

## Influence of synthesis conditions on the crystal structure of the powder formed in the $\text{ZrO}_2 - \text{Ce}_2\text{O}_3/\text{CeO}_2$ system.

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**Abstract.** Influence of synthesis conditions (type of atmosphere, reduction and oxidation, annealing temperature) on the chemical composition and structure of the compounds formed in the “ $\text{ZrO}_2 - \text{Ce}_2\text{O}_3 / \text{CeO}_2$ ” system has been investigated by X-ray absorption fine structure (XAFS) spectroscopy combined with X-ray diffraction (XRD) and thermogravimetric analysis (TGA). It is revealed that isothermal annealing of precursor at temperatures less than 1000 °C in air leads to formation of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  powders with cubic fluorite-type structure ( $Fm-3m$ ). Further increase of annealing temperatures above 1000 °C causes decomposition of formed crystal structure into two phases: cubic and tetragonal. Annealing in reduction hydrogen atmosphere causes formation of  $\text{Ce}^{4+}_{2x}\text{Ce}^{3+}_{2-2x}\text{Zr}_2\text{O}_{7+x}$  compounds with intermediate valency of cerium, where value of  $x$  depends on the reducing conditions and treatment parameters of precursor. Annealing in vacuum at 1400 °C strongly reduces the content of  $\text{Ce}^{4+}$  in a powder samples and leads to formation of pyrochlore structure (space group  $Fd-3m$ ) with practically  $\text{Ce}^{3+}$  valence state.

### 1. Introduction

The oxygen-containing cerium compounds are of great interest from the point of view of physics and chemistry due to the ability of cerium cation to change an oxidation state in dependence on the synthesis conditions. Materials based on cerium oxide are of great practical importance for obtaining the catalysts [1], solid oxide fuel cells [2], polishing composition, etc. [3].

The aim of the present work is to study the influence of the synthesis conditions and annealing in reduced atmosphere on chemical composition and structure of the powders formed in “ $\text{ZrO}_2 - \text{Ce}_2\text{O}_3/\text{CeO}_2$ ” system by means of X-ray diffraction, XAFS spectroscopy and TGA.

### 2. Experimental

The starting materials were  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.99% purity),  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (99% purity). Precursor was prepared by co-precipitation of metal salts solution with ammonia  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (analytical grade) [4]. The powders of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  were prepared by calcination of precursor at 600-1400°C for 3 h in air. Oxygen content reducing was made by two ways: isothermal annealing in vacuum at 1400°C for 3h and isothermal annealing in hydrogen at 1000°C for 4h (for more detailed experimental procedure refer [5], [6]).

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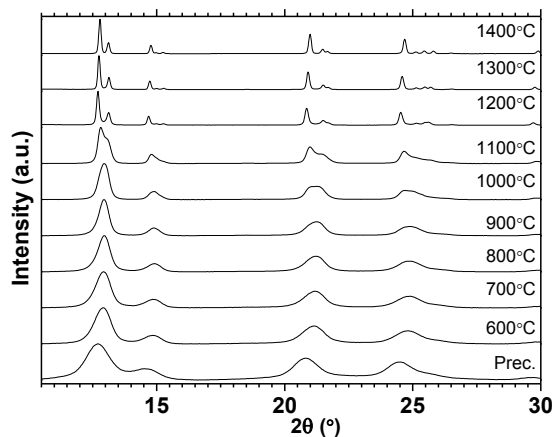
TGA of powders was measured at temperature range 30 - 1400°C using thermogravimetric analyzer SDT Q600 (TA Instruments) with a heating rate of 10 K/min in air flow. The composition and the oxidation degree of synthesized powders was determined by TGA method in measurements of sample mass during heating to 1000 °C and further isothermal annealing for 4 hours in air flow.

Crystal structure of synthesized powders was studied by X-ray powder diffraction at “Structural Materials Science” beamline of the Kurchatov synchrotron radiation source. Measurements were carried out in the transmission mode at  $\lambda = 0.68886$  Å, using XY detector Imaging Plate Fuji Film BAS-5000. The Rietveld full-profile analysis of X-ray diffraction patterns was performed with the Jana2006 software [7].

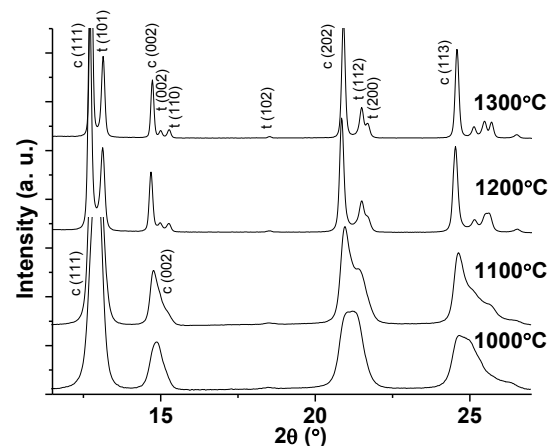
The X-ray absorption spectra (XANES) were measured above the  $L_3$ -Ce edge at i811 beamline of MAX-lab (Lund, Sweden) in transmission mode at room temperature. XANDA software pack [8] was used to fit the near-edge region of spectra.

