Influence of synthesis conditions on the crystal structure of the powder formed in the “HfO$_2$ - CeO$_2$/Ce$_2$O$_3$” system

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Abstract. Influence of synthesis conditions (type of atmosphere: reduction or oxidation, annealing temperature) on the chemical composition and structure of the compounds formed in the “HfO$_2$ - CeO$_2$/Ce$_2$O$_3$” system has been investigated by X-ray absorption fine structure spectroscopy combined with Raman spectroscopy, X-ray diffraction and thermogravimetric analysis. It was revealed that isothermal annealing of precursor at temperatures less than 1000°C in air leads to formation of Ce$_{0.5}$Hf$_{0.5}$O$_2$ powders with cubic fluorite-type structure (space group Fm$\overline{3}$m). Further increase of annealing temperatures above 1000°C causes decomposition of formed crystal structure into two phases: cubic and monoclinic. Annealing in reduction hydrogen atmosphere causes formation of Ce$_{x}$Hf$_{1-x}$O$_2$ compounds with intermediate oxidation state of cerium, where value of $x$ depends on the reducing conditions and treatment parameters. Annealing in vacuum at 1400°C strongly reduces the content of Ce$^{4+}$ in a powder samples and leads to formation of pyrochlore structure (space group Fd-3m) with predominant +3 oxidation state of cerium.

1. Introduction

Cerium based mixed oxides are of great interest from both theoretical and practical points of view due to their physical-chemical properties (firstly, the ability of cerium cation to change an oxidation state depending on the synthesis conditions) for applications in three-way catalysts and as material for anodes in Solid Oxide Fuel Cells (SOFC) [1]. Despite on the large number of investigations of Zr-based Ce$_2$Zr$_2$O$_7$/Ce$_2$Zr$_2$O$_7$ compounds [1-3] the information concerning hafnium analogue remains insufficient. The phase relation and the thermal expansion studies of Hf-based materials in the “HfO$_2$ - CeO$_2$” system are of considerable interest from the point of view of the use in nuclear reactors, oxygen storage capacitors and thermal barrier coatings [4]. Moreover CeO$_2$ is commonly used as a surrogate material for PuO$_2$, which is a nuclear fuel material. So that the phase relation studies in the “HfO$_2$ - CeO$_2$” system could be used to simulate the phase relation in the “HfO$_2$ - PuO$_2$” system [4]. Accordingly to [4, 5] the phase diagram of “HfO$_2$ - CeO$_2$” system involves not only the stable phase bounda-
ries (between monoclinic, tetragonal and cubic phases) but also some metastable boundaries which appear under prolonged heating at higher temperatures and quenched conditions. Unfortunately information about properties of Ce$_3$Hf$_2$O$_{12}$s compounds is very limited [6].

The aim of the present work is to study the influence of the synthesis conditions and annealing in reduced atmosphere on chemical composition, oxidation state of cerium and structure of the powders formed in “HIO$_2$ - CeO$_2$/Ce$_2$O$_3” system by means of X-ray diffraction, XAFS, Raman spectroscopy and thermogravimetric analysis.

2. Experimental

The starting materials were Ce(NO$_3$)$_3$·6H$_2$O (99.99%), HfOCl$_2$·8H$_2$O (99.7%). Precursor was prepared by co-precipitation of metal salts solution with ammonia NH$_3$·H$_2$O (analytical grade) [3, 7]. Powders of Ce$_{0.5}$Hf$_{0.5}$O$_2$ were prepared by calcination of precursor at 600-1000°C for 3 h in air. Two different reducing procedures were carried out: isothermal annealing in vacuum at 1400°C for 3h and isothermal annealing in hydrogen at 1000°C for 4h (for more detailed experimental procedure see [3]).

Thermogravimetric analysis (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 measurements of sample mass during heating to 1000°C and further isothermal annealing for 4 hours in air flow [3].

Crystal structures of synthesized powders were 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 λ = 0.68886 Å, using XY detector Imaging Plate Fuji Film BAS-5000 [8, 9]. The Rietveld full-profile analysis of X-ray diffraction patterns was performed with the Jana2006 software [10].

The Raman spectra were collected on a Nicolet iS50 FT-IR spectrometer (Thermo Fisher Scientific Inc.) with Thermo Scientific iS50 Raman module (λ=1064 nm) at room temperature [11].

X-ray absorption fine structure (EXAFS) spectra were measured above $L_\beta$-Ce and $L_\beta$-Hf edges at i811 beamline of MAX-lab (Lund, Sweden) and at “Structural Materials Science” beamline of the Kurchatov synchrotron radiation source in transmission mode at room temperature. The processing and simulation of the EXAFS spectra were performed using IFEFFIT [12] program packages. The back scattering amplitudes and phases were calculated with FEFF-8.20 [13] based on the known fluorite and pyrochlore crystal structure parameters and the diffraction data. The XANDA program [14] was used to fit the near-edge region of X-ray absorption spectra.

