INFLUENCE OF PRECURSOR DISPERSITY AND AGGLOMERATION ON MECHANICAL CHARACTERISTICS OF ZrO$_2$–Ce$_2$O$_3$ AND ZrO$_2$–Y$_2$O$_3$–Ce$_2$O$_3$ CERAMICS

Vladimir G. Konakov[1], Sudipta Seal[2], Elena N. Solovieva[1], Denis A. Ivanov-Pavlov[1], Michail M. Pivovarov[1], Sergei N. Golubev[1] and Alexandr V. Shorochov[3]

[1] St.Petersburg State University, St. Petersburg, Russia
[2] University of Central Florida, Oralndo, USA
[3] Smolensk State Production Union "Analitpribor", Smolensk, Russia

Abstract. Powder precursors of ZrO$_2$ – Ce$_2$O$_3$ and ZrO$_2$–Y$_2$O$_3$– Ce$_2$O$_3$ systems were synthesized by sol-gel method. Dispersity of the powders depended on concentrations of starting reagents and synthesis conditions. To characterize the powder dispersity and aggregated state, electron microscopy and laser scattering particle size distribution analysis were used. Ceramic samples were prepared from these powder precursors; their mechanical characteristics were studied by three points bending method at 1000 ºC. It was revealed that bending strength – particle size curve for ZrO$_2$–Ce$_2$O$_3$ system has a pronounced maximum. This phenomenon is explained by a change in cerium valence depending on powder precursor agglomerate size.

1. INTRODUCTION

Yttria-stabilized ZrO$_2$-based solid solutions with a fluorite-type cubic structure are widely used as a solid electrolyte in high-temperature oxygen sensors [1,2]. Fabrication of the solid electrolytes from nano-sized precursors considerably improves their characteristics. One can change properties of the end product by varying the dispersity of the powder precursor.

We carried out a series of investigations on the influence of the synthesis parameters (temperature of precipitation, the use of superficial active substances, the procedure of gel drying, concentration of starting solutions, and pH of the reaction mixture) for yttria-stabilized ZrO$_2$ on the size of crystallites and agglomerates of powder precursors in ZrO$_2$–Y$_2$O$_3$, ZrO$_2$–Ce$_2$O$_3$, ZrO$_2$–Y$_2$O$_3$–Ce$_2$O$_3$, and

ZrO$_2$–Y$_2$O$_3$–HfO$_2$ systems [3-5]. The influence of dispersity and agglomeration on mechanical characteristics of the ceramics on the basis of ZrO$_2$–Y$_2$O$_3$ system was also studied in [6]; the results on the dependence of the strength of 92ZrO$_2$–8Y$_2$O$_3$ ceramics synthesized in [6] on crystallite sizes in powder precursor is given in Fig.1.

The present work is a sequel of the above-mentioned investigations and deals with the influence of powder precursor dispersity on mechanical characteristics of the ceramics on the basis of ZrO$_2$–Ce$_2$O$_3$ and ZrO$_2$–Y$_2$O$_3$–Ce$_2$O$_3$ systems.

2. EXPERIMENTAL

The synthesis of 91ZrO$_2$–9Ce$_2$O$_3$ and 88ZrO$_2$–6Y$_2$O$_3$–6Ce$_2$O$_3$ (mol.%) ceramic samples consisted in obtaining of powder precursors by sol-gel method

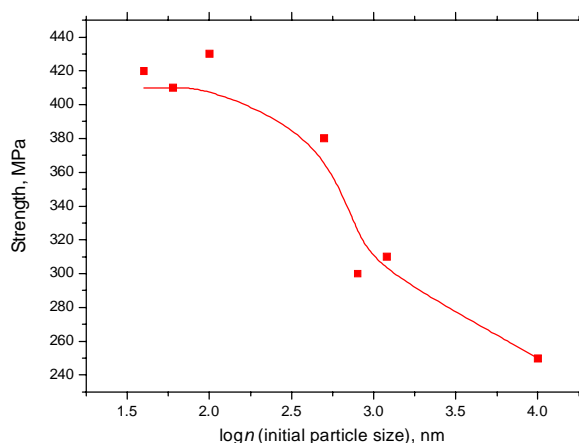Corresponding author: Vladimir G. Konakov, e-mail: konakov@mail.wplus.net

Fig. 1. Crystallite size dependence of the fracture strength for $92ZrO_2–8Y_2O_3$ ceramics [6].