### 3. Results and discussion

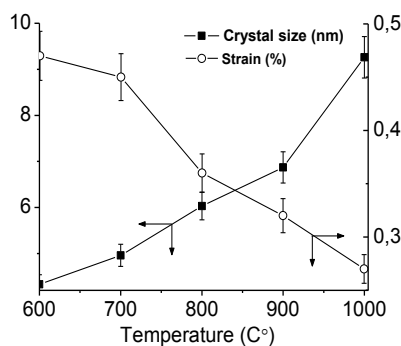
It is revealed that isothermal annealing of precursor at 600-1000°C temperatures in air leads to formation of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  powders with FCC fluorite-type structure (space group  $Fm-3m$ ) (Figure 1). Further increase of annealing temperatures above 1000 °C causes decomposition of formed crystal structure into the two phases: cubic  $\text{Ce}_{0.55}\text{Zr}_{0.45}\text{O}_2$  and tetragonal  $\text{Ce}_{0.07}\text{Zr}_{0.93}\text{O}_2$  (Figure 2).



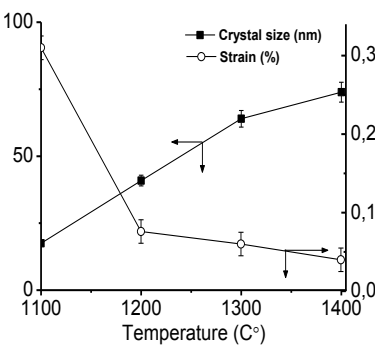
**Figure 1** XRD patterns of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  powders obtained by calcination of the precursor at different temperatures (shown on the corresponding curves)



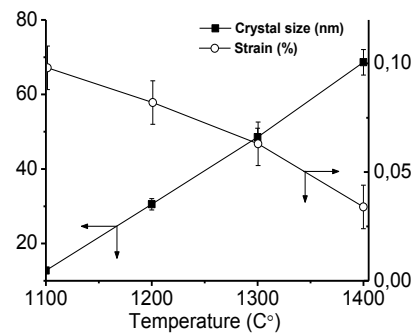
**Figure 2** XRD patterns of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  powders in a narrower  $2\theta$  range.



**Figure 3** Crystal size and strain for  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  compound with cubic fluorite-type structure at 600-1000 °C annealing temperatures.



**Figure 4** Crystal size and strain for cubic phase at 1100 – 1400 °C



**Figure 5** Crystal size and strain for tetragonal phase at 1100-1400 °C.

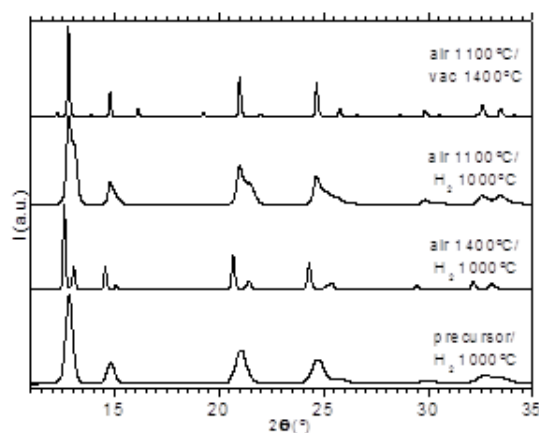
**Table 1.** . Structural parameters of  $\text{Ce}^{4+}_{2x}\text{Ce}^{3+}_{2-2x}\text{Zr}_2\text{O}_{7+x}$  reduced samples.

Sample	Structure	Phase fraction (%)	CSL (nm)	Strain (%)	Compound (TGA)	Compound (XANES)
precursor / $\text{H}_2$ 1000°C	-	-	-	-	$\text{Ce}^{4+}_{0.984}\text{Ce}^{3+}_{1.016}\text{Zr}_2\text{O}_{7.508}$	$\text{Ce}^{4+}_{0.693}\text{Ce}^{3+}_{1.307}\text{Zr}_2\text{O}_{7.347}$
Air 1100°C / $\text{H}_2$ 1000°C	$P4_2/nmc$ $Fm-3m$	$\sim 30$ $\sim 70$	16 23	0.140 0.095	$\text{Ce}^{4+}_{0.924}\text{Ce}^{3+}_{1.076}\text{Zr}_2\text{O}_{7.462}$	-
Air 1400°C / $\text{H}_2$ 1000°C	$P4_2/nmc$ $Fm-3m$	$\sim 30$ $\sim 70$	92 110	0.014 0.069	$\text{Ce}^{4+}_{0.488}\text{Ce}^{3+}_{1.512}\text{Zr}_2\text{O}_{7.244}$	$\text{Ce}^{4+}_{0.356}\text{Ce}^{3+}_{1.644}\text{Zr}_2\text{O}_{7.178}$
Air 1100°C / Vac 1400°C	$Fd-3m$	$\sim 100$	155	0.090	$\text{Ce}^{4+}_{0.206}\text{Ce}^{3+}_{1.794}\text{Zr}_2\text{O}_{7.103}$	$\text{Ce}^{4+}_{0.135}\text{Ce}^{3+}_{1.865}\text{Zr}_2\text{O}_{7.068}$