3. Results and discussion

It is revealed that isothermal annealing of precursor at 600-1000°C temperatures in air leads to formation of Ce$_{0.5}$Hf$_{0.5}$O$_2$ powders with FCC fluorite-type structure (space group Fm-3m) (Figure 1) with the lattice parameter $a$ ~ 5.26 Å (low temperature cubic phase). Increasing synthesis temperature leads to the narrowing the main peaks, due to increase in the crystal size (or coherent scattering length - CSL) and to decrease of microstrain ($\varepsilon$) values.

In samples annealed at 1000°C we observed three phases: low temperature cubic phase (55 %), monoclinic (7 %) and high temperature cubic phase with $a$ ~ 5.36 Å (38 %). Further increase of annealing temperature $\geq$ 1000°C led to formation of biphasic system: high temperature cubic Ce$_{0.6}$Hf$_{0.4}$O$_2$ and monoclinic Ce$_{0.12}$Hf$_{0.88}$O$_2$ (with content 40 - 43 %, at annealing temperature 1200 - 1400°C). The formation of biphasic system for Ce-Hf-O system is in good agreement with reported in [4]. The XRD study showed that increase of annealing temperature in the range 1000-1400°C causes increase of CSL and decrease of microstrains for both types of the formed phases (Figure 2).

The structural information was confirmed by Raman-spectroscopy data. It was observed that Raman spectra of powders with fluorite structure (prepared at $< 1000^\circ$C) have only one Raman mode ($F_{2g}$) around 470 cm$^{-1}$ originating from the symmetric vibrations of the oxygen anions around the Ce$^{4+}$ cation in Ce-O$_6$ cubic cell. Increasing the annealing temperature to $> 1000^\circ$C leads to the appearance.
of the some additional modes due to the formation of additional monoclinic phase in prepared samples (Figure 3). The concentration of monoclinic phase increases with the annealing temperature increase (Figure 4). It is worth to note that Raman-spectra analysis have shown that the samples prepared at low temperature (< 1000°C) may contain an admixture of the tetragonal phase (Figure 4). Thus these samples with low temperature FCC fluorite-type structure can be characterized by not clear cubic structure but the $t''$-structure. Analogous $t''$-structure (according to Raman data) was identified in cubic (according to XRD) $(1-x)\text{HfO}_2:x\text{Y}_2\text{O}_3$ [15].

**Figure 1.** XRD patterns of $\text{Ce}_{0.5}\text{Hf}_{0.5}\text{O}_2$ powders obtained by calcination of the precursor at different temperatures.

**Figure 2.** Crystal size and microstrains of $\text{Ce}_{0.5}\text{Hf}_{0.5}\text{O}_2$ powders.

**Figure 3.** Raman spectra of $\text{Ce}_{0.5}\text{Hf}_{0.5}\text{O}_2$ powders prepared at different temperature using 1064 nm excitation. The most intensive monoclinic phase modes indicated by rectangle.

**Figure 4.** The temperature dependence of ratio $I_{(112\text{ cm}^{-1})}/I_{(470\text{ cm}^{-1})}$ (for tetragonal phase) (1) and $I_{(146\text{ cm}^{-1})}/I_{(470\text{ cm}^{-1})}$ (for monoclinic phase) (2).

Using XAFS spectroscopy we have traced the $\text{Ce}_{0.5}\text{Hf}_{0.5}\text{O}_2$ local atomic structure evolution upon the progressive heat treatment from initially amorphous precursors to well-crystallized powders. XANES-analysis of $L_3$-Ce absorption edge of precursors and samples synthesised by annealing in air have shown that all these compounds contain only Ce$^{4+}$ cations (similar to CeO$_2$ [16]). It was observed that the width and magnitude of the splitting of the XANES peak increases with the annealing temperature increase (Figure 5) probably due to the formation of an additional monoclinic phase.

The analysis of EXAFS-data showed that spectra of samples calcinated at temperature < 1000°C are well fitted by using the fluorite structure model. It was found that the difference between the Ce-O and Hf-O bond lengths appears to be about 0.15 Å in full range of annealing temperature, which significantly exceeds the standard error of the interatomic distances determination by EXAFS (0.01-0.02
It means that the local environment of the Ce\textsuperscript{4+} and Hf\textsuperscript{4+} cations in fluorite powders (< 1000°C) cannot be described by the ideal fluorite model, and is rather characterized by the defect-fluorite structure with nonequivalent positions of cations. Further increasing of the annealing temperature > 1000°C leads to a remarkable splitting of the both Ce-O and Hf-O coordination shell into two components due to the formation of the additional monoclinic phase.

![Graph showing Ce-O bond lengths in Ce\textsubscript{0.5}Hf\textsubscript{0.5}O\textsubscript{2} powders annealed at different temperatures on air.](image)

**Figure 5.** The $L_{3}$-Ce XANES spectra of Ce\textsubscript{0.5}Hf\textsubscript{0.5}O\textsubscript{2} powders annealed at different temperatures on air.

