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Sol–gel synthesis and phase composition of ultrafine ceria-doped zirconia powders for functional ceramics

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Abstract

Ultrafine ceria-doped zirconia powders with the general formula $Ce_xZr_{1-x}O_2$ oriented for functional ceramic materials for different purposes were prepared by modified sol–gel synthesis with use of monoethanolamine or tetraethylammonium hydroxide. All powders were high crystallized single-phase systems with average crystallite size 8–11 nm. It was established that doping of zirconia by ceria led to a decrease in the crystallite size. At the same time the nature of the zirconium salt anion has little effect on crystallite size. However, only powders obtained from zirconyl chloride had crystallites with sizes below 10 nm. When $x = 0.150$–0.155, a sharp increase in the crystallite size was observed regardless of the used organic components. Use of tetraethylammonium hydroxide resulted in formation of $Ce_xZr_{1-x}O_2$ crystallites of 2–3 nm smaller than that which was obtained in the presence of monoethanolamine.

Keywords: Sol–gel processes; Nanocomposites; CeO_2–ZrO_2; Grain size; X-ray methods

1. Introduction

In the last 10–15 years, solid solutions CeO_2–ZrO_2 attract increasing attention of researchers in the field of physical chemistry, technology of ceramics and nanotechnology. The practical use of these materials involves the production of solid fuel cells, gas sensors, oxygen-conducting materials and catalysts for the large number of chemical processes. It is known solid solutions CeO_2–ZrO_2 to have a high oxygen capacity, a high mobility of lattice oxygen and high thermal stability.[1] Relevance of these materials cause a high demand for its methods of production, and the solid solutions with particle size up to 20 nm are of particular interest.[2] In this case, the materials acquire special physical and chemical properties due to size effect. Achievement of a high dispersion is possible by using wet chemistry methods for synthesis, one of which is the sol–gel synthesis. This method enables to obtain the particles, texture and morphology of that can be programmed in the synthesis implementation. The main advantages of this low temperature process are to give solids with large specific surface area and meso porosity. The sol–gel process is a useful synthesis approach for the preparation of amorphous as well as structurally ordered materials. The solid network is formed from the solution via the hydrolysis and condensation of molecular precursors in solution.[3] Modified sol–gel is a method which varies the technique to prepare a sol–gel as well as reaction condition.

Previously, we reported about modified sol–gel synthesis of ultrafine Cu–Ce– and Mn–Ce–oxides composites with crystallite size of 6 nm with use *N*,*N*-dimethyloctylamine (DMOA) for sol stabilization.[4] The aim of the present work was to investigate the optimum conditions on the formation of single phase solid solutions with general formula $Ce_xZr_{1-x}O_2$ during the modified sol–gel synthesis with use of monoethanolamine (MEA) or tetraethylammonium hydroxide (TEAH). The powders synthesized were oriented to medical ceramics (endoprostheses) and catalytic purposes (environmental catalysis and petrochemistry).

2. Experimental

2.1. Preparation of ultrafine ceria-doped zirconia powders

Our method for ceria-doped zirconia powders synthesis consists of several steps as shown in Fig. 1. Zirconyl nitrate and chloride were used as zirconium sources and cerium nitrate was used as cerium source. Deionized water used for the preparation

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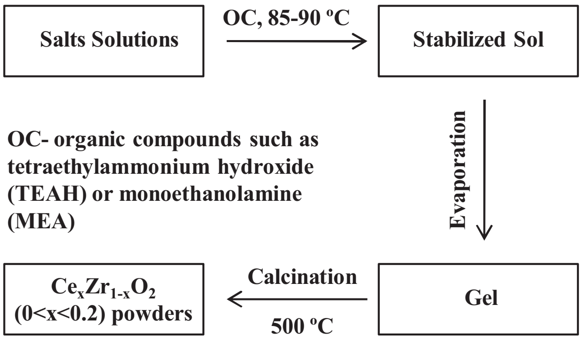

Fig. 1. Experimental scheme of ultrafine composites produced by modified sol–gel synthesis.

of salt aqueous solutions was prepared by use of reverse osmosis and electrodeionization (RAIFIL membranes). Synthesis was carried out in the presence of sol stabilizers TEAH or MEA – organic compounds (OC) – under OC/Me = 1 or 0.5 molar ratio value (Me = Ce, Zr). The first stage: 0.05 M cerium nitrate aqueous solution was slowly added to 0.4–0.8 M zirconyl nitrate or chloride aqueous solution under magnetic stirring at 85–90 °C. The stirring of mixed solution was continued for 40 min, and then OC was added to it under stirring. The formation of the stabilized sol was carried out for 40 min under stirring at 85–90 °C followed by evaporation at 90–95 °C for 2–2.5 h. $Ce_{0.03}Zr_{0.97}O_2$ powder was prepared by precipitation using of aqueous NH_4OH as precipitant. Pure ultrafine ZrO_2 was obtained by use of zirconyl chloride. The final stage: substance obtained was calcined at 500 °C for 1 h.