(back coprecipitation from solutions) with subsequent calcination, compacting, and high-temperature annealing.

As starting components, the following salts were used: $ZrO(NO_3)_2 \cdot 2H_2O$ (c.p.g.), $Y(NO_3)_3 \cdot 6H_2O$ (c.p.g.), and $Ce(NO_3)_3 \cdot 6H_2O$ (p.p.a.). Concentrations of starting aqueous solutions of these salts ranges from 0.001 to 0.1 mol/l. Concentration of the precipitant – ammonium aqueous solution – varies between 0.1 and 1.5 mol/l. The temperature of coprecipitation ranges from 0 to 40 ºC. The procedure of coprecipitation and washing of the precipitates is described in [4]. After washing, the precipitates were dried under the pressure of 5 kg/cm² between polished glass plates at 120 ºC. As-obtained powder was calcined at 550 ºC. The moulding of ceramic samples was carried out in a cylindrical steel mould (30 mm in diameter) under the pressure of 45 atm without a binder. Then the blanks were enclosed in latex shells and treated in a hydrostat under the pressure 1500 atm. The samples obtained were sintered at 1600 ºC during 2 hours.

Dispersity of powder precursors after drying and calcination was determined by laser scattering particle size distribution analysis using HORIBA LA-950. The grain size was measured by field-emission transmission electron microscopy (JEOL JEM 3000F) with an accelerating voltage of 300 kV.

Phase formation processes were studied in each stage of the synthesis using Shimadzu X-ray diffractometer XRD-6000 and by DSC method with Netsch Pegasus 407.

Contents of CeO_2 and Ce_2O_3 in the samples was determined on X-ray photoelectronic spectrometer ESCA-5400, PHI (MgKα radiation).

Mechanical characteristics of ceramics obtained were defined by three points bending method at 1000 ºC.

3. RESULT AND DISCUSSION

Fig.2 presents microphotographs of the powder precursors in the system of $ZrO_2–Ce_2O_3$ obtained from solutions of different concentrations. It is obvious from this figure that an increase in concentrations of starting salt solutions favours particle growth and appearance of agglomerates. Analogous results were obtained for $ZrO_2–Y_2O_3–Ce_2O_3$ system.

In Fig.3 the data of sedimentometry is shown: distribution of agglomerate sizes of powder precursors synthesized from solutions of different concentrations for the system $ZrO_2 – Ce_2O_3$. This figure presents some of the diagrams taken for this system which are the most typical. They have no fundamental distinctions from the diagrams of $ZrO_2–Y_2O_3–Ce_2O_3$ system.

We supposed in [6] that a particle radius measured in sedimentometric analysis conforms to a crystallite radius in a powder-precursor. However, a correlation of the results of sedimentometry and TEM obtained in the present work with the results of [6] allows to conclude that actually an agglomerate radius is measured.

On the basis of sedimentometric results the dependence of the mean agglomerate size in precursors on concentration of salt solutions in the reaction mixture was constructed (Fig. 4). As seen from the Fig. 4a, for both systems under investigation there is a low-concentration range where the concentration has a slight effect on an increase in the size of agglomerates in precursor powders obtained from the solutions. When the concentrations of starting solutions exceed 0.6 mol/l, a drastic increase in agglomerate sizes is observed. The same effect was detected in our investigation on the system of $92ZrO_2–8Y_2O_3$ [6]. Most likely, in solutions of such concentrations a great quantity of particle nuclei is formed which begin to integrate and to grow producing a sharp rise of agglomerate size.

