Refinements were made with the assumption that some of Al atoms are on Zr sites in the tetragonal or cubic zirconia lattice and the rest form a separate alumina phase (amorphous and/or crystalline transitional  $\eta$ ,  $\gamma$  or  $\upsilon$ -Al<sub>2</sub>O<sub>3</sub>). Occupation numbers were calculated according to the assumption that in both tetragonal and cubic ZrO<sub>2</sub>, Al atoms randomly occupy the Zr sites in lattice and charge balance is achieved by formation of vacancies on the O sites. Space group Fd3m is used for the transitional  $\eta$  and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phases and C2/m for the  $\upsilon$ -Al<sub>2</sub>O<sub>3</sub>. Broadening of the diffraction peaks was analyzed through the refinement of the regular TCH-pseudo Voigt function parameters and the multipolar functions.

The alumina contents in the as-synthesized nanopowders were determined by energy dispersive X-ray analysis (EDX), using a scanning electron microscope, SEM JEOL 6460LV and appropriate standards.

# 3. Results

The as-synthesized nanopowders were prepared in such a way that the pyrolysed product would contain 0, 20 and 35 at%  $Al^{3+}$  relative to  $Zr^{4+}$ , which are close to the values of 0, 10 and 20 mol%  $Al_2O_3$  used in this paper as the nominal compositions (Table 1).

The as-synthesized powders are amorphous, have very high specific surface area (Table 1) and the corresponding particle size, calculated from BET data, smaller than 4 nm. The increase of the specific surface area with the alumina content from 293.7 m<sup>2</sup>/g for the powder 0-AZ to 397.9 m<sup>2</sup>/g for the powder 20-AZ (Table 1) indicates the size-reducing effect of alumina on zirconia particles.

Fig. 1 shows DTA curves with a sharp exothermic peak resulting from the crystallization of a zirconia phase. Position of the peak depends on alumina content and is at 460, 692 and 749 °C for the 0-AZ, 10-AZ and 20-AZ samples, respectively. The selected XRD patterns, shown in Figs. 2–4, confirm this observation. The pure zirconia powder annealed at 500 °C for 1 h consists of a mixture of the monoclinic  $ZrO_2$  and the high-temperature zirconia phase (the tetragonal or cubic zirconia). On the other side, in the  $ZrO_2/Al_2O_3$  nanopowders annealed at relative high temperatures ( $\leq 1000$  °C) there are no traces of the monoclinic phase (i.e. the transition t  $\rightarrow$  m ZrO<sub>2</sub> started even after heating at 1150 °C in the 10-AZ nanopowder). In addition, XRD patterns of the annealed  $ZrO_2/Al_2O_3$  nanopowders have only reflection belonging to the zirconia phase without any traces of crystalline alumina phases. This means that alumina addition stabilizes the high-temperature zirconia is reduction of particle size (Fig. 5). Thus, in the powder 0-AZ annealed at 850 °C the average particle size is higher than 50 nm, whereas in the powder 20-AZ annealed at the same temperature the average particle size is only about 10 nm and reaches 25 nm after heating at 1000 °C.

## 4. Discussion

According to the presented results it is clear that addition of alumina to zirconia stabilizes the high-temperature zirconia phase. This could be explained by the formation of  $ZrO_2/Al_2O_3$  solid solutions. However, due to the considerable line broadening and overlapping of the corresponding X-ray reflections, it was not possible to determine whether the high-temperature phase (denote with \* in Figs. 3 and 4) has the tetragonal or cubic symmetry. In addition, there was no any information about type of  $ZrO_2/Al_2O_3$  solid solution and portion of  $Al^{3+}$  ions which could be



Fig. 1. DTA curves for alumina/zirconia nanopowders with 0, 10 and 20 mol% Al<sub>2</sub>O<sub>3</sub>.



Fig. 2. XRD patterns of pure zirconia nanopowders, 0-AZ, annealed at 400 and 500 °C (letters t and m denote tetragonal and monoclinic ZrO<sub>2</sub> phases, respectively).

incorporated in the zirconia lattice. Because of that the structural analysis of X-ray diffraction data was done with the Rietveld analysis. Refinements were performed with the pure monoclinic  $\text{ZrO}_2$  phase, the tetragonal or cubic  $\text{ZrO}_2$  structure having some of Al atoms on Zr sites and the corresponding quantity of the amorphous and/or transitional alumina phase (formed by the rest of Al<sup>3+</sup> ions). The obtained results are listed in detail in Table 2 (for the 10-AZ nanopowders) and Table 3 (for the 20-AZ nanopowders), and one typical refined XRD pattern with weighted difference plot is illustrated in Fig. 6.