2.2. Characterization

The powders obtained were characterized using several techniques to determine the particle size, composition, and morphology. The morphology of composites was observed by transmission electron microscopy (TEM) using LEO 912 ab_Omega Carl Zeiss and scanning electron microscopy (SEM) using Carl Zeiss AG NVision 40-38-50 instrument. The Brunauer–Emmett–Teller surface area (S_{BET}), pore volume, pore size, and pore-size distribution of the powders were obtained from N_2 adsorption/desorption isotherms obtained at 77 K (NOVA 2200). The pore size distribution for the mesoporous materials was analyzed using the Barrett–Joyner–Halenda (BJH) method. S_{BET} and pore size distribution were calculated from the desorption branch of the isotherms. Powders XRD data were obtained at room temperature (DRON-3 M, Russia) with Cu K_α radiation. The crystalline phases were identified by matching the experimental patterns to the JCPDS powder diffraction file. The average crystallite size was estimated from peak broadening using the Scherrer equation: $D = 0.9\lambda/(\beta\cos\theta)$, where D is the crystallite size, λ is the wavelength of the XRD (Cu K_α, 1.5406 Å), θ is the diffraction angle, and β is the corrected half-width of the diffraction peak for the (1 1 1) plane. Particles size distribution was obtained using the diffusion aerosol spectrometer (AeroNanoTech, DAS 2702). The elemental analysis made by atomic

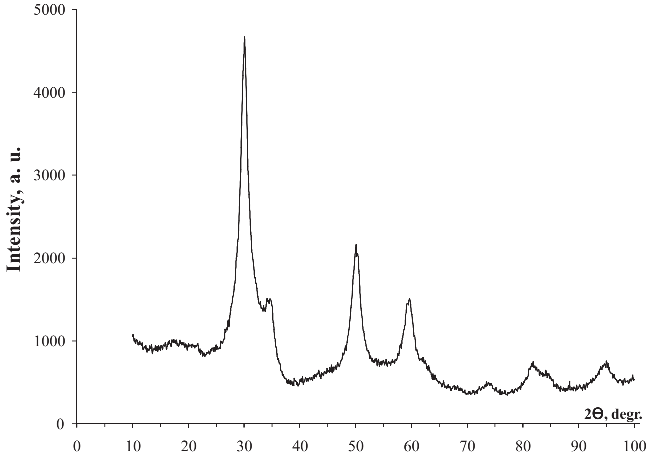

Fig. 2. XRD profile of $Ce_{0.03}Zr_{0.97}O_2$ obtained by precipitation.