The results of DSC-investigations of powder precursors of $91ZrO_2–9Ce_2O_3$ and $88ZrO_2–6Y_2O_3 –6Ce_2O_3$ samples after the drying at 200 °C under
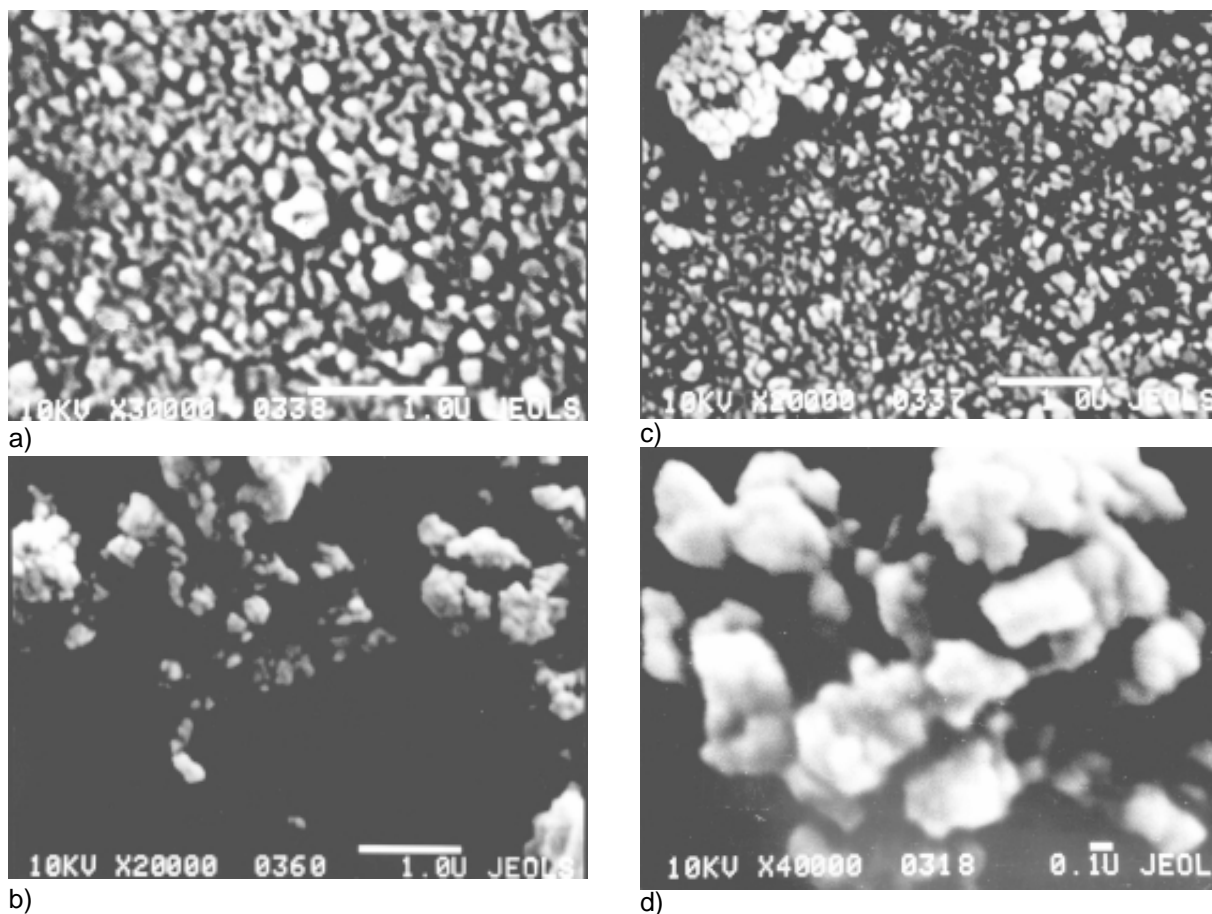
Fig. 2. Microphotographs of powder precursors in the system of $92ZrO_2$–$8Ce_2O_3$ obtained at starting concentrations in reaction mixture a) 0.05, b) 0.1, c-d) 0.85 mol/l.
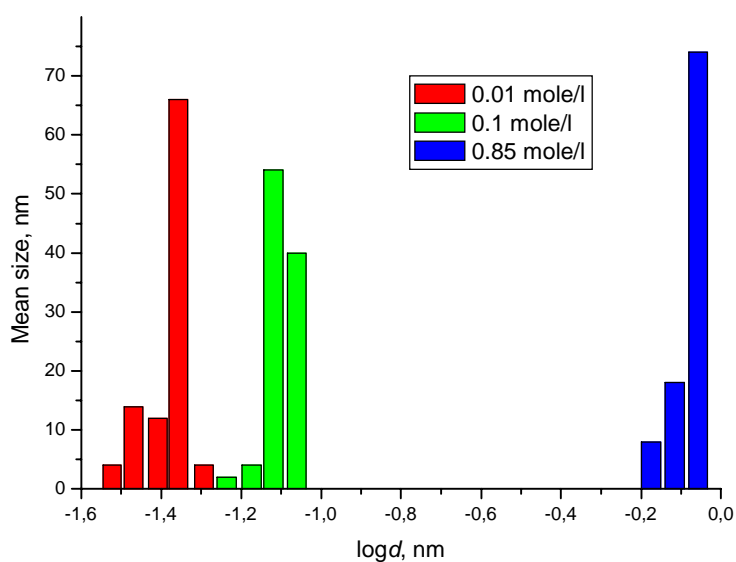