For the 10-AZ nanopowders annealed at 700 °C the best fit was obtained when all Al atoms are on Zr sites of the dominant zirconia phase (Table 2). However, even with the Rietveld analysis it was difficult to distinguish whether the high-temperature zirconia phase has the tetragonal or cubic symmetry. It is well known that tetragonal zirconia is formed if small amount of oversized trivalent dopants is added, whereas for the stabilization of cubic phase higher concentration is necessary (>8 mol% M<sub>2</sub>O<sub>3</sub>) [2,3]. This boarder corresponds very closely to the structure having almost every second Zr<sup>4+</sup> ion in seven-fold coordination. On the other side, undersized trivalent dopants take oxygen vacancies from Zr<sup>4+</sup> ions and provide only half as many Zr<sup>4+</sup> ions with seven-fold coordination, for the same dopant content [5]. Thus, it is expected that for the stabilization of cubic zirconia phase M<sub>2</sub>O<sub>3</sub> content should be above



Fig. 3. XRD patterns of alumina/zirconia nanopowders, 10-AZ, annealed at different temperatures (\* indicates high-temperature ZrO<sub>2</sub> phases and letter t tetragonal ZrO<sub>2</sub> phase).



Fig. 4. XRD patterns of alumina/zirconia nanopowders, 20-AZ, annealed at different temperatures (\* indicates high-temperature ZrO<sub>2</sub> phases and letter t tetragonal ZrO<sub>2</sub> phase).

15 mol%. This is the reason why it is believed that the 10-AZ nanopowder annealed at 700 °C, having only 10 mol % of Al<sub>2</sub>O<sub>3</sub>, consists of tetragonal zirconia, with very low tetragonality, c/a = 1.0108.

Rietveld analysis for the 10-AZ nanopowders annealed at 850, 950 and 1050 °C showed that the best fits were obtained with the tetragonal solid solution and almost all Al atoms on Zr sites. Changes of lattice parameters and unit cell volume with annealing temperatures are presented in Figs. 7 and 8, respectively. The changes are very pronounced at low annealing temperatures, whereas at 1050 °C lattice parameters and unit cell volume reach values characteristic for the pure zirconia. On the other side, refinement of the XRD data showed that the 10-AZ sample annealed at 1150 °C has small portion of tetragonal phase (13.1 vol%) and decreased portion of Al atoms on zirconia sites. This clearly indicates on simultaneous t  $\rightarrow$  m ZrO<sub>2</sub> transition and segregation of alumina phases.

Rietveld refinement for the 20-AZ nanopowder annealed at 750 °C showed that the best fit was obtained with tetragonal solid solution and when almost all aluminum ions (27.0 at%  $Al^{3+}$ ) are incorporated in zirconia lattice. However, the difference in the refined data obtained with cubic and tetragonal phase is relatively small. The observed high solubility of  $Al^{3+}$  in tetragonal lattice was not expected, since aluminum is trivalent undersized dopant, having much smaller size than  $Zr^{4+}$ . When  $Al^{3+}$  ions substitute  $Zr^{4+}$  (having eight-fold coordination) in zirconia lattice, they



Fig. 5. Particle size, estimated from XRD and BET, as a function of annealing temperature of 0-AZ, 10-AZ and 20-AZ nanopowders.

introduce oxygen vacancies and in same time tend to form six-fold coordination. The six-fold coordination for aluminum can be achieved if  $Al^{3+}$  ions incorporate mostly in the surface region of nanoparticles. Cations that reside on the surface (shell of a particle) are expected to have a lower coordination than those in the bulk (core of a particle). For small particles (less that 10 nm) the surface area becomes significantly large, thus, high quantity of  $Al^{3+}$  ions can be incorporated in surface region [17]. This could be the reason for the observed high solubility of  $Al^{3+}$  in zirconia lattice. However, it is surprising that even of the observed high solubility the structure of the 20-AZ powder annealed at 750 °C is characterized with tetragonal zirconia. This can be explained as follows. The six-fold coordination for  $Al^{3+}$  ions can also be achieved if  $Al^{3+}$  ions take oxygen vacancies from  $Zr^{4+}$ . In this case decreasing of Al-coordination number by taking oxygen vacancies from  $Zr^{4+}$  will decrease the number of  $Zr^{4+}$  ions with seven-fold coordinated. Thus, it seems that in the 20-AZ nanopowder annealed at 750 °C portion of  $Zr^{4+}$  ions with seven-fold coordination is relatively high to

Table 2

Structural parameters of annealed alumina/zirconia nanopowders, 10-AZ, determined from XRD data by Rietveld refinement