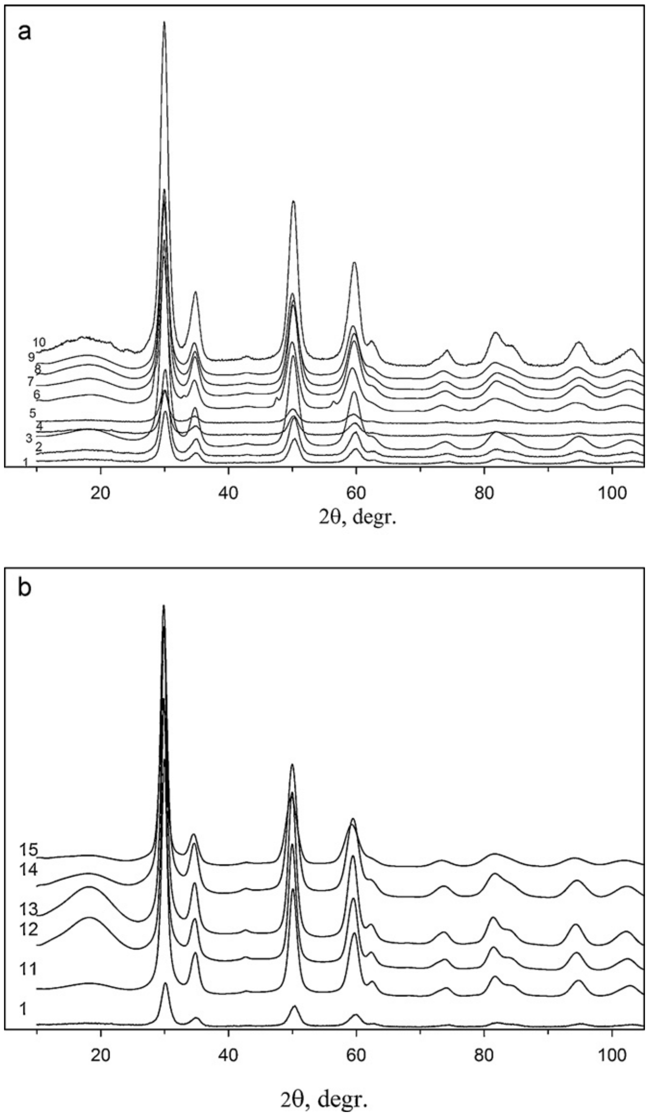

Fig. 3. XRD patterns of $Ce_xZr_{1-x}O_2$ powders obtained by using of zirconyl chloride (a) and nitrate (b).

emission spectrometry with use of inductively coupled plasma (Optima-5300) has shown that residual contents of carbon and nitrogen in all samples were less than 0.08 wt%.

3. Results and discussion

3.1. Precipitation

As an example of powders with a total gross formula $Ce_{0.03}Zr_{0.97}O_2$ the texture of samples was compared for the samples obtained by precipitation (1) and modified sol–gel synthesis (2). In the first case oxide calcined at 500 °C constituted a crude yellow powder with a block size about 8 mm and an average crystallite size equal 6 nm, according to X-ray diffraction data (Fig. 2). However, only ∼50% cerium was included in the cubic sublattice of the solid solution composition $Ce_{0.03}Zr_{0.97}O_2$. Apparently the rest of the cerium was affiliated as an non-crystalline oxide species or as crystallites with a size not exceeding 4 nm.

3.2. Modified sol–gel synthesis

The summary Table 1 shows the initial molecular ratio values of Ce/Zr and OC/ΣMe (Me = Ce + Zr) and crystallite sizes of powders obtained by modified sol–gel synthesis using TEAH and MEA. The powders yield from speculative value was equal to 96–99% throughout the experiment. At the same time, according to X-ray diffraction data (Fig. 3a and b), the powders obtained were single-phase systems with the general formula

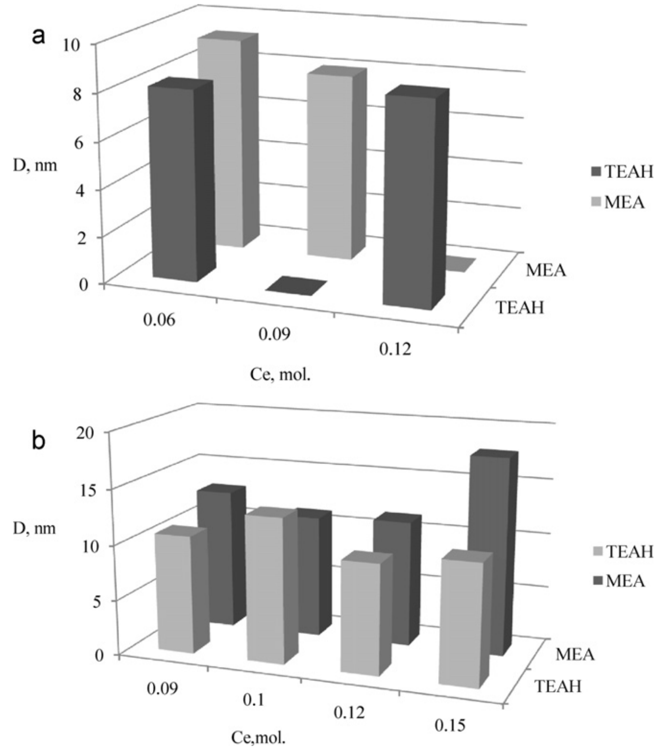

Fig. 4. Histograms of the crystallite size of single-phase composites with general formula $Ce_xZr_{1-x}O_2$ for the series of samples obtained from the zirconyl chloride (a) and nitrate (b) using different OC.