Fig. 3. Distribution of agglomerate sizes of powder precursors synthesized from solutions of different concentration for $91ZrO_2$–$9Ce_2O_3$ sample (d – agglomerate diameter, nm).
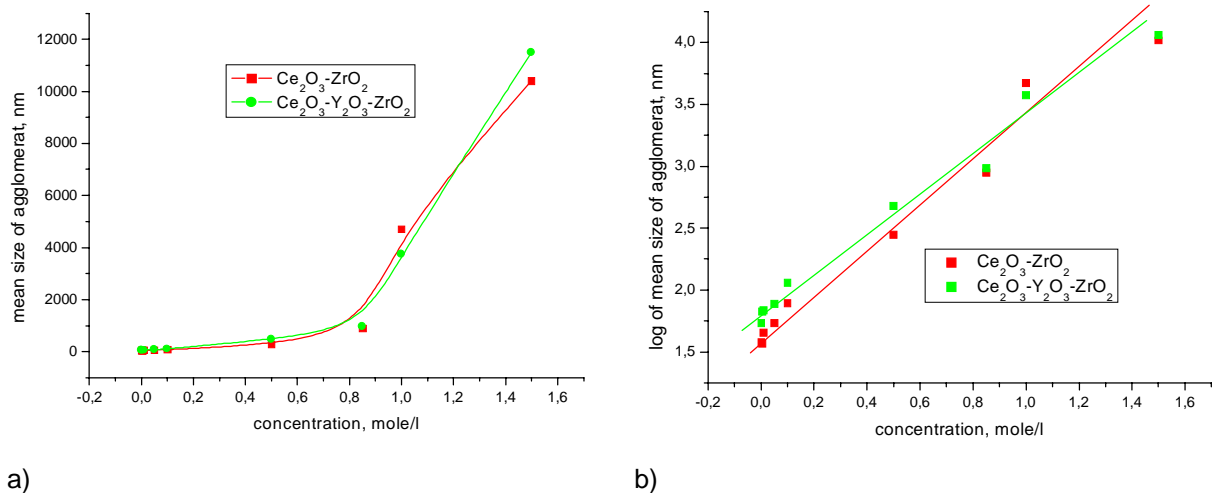
a)   b)

Fig. 4. Dependence (a- common, b – logarithmic) of mean agglomerate size (nm) on concentration of the reaction mixture for $91ZrO_2–9Ce_2O_3$ and $88ZrO_2–6Y_2O_3–6Ce_2O_3$ samples.

pressure are presented in Fig. 5. Endothermal effects at the temperature about 150 °C are due to dehydration of amorphous gels. A deep exothermal effect (~ 400 °C) observed on heating of powder precursors is caused by phase transformation of ZrO_2 from amorphous to crystalline state (cubic phase), as it was seen in [6].