![Graph showing interatomic bond lengths Ce-O and Hf-O in Ce\textsubscript{0.5}Hf\textsubscript{0.5}O\textsubscript{2} extracted from the EXAFS date.](image)

**Figure 6.** The interatomic bond lengths Ce-O and Hf-O in Ce\textsubscript{0.5}Hf\textsubscript{0.5}O\textsubscript{2} extracted from the EXAFS date.

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

| Sample          | Structure | CSL (nm) | $\varepsilon$ (%) | Composition (TGA)                  | Composition (XANES)          |
|-----------------|-----------|----------|-------------------|------------------------------------|------------------------------|
| Precursor / H$_2$ 1000°C | $P2_1/c$ Fm-3m | 23       | 0.199             | Ce\textsuperscript{4+}0.87Ce\textsuperscript{3+}1.12Hf\textsubscript{2}O\textsubscript{7.438} | Ce\textsuperscript{4+}0.68Ce\textsuperscript{3+}1.32Hf\textsubscript{2}O\textsubscript{7.34} |
| Air 1100°C / H$_2$ 1000°C | $P2_1/c$ Fm-3m | 27       | 0.13              | Ce\textsuperscript{4+}1.25Ce\textsuperscript{3+}0.75Hf\textsubscript{2}O\textsubscript{7.625} | Ce\textsuperscript{4+}1.36Ce\textsuperscript{3+}0.64Hf\textsubscript{2}O\textsubscript{7.68} |
| Air 1400°C / H$_2$ 1000°C | $P2_1/c$ Fm-3m | 57       | 0.05              | Ce\textsuperscript{4+}1.53Ce\textsuperscript{3+}0.46Hf\textsubscript{2}O\textsubscript{7.769} | Ce\textsuperscript{4+}1.50Ce\textsuperscript{3+}0.50Hf\textsubscript{2}O\textsubscript{7.75} |
| Air 1100°C / Vac 1400°C | Fd-3m | 220      | 0.035             | Ce\textsuperscript{4+}0.16Ce\textsuperscript{3+}1.83Hf\textsubscript{2}O\textsubscript{7.081} | Ce\textsuperscript{4+}0.18Ce\textsuperscript{3+}1.82Hf\textsubscript{2}O\textsubscript{7.09} |

Oxidation state of cerium in synthesized Ce\textsuperscript{4+}$_{x}$Ce\textsuperscript{3+}$_{2-x}$Hf\textsubscript{2}O\textsubscript{7+x} powders excluded from TGA and XANES data analysis is presented in Table 1. It worth to notice the good agreement between the data obtained by these two methods.

The presented results (Table 1) point to the reducing ability of Ce$_2$Hf$_2$O$_8$ powders in hydrogen decreasing with increasing of the annealing temperature of the preliminary treatment. Moreover the reducing ability of Ce$_2$Hf$_2$O$_8$ powders (after thermal treatment) are less than that of Zr-based compounds Ce$_2$Zr$_2$O$_8$ [3]. These results are in good agreement with reported in [6].

As seen in Figure 8, the powders obtained by heat treatment in air at 1100 and 1400°C/3h has the the $L_{3}$-Ce XANES spectrum splitted “white line” corresponding to compounds containing Ce\textsuperscript{4+} cations, particularly to CeO$_2$ [16]. Herewith the decrease in the degree of oxidation of cerium cations causes shifting the position of the absorption edge to lower energies, corresponding to +3 oxidation.
state of cerium (Figure 8). Similar results were obtained by us for cerium aluminate [17] and cerium zirconate [3].

Figure 7. XRD patterns of reduced samples obtained under different conditions.

Figure 8. The L$_3$-Ce XANES-spectra of cerium hafnate powders obtained under different conditions: 1 – CeO$_2$ (standard); 2 – Ce$_0.4$Hf$_{0.6}$O$_2$ (1100°C); 3 – Ce$_0.4$Hf$_{0.6}$O$_2$ (1400°C); 4 – Air 1400°C / H$_2$ 1000°C; 5 - Air 1100°C / H$_2$ 1000°C; 6 - Precursor / H$_2$ 1000°C; 7 - Air 1100°C / Vac 1400°C; 8 – CeAlO$_3$ (standard).

Conclusion

Isothermal annealing of mixed hydroxides of cerium and hafnium at 600-1000°C in air leads to the formation of Ce$_0.5$Hf$_{0.5}$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 Ce$_0.6$Hf$_{0.4}$O$_2$ and monoclinic Ce$_{0.12}$Hf$_{0.88}$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 was found that the reduction in vacuum or in hydrogen atmosphere causes formation of Ce$^{4+}$2Ce$^{3+}$$\times_2$Hf$_2$O$_7$$\times_4$ compounds with intermediate oxidation state of cerium. In addition it was observed that the reduction in vacuum leads to formation of a compound with predominant +3 oxidation state of cerium which has the pyrochlore-type structure (space group Fd-3m).

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