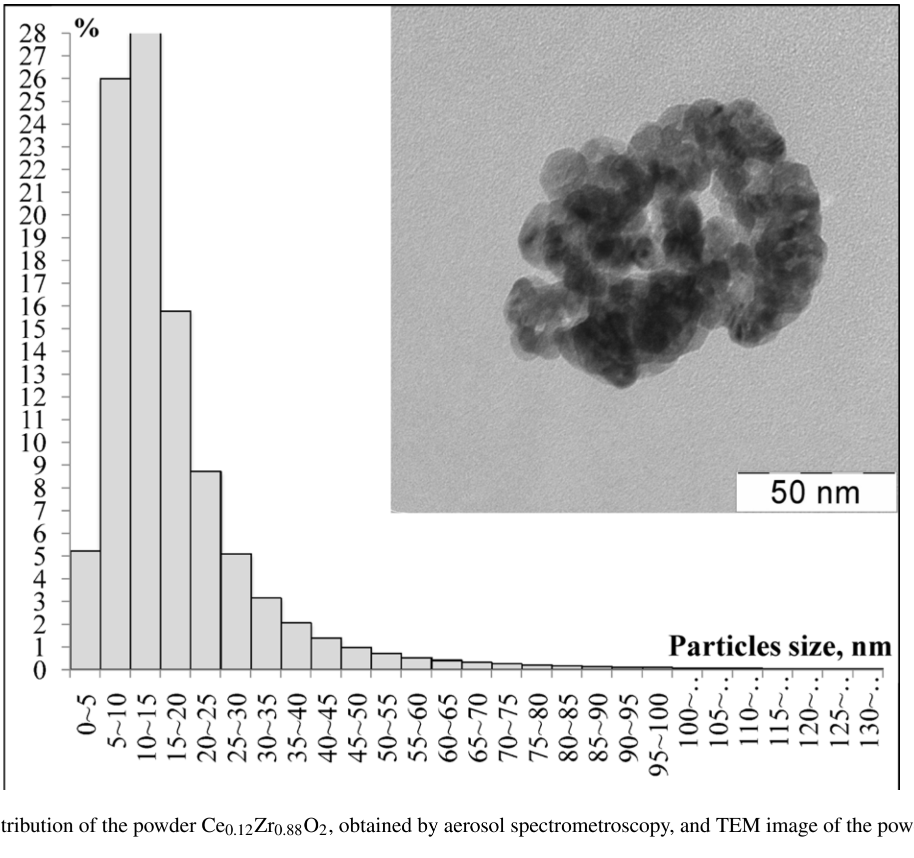

Fig. 5. The particles size distribution of the powder $Ce_{0.12}Zr_{0.88}O_2$, obtained by aerosol spectrometroscopy, and TEM image of the powder $Ce_{0.12}Zr_{0.88}O_2$ (insert).