The results of XRD investigations of powder precursors before and after calcination are shown in Fig. 6. These diagrams demonstrate appearance in amorphous samples a well-formed fluorite-type cubic structure of ZrO_2-based solid solution. On the basis of these data crystallite sizes can be calculated and correlated with sizes of stable agglom-
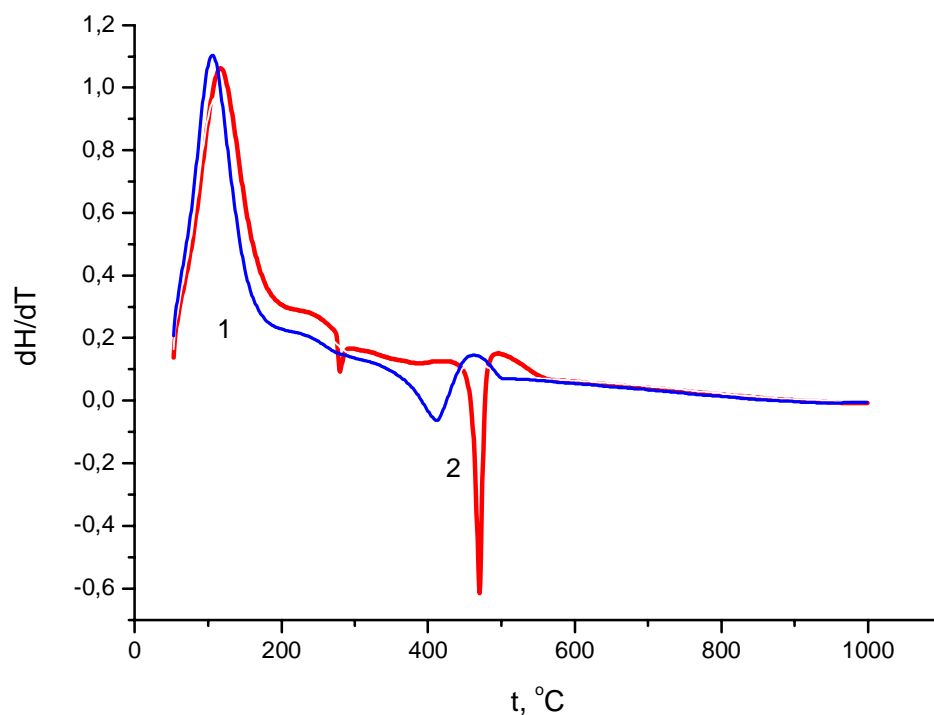

Fig. 5. DTA curves for the samples of amorphous precursors: 1 – $91ZrO_2–9Ce_2O_3$, 2 – $88ZrO_2–6Y_2O_3–6Ce_2O_3$.

Table 1. Contents of cerium compounds of different valence determined on ESCA in powders and ceramics of the system $91ZrO_2 - 9Ce_2O_3$.