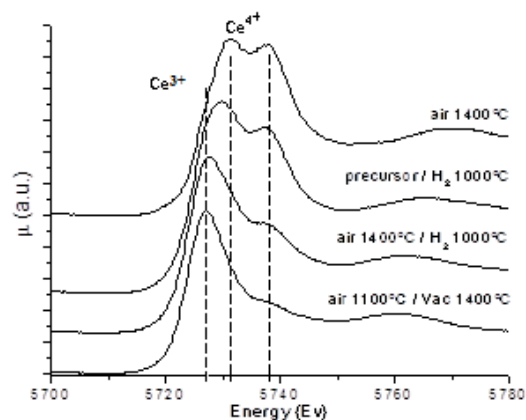
The increasing of synthesis temperature from 600 to 1000°C leads to the narrowing of the main peaks, due to the increase in the size of the coherent scattering length (CSL) and the decrease in microstrain values (Figure 3). Further increase in temperature at range 1100-1400 °C causes also an increase of CSL and a decrease in the microstrain for both types of formed phases (Figure 4 and Figure 5).

Annealing in reduction hydrogen atmosphere causes formation of  $\text{Ce}^{4+}_{2x}\text{Ce}^{3+}_{2-2x}\text{Zr}_2\text{O}_{7+x}$  compounds with intermediate valency of cerium, where value of  $x$  depends on the reducing conditions and treatment parameters of precursor (Figure 6 and Table 1). Annealing in vacuum at 1400 °C strongly reduces the content of  $\text{Ce}^{4+}$  in a powder samples and leads to formation of pyrochlore structure (space group  $Fd-3m$ ) with practically  $\text{Ce}^{3+}$  valence state.

Valence state of cerium for the synthesized powders  $\text{Ce}^{4+}_{2x}\text{Ce}^{3+}_{2-2x}\text{Zr}_2\text{O}_{7+x}$  was obtained from XANES spectroscopy at  $L_3$  absorption edge of cerium, corresponding to electron dipole transition from the domestic level  $2p_{3/2}$  to valence  $5d_{5/2}$  level (Figure 7). As seen from Figure 7 the powder obtained by heat treatment in air at 1400 °C/3h has the  $L_3$ -Ce XANES spectrum in the form of split “white line” corresponding to compounds containing  $\text{Ce}^{4+}$  cations, particularly to  $\text{CeO}_2$  [9]. Variation of the absorption peak for the reduced samples were seen owing to the excitation of two possible channels due to the difference in the electronic structure of the cations  $\text{Ce}^{3+}$  ( $4f^1$ ) and  $\text{Ce}^{4+}$  ( $4f^0$ ). Herewith the decrease in the degree of oxidation of cerium cations causes shifting the position of the absorption edge to lower energies (Figure 7). It should be noted that the variation of the XANES-spectra for reduced samples correlates qualitatively with the chemical compositions of the samples determined by thermogravimetric method (table 1).



**Figure 6** XRD patterns of reduced samples obtained under different conditions.



**Figure 7** XANES-spectra of reduced samples obtained under different conditions.

#### 4. Conclusion

Isothermal annealing of mixed hydroxides of cerium and zirconium at 600-1000 °C in air leads to formation of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  powders with FCC fluorite-type structure (space group  $Fm-3m$ ). Increase of annealing temperatures above 1000 °C causes decomposition of formed crystal structure into the two phases: cubic  $\text{Ce}_{0.55}\text{Zr}_{0.45}\text{O}_2$  and tetragonal  $\text{Ce}_{0.07}\text{Zr}_{0.93}\text{O}_2$ . It is shown that type and parameters of crystal structure of obtained powders strongly depends on the reducing conditions and treatment parameters of precursor. It has been found that the reduction in vacuum or in hydrogen atmosphere causes formation of  $\text{Ce}^{4+}_{2x}\text{Ce}^{3+}_{2-2x}\text{Zr}_2\text{O}_{7+x}$  compounds with intermediate valency of cerium. Also shown, that the reduction in vacuum leads to formation of a compound with a minimum content of  $\text{Ce}^{4+}$  which has the pyrochlore-type structure (space group  $Fd-3m$ ).

#### Acknowledgements

The authors thank S. Carlson (MAX IV lab.), A.A. Ivanov (NRNU MEPhI) for their help in experiments. This work was partly supported by the Ministry of Education and Science of the Russian Federation within the framework of the state assignment 3.1540.2014/K and by Russian Foundation for Basic Research (grant No. 14-22-01002-ofi\_m).

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