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Synthesis and sintering behaviour of hydrothermally synthesised YTZP nanopowders for ion-conduction applications

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Abstract

The influence of hydrothermal synthesis parameters (pH, temperature, initial Zr concentration) on the chemical composition, crystalline structure, crystallite sizes and grain sizes of 4 mol% YTZP powders was investigated. Tetragonal, cubic, and monoclinic phases were formed as a function of the synthesis conditions. Tetragonal zirconia was formed as major phase at lower pH, in correlation with the synthesis parameters and precipitate chemical composition. Hydrothermal temperature increases the crystallization degree and crystallite sizes while decreasing particle sizes, particle sizes also decreasing with decreasing pH. The analysis of sintering curves revealed that a densification process takes place in the temperature range 800–1300 °C with a well-defined maximum around 1100 °C, leading to the formation of ceramic materials with fine equal grains. The dense sintered pellets obtained were used to study the oxygen transport properties in zirconia nanomaterials.

Keywords: Nanomaterials; Powders-hydrothermal synthesis; Sintering; Solid electrolytes; Yttria-tetragonal zirconia

1. Introduction

Solid electrolytes based on stabilized Y_2O_3–ZrO_2 ceramics (YSZ) are used in various applications as oxygen sensors or fuel cells due to their high oxygen vacancies concentrations.[1] Recently it has been reported that tetragonal zirconia (YTZP) shows also interesting ionic conductivity properties.[2,3] Knowing that YTZP ceramics possess also higher strength and toughness compared with YSZ materials their utilization as sintered parts or membranes is expected to improve the quality of the electrochemical devices.

Hydrothermal methods are mentioned to have important advantages in the manufacture of zirconia powders and films[4–6] such as: direct producing of nanocrystalline powders in one step at low temperatures, utilization of low-cost inorganic precursors and lower polluting effluents resulting from the synthesis process. The homogeneous nucleation and grain growth processes taking place in the aqueous solutions need a better understanding to obtain materials with the desired microstructure and properties. The present paper investigates the influence of the hydrothermal synthesis parameters on the phase evolution, crystallite sizes and particle sizes of 4 mol% YTZP nanopowders starting from soluble Zr (IV) precursors and their presureless sintering behaviour in normal atmosphere.

2. Experimental

The precursor solution was prepared by dissolution of pure $ZrCl_4$ into distilled water, filtering to eliminate insoluble particles and dissolving yttrium oxide in the appropriate amount corresponding to 4 mol% ratio under vigorous stirring. The pH of the solution was adjusted to the desired value by mixing it with ammonium hydroxide solution. YTZP powders were then obtained by hydrothermal treatment of the suspension in a 2 l Teflon autoclave (CORTEST, USA) for 2 h in the temperature range 150–250 °C. The precipitates were filtered, washed with distilled water to remove the

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soluble chlorides and ethanol to reduce agglomeration and dried for several hours in air at 110 °C. Phase composition of powders was investigated by XR diffraction. The mean crystallite sizes were calculated according to the Sherrer formula from the broadening of the [111] characteristic peak of the crystalline phases. Raman spectroscopy was performed on a Raman System R2001 with the operating range 200–2800 cm^{-1}. Particle sizes were measured using a CILAS Granulometer HR 850-B using izopropanol as suspension fluid. Complex thermal analysis of powders was performed on a computer-controlled Derivatograph C-MOM up to 1500 °C in air.

Soft agglomerated powders were obtained by attrition milling in water for 2 h and green specimens were prepared by uniaxial pressing at 100 MPa. Sintering behaviour of green pellets was studied on a heating-stage microscope up to 1500 °C. The microstructure of sintered pellets was then investigated by SEM (Jeol JEM 2000 FX). The sintered pellets were used to measure the ionic conductivity. The results of the impedancemeter measurements are reported in a separate paper.

3. Results and discussions

Phase composition, calculated mean crystallite sizes (d_{111}) and particle sizes (D_p) for different hydrothermal treatment conditions are presented in Table 1. Powders with large peaks, typical for the nanopowders have been prepared (Fig. 1). The calculated mean crystallite sizes were in the range 8–23 nm, increasing with hydrothermal synthesis temperature and having a maximum in the neutral pH domain. Particle sizes decrease with hydrothermal synthesis temperature and strongly depend on solution pH. A maximum agglomeration process is observed in the same neutral pH domain.