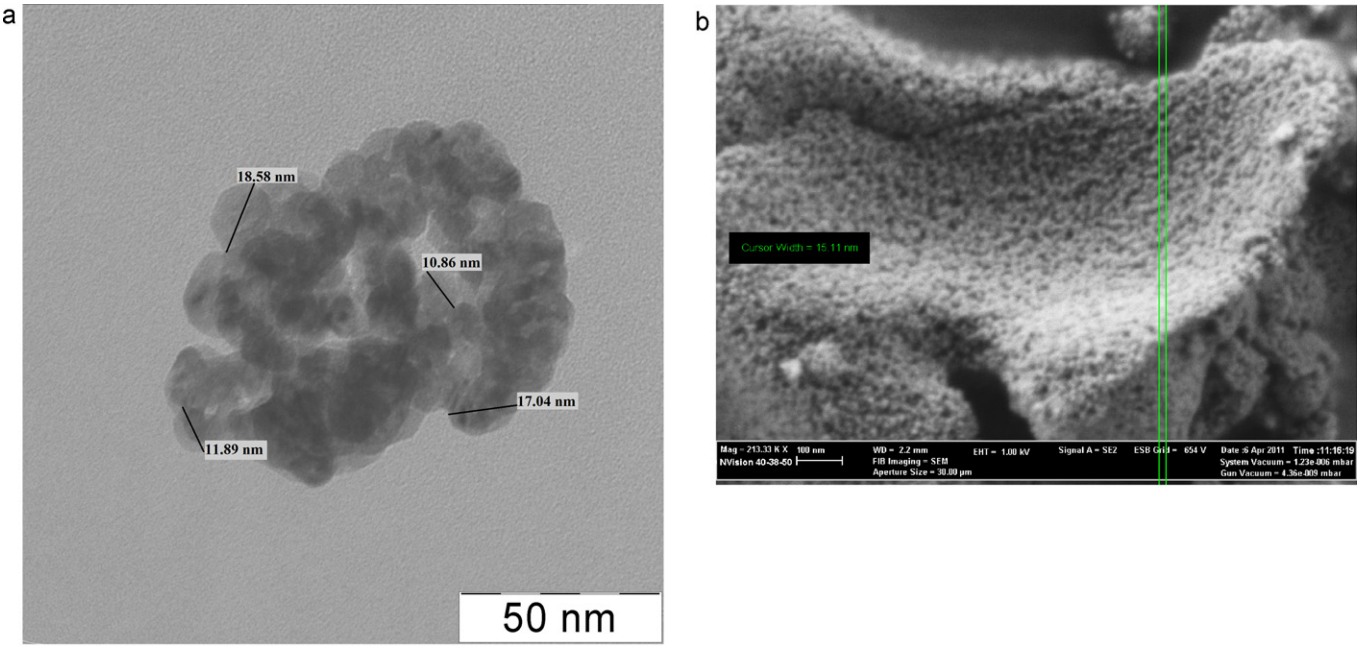

Fig. 6. TEM (a) and SEM (b) images of the powder $Ce_{0.12}Zr_{0.88}O_2$.

$Ce_xZr_{1-x}O_2$ ($0 \leq x \leq 0.155$) in which the ratio $x/(1-x)$ corresponded to initial atomic ratio Ce/Zr in the reaction medium. All of them concerned to the nanopowders, because the size of their crystallites does not exceed 18 nm.

According to the XRD data average crystallite size of as-prepared pure zirconia was 11.8 nm (Sample 1, Table 1). The doping of nanodispersed zirconia by ceria leads to decreasing of crystallite size to 10.4 and 8.1 nm (Samples 11 and 8) without phase separation, if TEAH and MEA were used accordingly. All obtained solid solution powders had a pseudocubic crystal lattice with ceria face-centered cubic sublattice. Only when x was equal to 0.155 the increase of crystallite size up to 17.8 nm

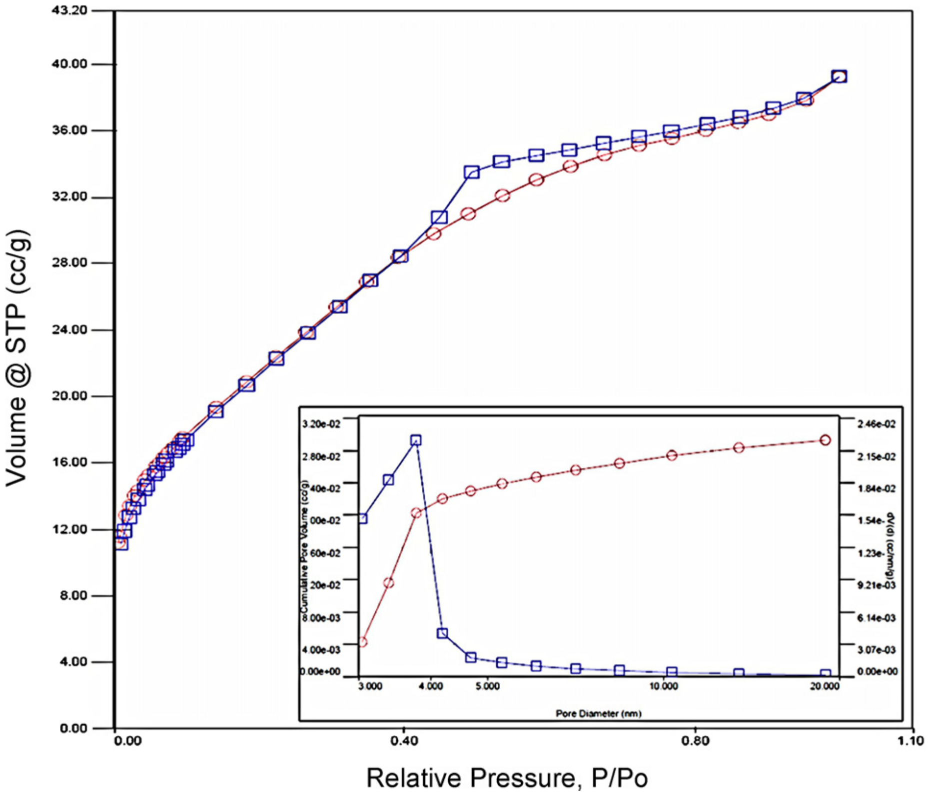

Fig. 7. N_2 adsorption–desorption curves and pore size distribution (insert) for the powder $Ce_{0.12}Zr_{0.88}O_2$.