	850 °C	950 °C	1050 °C	1150 °C	
Space group Composition	P4 <sub>2</sub> /nmc	P4 <sub>2</sub> /nmc	P4 <sub>2</sub> /nmc	<i>P</i> 2 <sub>1</sub> / <i>c</i> 86.92%	P4 <sub>2</sub> /nmc 13.08%
Lattice parameters					
a (Å) b (Å)	3.5936(19)	3.5927(22)	3.5943(21)	5.1561 5.1885	3.6019(19)
c (Å) β (°)	5.1407(20)	5.1747(20)	5.1902(18)	5.3193 98.76	5.1929(18)
Occupation paramet	ters				
N(Zr) N(O)	0.418(3) 0.838(4)	0.417(3) 0.841(4)	0.425(3) 0.870(4)		0.426(2)
N(Al)	0.082(3)	0.083(3)	0.075(3)		0.053(2)
Thermal coefficient	S				
$U_{2b}$ [Å <sup>2</sup> )	0.007(1)	0.012(2)	0.004(1)		0.018(3)
$U_{4d}$ [Å <sup>2</sup> )	0.018(3)	0.008(2)	0.022(3)		0.025(4)
Agreement factors					
cRp%	8.37	8.27	7.73		9.15
cRwp%	10.10	8.90	8.38		10.60
$R_{ m B}\%$	1.77	1.12	1.49		1.30
$\chi^2$	1.27	1.43	1.52		1.84

Table 3 Structural parameters of annealed alumina/zirconia nanopowders, 20-AZ, determined from XRD data by Rietveld refinement

	750 °C	850 °C	1000 °C
Space group	$P4_2/nmc$	P4 <sub>2</sub> /nmc	P4 <sub>2</sub> /nmc
Lattice parameters			
a (Å)	3.5841(21)	3.5853(20)	3.5944(19)
<i>c</i> (Å)	5.1258(18)	5.1489(19)	5.1884(18)
Occupation parameters			
N(Zr)	0.365(3)	0.357	0.393
N(O)	0.933(5)	0.852	0.800
N(Al)	0.135(3)	0.143	0.107
Thermal coefficients			
$U_{2b}$ (Å <sup>2</sup> )	0.016(5)	0.012(4)	0.009(3)
$U_{4d}$ (Å <sup>2</sup> )	0.069(3)	0.046(3)	0.019(3)
Agreement factors			
cRp%	7.54	10.90	7.79
cRwp%	8.24	12.40	8.91
R <sub>B</sub> %	1.40	2.13	1.57
$\chi^2$	1.45	1.44	1.79



Fig. 6. XRD pattern of the 20-AZ nanopowder annealed at 850 °C refined by Rietveld analysis.

considerably decrease the tetragonality (c/a = 1.0110), but is still not enough to completely stabilize cubic zirconia phase.

Rietveld analysis for the annealed 20-AZ nanopowder showed that solubility of alumina in tetragonal zirconia is very high ( $\sim$ 28.6 at% Al<sup>3+</sup> at 850 °C) and decreases with temperature to 21.4 at% Al<sup>3+</sup> at 1000 °C. The observed decrease in solubility is accompanied with continuous increase of tetragonality and unit cell volume (Figs. 7 and 8), but not with the appearance of transitional alumina phases. Thus, no any traces of alumina phases were observed even in the 20-AZ powder annealed at 1000 °C. Segregation starts, most probably, in the surface region of small particles, but the formed structures are too small to be detected by XRD.

The fraction of Al on Zr sites in the tetragonal zirconia lattice as a function of temperature and alumina content is presented in Fig. 9. The fraction is equal to the doping level for the 10-AZ nanopowder annealed at temperature up to 950 °C. In the powder with higher alumina content only a fraction of  $Al^{3+}$  ions is remaining on the Zr sites, and the fraction continuously decreases with temperature. These observations are in agreement with data already published before [15] for CVS nanopowders. However, the main difference is in the solubility maximum, which is much higher in the case of WCS nanopowders.



Fig. 7. Lattice parameters (*cell constant a*—solid lines; *cell constant c*—dash lines) as a function of annealing temperature for different alumina/ zirconia nanopowders.



Fig. 8. Unit cell volume as a function of annealing temperature for different alumina/zirconia nanopowders.



Fig. 9. Fraction of  $Al^{3+}$  ions on Zr sites in the tetragonal zirconia lattice, obtained by Rietveld refinement. Corresponding curve obtained for CVS nanopowder [15] is presented with dash line.

## 5. Conclusions

Alumina/zirconia nanopowders were prepared by controlled hydrolysis of alkoxides. The as-synthesized powders are amorphous, have very high specific surface area (with corresponding particle size smaller than 4 nm) and crystallize in tetragonal alumina/zirconia solid solution after heating at 700–750 °C. Rietvled refinement of X-ray diffraction data enabled the detailed structural analysis of annealed nanopowders. In the nanopowders with 10 mol%  $Al_2O_3$ , annealed at lower temperatures, the tetragonal solid solutions with almost all Al atoms on Zr sites were formed, whereas at 1150 °C simultaneous t  $\rightarrow$  m ZrO<sub>2</sub> transition and segregation of alumina phases were observed. The nanopowder with 20 mol%  $Al_2O_3$ , annealed at 750 °C characterizes also the tetragonal solid solution, but relatively high solubility of alumina in zirconia. However, the observed high solubility (28.6 at%  $Al^{3+}$ ) is still not enough to completely stabilize cubic zirconia phase. Solubility of alumina in tetragonal zirconia decreases with temperature and is accompanied with continuous increase of tetragonality and unit cell volume.

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