The correlation between mean crystallite sizes, particle sizes and synthesis parameters (pH and temperature) are respectively given in the equations:

$$d_{111} = -7.704 + 0.169\ \text{pH} + 0.109\ \text{T} \quad (1)$$

$$D_p = 0.6429 + 2.49.10^{-2}\ \text{pH} - 1.5797.10^{-3}\ \text{T} \quad (2)$$

Increasing concentration of Zr(IV) and Y(III) in the initial solution from 0.047 to 0.21 M (samples denoted

Table 1
Phase evolution, mean crystallite sizes (d_{111}) and particle sizes (D_p) of hydrothermally synthesized zirconia powders vs. synthesis conditions

Sample	pH	T°C	Phases	d_{111} nm	D_p μm	Sample	pH	T °C	Phases	d_{111} nm	D_p μm
H2/150	2.01	150	A +, C	7	0.51	H6/200	5.98	200	C (T?)+, M	19	
H2/200	2.00	200	*Colloidal*			H6/250	5.98	250	C (T?)+, M	23	0.40
H2/250	2.00	250	C (T?)+, M	14	0.29	H7/150	7.08	150	A+, C	10	
H3/150	2.99	150	A +, C	8	0.51	H7/200	7.05	200	C (T?)+, M	17	0.49
H3/200	3.01	200	C+, M+, A	15	0.43	H7/250	7.07	250	C(T?)+	20	0.41
H3/250	3.01	250	C (T?)+, M	18	0.26	H8/150	8.02	150	A+, C	9	0.58
H4/150	4.01	150	A+, C	10	0.47	H8/200	7.98	200	C (T?)+, M	15	
H4/200	4.02	200	C(T?)+, M	17		H8/250	8	250	C (T?)	22	0.48
H4/250	4.01	250	C(T?)+, M+	21	0.35	H9/150	9	150	A+, C	6	
H5/150	5.02	150	A+, C	10		H9/200	9	200	C(T?)+, M	14	0.56
H5/200	5.05	200	C (T?)+, M	19	0.43	H9/250	9.01	250	C (T?)+, M	18	0.51
H5/250	5.03	250	C (T?)+, M	22	0.36	HC/8/250	7.99	250	C (T?)+, M	21	50.5
H6/150	5.94	150	A+, C	11	0.53	HC/4/250	4	250	C (T?)+, M	15	28.15

A, amorphous; C, cubic; T, tetragonal; M, monoclinic; + denote major phases.

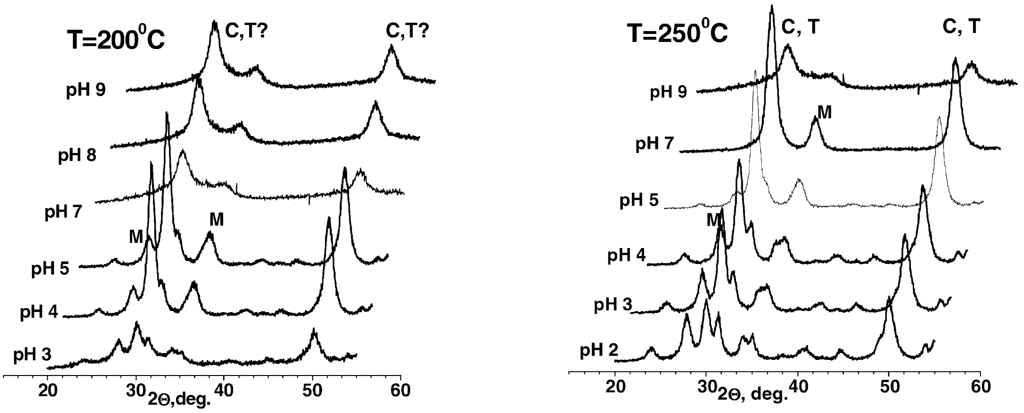

Fig. 1. XRD spectra of samples obtained by hydrothermal procedure vs. synthesis parameters.

HC in Table 1) has a weak influence on the particle size but largely affects the agglomeration process, mainly in the alkaline solutions.