Size of agglomerates, nm	Material condition	$[Ce_2O_3]$, rel. %	$[CeO]$, rel. %	Temperature of heat-treatment, °C
>100	Powder	5	95	200
> 100	Powder	20	80	550
100-400	Powder	35	65	550
100-400	Ceramics	75	25	1600
>400	Ceramics	90	10	1600
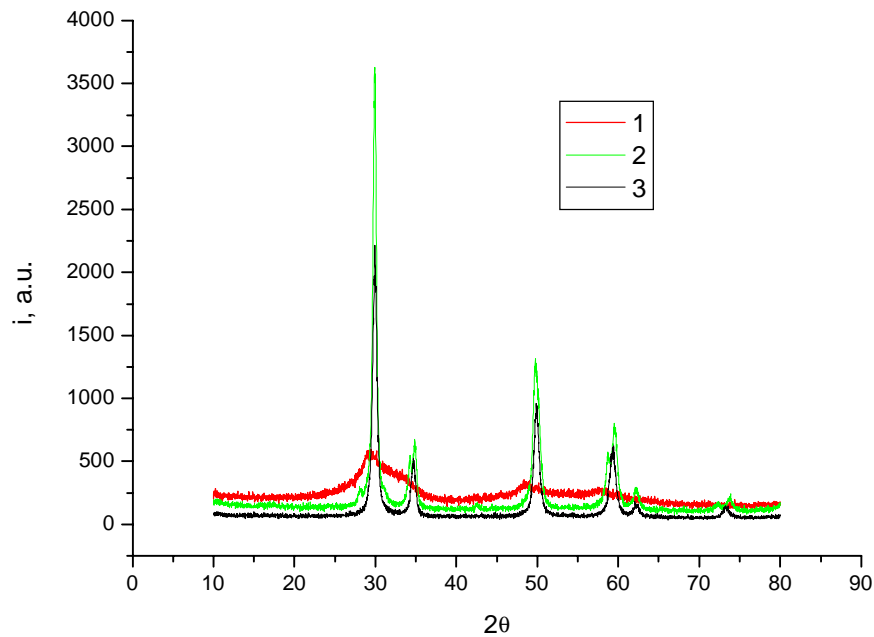
Fig. 6. X-ray diffraction patterns for powder $91ZrO_2$–$9Ce_2O_3$ before (1) and after calcination for $91ZrO_2$–$9Ce_2O_3$ (2) and $88ZrO_2$–$6Y_2O_3$–$6Ce_2O_3$ (3).
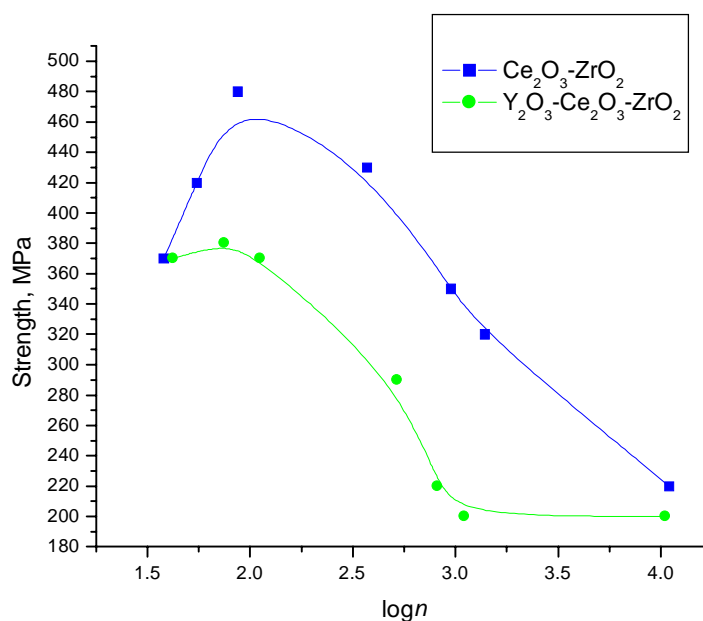
Fig. 7. High-temperature mechanical characteristics obtained by three points bending for $91ZrO_2$–$9Ce_2O_3$ and $88ZrO_2$–$6Y_2O_3$–$6Ce_2O_3$ samples. *n* - initial partical size in nm.

erates which we observed in the present work. These calculations will be performed in our next investigation.

Mechanical characteristics of the $91ZrO_2$–$9Ce_2O_3$ and $88ZrO_2$–$6Y_2O_3$–$6Ce_2O_3$ samples sintered at 1500 °C are presented in Fig. 7. As can be seen from the figure, strength – particle size curve for the system of ZrO_2–Ce_2O_3 has a pronounced maximum in the range of values of powder precursor particle size about 100 nm. We suppose that this maximum is explained by the change in cerium valence both in powder precursors and in the end ceramics. Contents of cerium compounds of different valence determined on ESCA in powders and ceramics of the system $91ZrO_2$–$9Ce_2O_3$ are shown in Table 1. As seen from the table that Ce^{4+} contents in powder precursors increases when sizes of stable agglomerates decreases. On annealing of the end ceramics, Ce^{4+} contents decreases; at the same time, the tendency for an increase in Ce^{4+} contents with a decrease in agglomerate sizes remains.

The strength – particle size curve for the system of ZrO_2–Y_2O_3–Ce_2O_3 has not any pronounced maximum. However, in the range of values of powder precursor particle size less than 100 nm one can observe practically constant value of strength. This effect is not observed in the strength – particle size curve for the system of ZrO_2–Y_2O_3 (Fig.1); it can be explained firstly by a decrease in cerium concentration in the system of ZrO_2–Y_2O_3–Ce_2O_3 and secondly by stabilizing effect of yttrium.

4. CONCLUSIONS

Influence of stable agglomerates sizes of powder precursors in the systems of $91ZrO_2$–$9Ce_2O_3$ and $88ZrO_2$–$6Y_2O_3$–$6Ce_2O_3$ on mechanical characteristics of ceramic samples obtained from these precursors was revealed in the present work. This effect is explained by a changing valence of cerium which depends on both agglomerate size and heat-treatment temperature.

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