Table 1
Synthesis conditions and average crystallite sizes of powders $Ce_xZr_{1-x}O_2$ (according XRD data) obtained by using of $ZrOCl_2 \cdot 8H_2O$ as zirconium source.

No.	Ce/Zr (mol%)	OC/(Zr + Ce) (mol)	*D* (nm)
1	0/100	TEAH/(Zr + Ce) = 0.5	11.8
2	3/97		8.9
3	6/94		9.8
4	7.5/92.5		8.5
5	9/91		9.5
6	12/88		8.4
7	15.5/84.5		10.7
8	6/94	TEAH/(Zr + Ce) = 1	8.1
9	12/88		8.5
10	6/94	MEA/(Zr + Ce) = 1	9.2
11[a]	6/94		10.4
12[a]	8/92		12.8
13[a]	10/90		11.1
14[a]	12/88		11.4
15[a]	15/85		17.8

[a] Zirconium source – $ZrO(NO_3)_2 \cdot 2H_2O$.

(∼1.5 times) was observed in case of using MEA (Sample 15). However, in case of TEAH crystallite size increased not more than 1.3 times and it was equal 10.7 nm for $Ce_{0.155}Zr_{0.845}O_2$ powder (Sample 7).

Table 1 shows that the nature of the anions of zirconyl salt has no significant effect on the texture and the morphology of composites. Thus, in the case of nitrate, the crystallite size increased from 10 to 18 nm, and in the case of chloride its crystallite size increased from 8 to 10 nm. According to X-ray diffraction, the powders obtained were single phase with the general formula $Ce_xZr_{1-x}O_2$ ($0 < x < 0.155$). XRD patterns of samples 2, 3, 5, 6 and 15 (Fig. 3) show the absence of amorphous phases in composite materials. The appearance of weak halo in the diffraction patterns of samples 1, 4, 7–14 (Fig. 3) is the special result of using petroleum vaseline for sample preparation.

Fig. 4 shows the histograms of the crystallite sizes of the powdery composites obtained by using zirconyl chloride (Fig. 4a) and nitrate (Fig. 4b) and different OC. The crystallite size is obviously to difference in the 2–4 nm exists for these two groups (Fig. 4), although it is a tendency.

The particles size distribution was characterized by use of the aerosol spectrometroscopy (Fig. 5). Crystallites were shown on the example of powder $Ce_{0.12}Zr_{0.88}O_2$ to be able to associate in the particles of 2–3 ones (Fig. 5, insert), however, there are no particles with a size > 80 nm. Thus the substances obtained suit the definition of nanopowders completely in accordance with IUPAC nomenclature. This fact was confirmed by TEM (Fig. 6a) and SEM analyses (Fig. 6b) which determined the average particle size equal to 15.11 nm. According to the N_2 adsorption–desorption data powders obtained were mesoporous systems (Fig. 7) with a pore size of 3.4 nm (Fig. 7, insert). The BET surface was equal 80 m^2/g.

4. Conclusions

1. The developed modified sol–gel method was shown to have advantages over the traditional coprecipitation method, as it allows to obtain high crystallized ultrafine solid solution powders with a homogeneous component distribution.
2. Ultrafine ceria-doped zirconia powders of the general formula $Ce_xZr_{1-x}O_2$ oriented for functional ceramic materials for different purposes were prepared by modified sol–gel synthesis using of TEAH or MEA.
3. All obtained powders were high crystallized single-phase systems with average crystallite size 8–11 nm.
4. Doping of zirconia by ceria was established to lead to a decrease in the crystallite size. At the same time the nature of the zirconium salt anion little affected on crystallite size. However, only powders obtained from zirconyl chloride had crystallites with sizes below 10 nm. When $x = 0.150$–0.155, a sharp increase in the crystallite size was observed regardless of the used OC (TEAH or MEA).
5. The using of TEAH resulted in formation of $Ce_xZr_{1-x}O_2$ crystallites of 2–3 nm smaller than that which was obtained in the MEA presence.

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