At lower temperatures (<150 °C) cubic zirconia was formed with a lower crystallization degree, for the whole range of solution pH. A large amount of zirconia is amorphous or quasi-crystalline. Increasing the synthesis temperature to 200 and 250 °C, respectively the crystallization degree increases and the amount of amorphous material significantly decreases (Fig. 1). Cubic or tetragonal zirconia forms as major phase and monoclinic zirconia as secondary one. The amount of monoclinic and tetragonal zirconia is higher in the acidic range of pH. Observing that mean crystallite sizes are in all samples less then the critical value, a reasonable explanation for this phase evolution could be the decreasing of yttria content at lower pH due to its incomplete precipitation from the initial solution (Fig. 2) and consequently moving toward the region of M and T stabilization in the phase diagram of ZrO_2–$YO_{1.5}$ system.

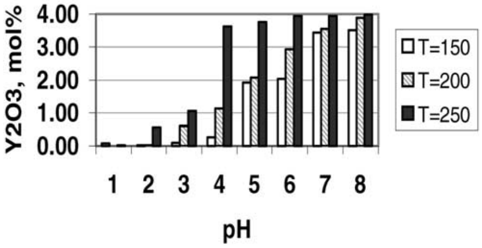

Fig. 2. Molar yttria content of powders vs. synthesis conditions.

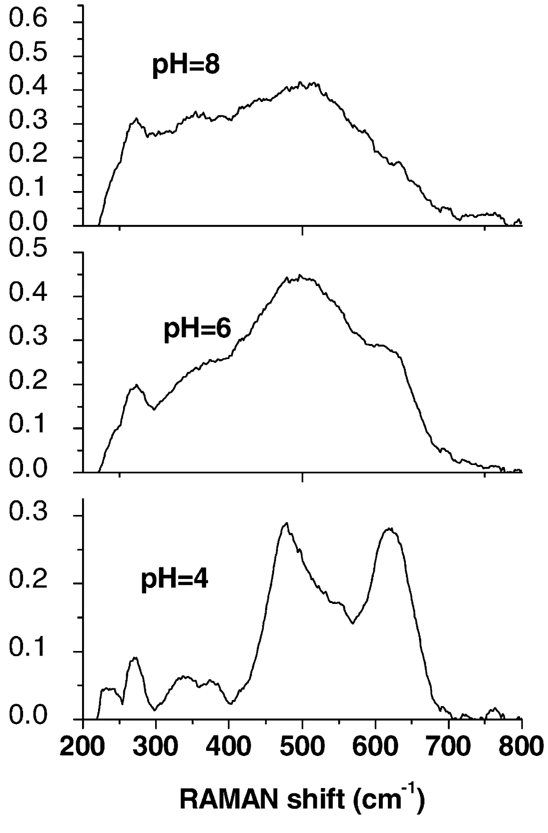

Fig. 3. RAMAN spectra of YTZP powders synthesized at 200 °C and different pH.

Due to the broad peaks characteristic to nanometric crystallite sizes it is difficult to observe the tetragonal splitting of zirconia. In order to confirm the existence of the tetragonal phase, three methods were used: RAMAN spectroscopy, milling of powders and thermal treatment. RAMAN spectroscopy (Fig. 3) directly evidenced the presence of tetragonal zirconia characteristic peaks (from 260.7, 334.1, 472.7, 547.4 and 628.4 cm^{-1}). Compared with the standard tetragonal sample, in the as-obtained powders the peaks are shifted probably due both to the synthesis history and the presence of cubic phase (standard cubic phase having the characteristic peaks at 255.4, 510.1 and 612.6 cm^{-1}). It can also be observed from the RAMAN patterns that the content of the tetragonal phase increases with decreasing pH. Indirect evidence of the presence of transformable tetragonal zirconia phase results from additional milling

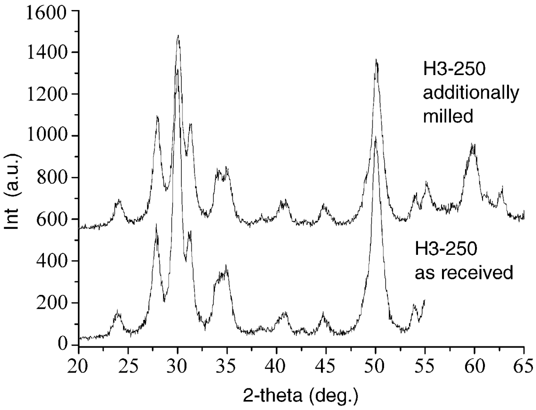

Fig. 4. XRD spectra of sample obtained in acid solution as prepared and after milling showing the presence of transformable tetragonal zirconia.

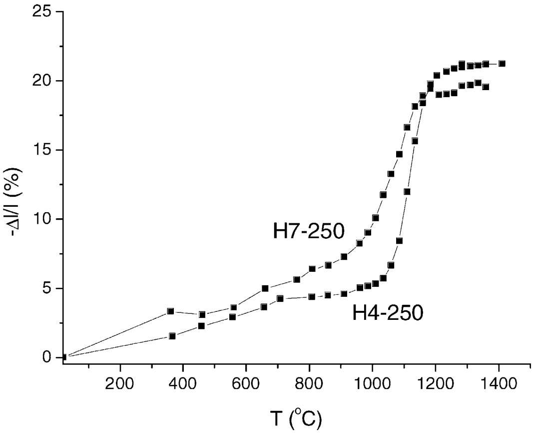

Fig. 5. Dynamic sintering curves of YTZP powder compacts.

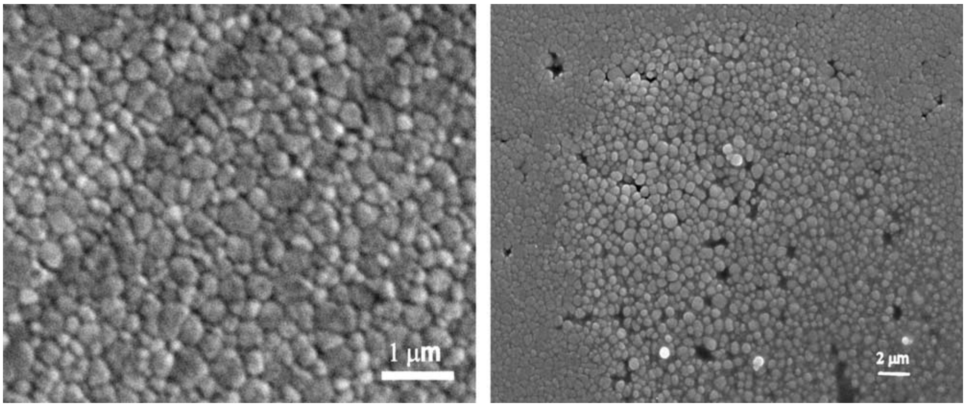

Fig. 6. SEM of sintered YTZP pellets obtained from powders H5/250 and H7/250 at 1400 °C.

of some samples and performing XRD analysis after milling. The increase of the monoclinic phase in the sample H3/250 synthesized in acidic pH is probably due to the transformation of tetragonal zirconia (Fig. 4).

Dynamic sintering curves of samples obtained in optimum conditions (pH = 8, T = 250 °C) after attrition milling of the respective samples and uniaxial pressing at 100 MPa are presented in Fig. 5. Powder compacts exhibited the highest shrinkage rate at temperatures around 1100 °C. Dense samples (>95% from the theoretical density, mean grain sizes 300 nm) are obtained for samples sintered at temperatures over 1300 °C from powders synthesized at pH arround 5.0. Samples obtained from powders synthesized at pH 7 show a larger porosity (Fig. 6). This could be related to the presence of agglomerates in the initial powders. These materials were used to study the oxygen transport properties in zirconia nanomaterials. Results are reported in a separate paper.

4. Conclusions

YTZP powders with crystallite sizes in the range 8–22 nm have been obtained by hydrothermal treatment of amorphous hydrous oxides. The crystallization degree increases with hydrothermal treatment temperature, agglomeration degree decreasing with temperature increasing and pH decreasing. A mixture of tetragonal and cubic zirconia is formed, with increasing tetragonal phase content with decreasing pH. Dense sintered materials could be produced by pressureless sintering at around 1300 °C from powders obtained at 250 °C and pH = 4–5 to be used in the design of materials with improved ionic conductivity.

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