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Structural Features of ZrO_2–Y_2O_3 and ZrO_2–Gd_2O_3 Nanoparticles Formed under Hydrothermal Conditions

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Abstract—We synthesized nanoparticles of variable composition based on zirconium dioxide in the ZrO_2–Y_2O_3 (or Gd_2O_3)–H_2O systems under hydrothermal conditions. By X-ray diffraction and small-angle X-ray scattering studies revealed that the nanoparticles consist of crystalline core and amorphous shell. Increase of Y_2O_3 (or Gd_2O_3) content yields increases of shell size and decreases of core size. The effect is due to suppressed ZrO_2 crystallites growth caused by development of the shell preventing zirconium ions transport.

Keywords: nanoparticles, variable composition phase, core–shell, hydrothermal synthesis

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Inorganic nanoparticles often reveal peculiar features. For instance, they can exist in structural modifications unusual for macroscopic phases of the same composition [1–9]. In some cases, parameters of the elementary cell of nanoparticles depend on their preparation method [10–16]. Several studies [10, 17, 18] have revealed that parameters of the elementary cell as function of composition are different in the cases of nanoparticles and macroscopic phases of variable composition. Alternation of the solubility limit upon formation of nanoscopic phases of variable composition has been revealed as well [17–20]. The above-mentioned experimental observations have not been explicitly explained so far.

In view of the above, systematic comparison of the effects of chemical composition, particles size, and preparation conditions on structure of nanoparticles of variable composition is of definite interest. In this work, we used the fluorite-type nanoparticles prepared under hydrothermal conditions in the ZrO_2–Y_2O_3 and ZrO_2–Gd_2O_3 systems as model objects. It has been demonstrated [10, 13, 20] that such nanoparticles reveal the above-mentioned structural features not yet explained. At the same time, information on structure of such and similar nanoparticles is of considerable interest in view of development of functional and engineering nanocomposites [21–26], including novel catalysts [27–29], luminophors [30–32], and biomedical materials [31, 33].

Figure 1 displays results of X-ray diffraction studies of the samples prepared via hydrothermal treatment of co-precipitated hydroxides of zirconium and yttrium, or of zirconium and gadolinium. From the presented data it follows that within the whole studied range of the Zr : Y(Gd) ratio the only crystalline phase present in the samples was that of cubic zirconium dioxide (fluorite structural type).

From the X-ray diffraction patterns, the parameter of elementary unit cell (Fig. 2) and the crystallite size (Fig. 3) of the prepared nanoparticles were determined.

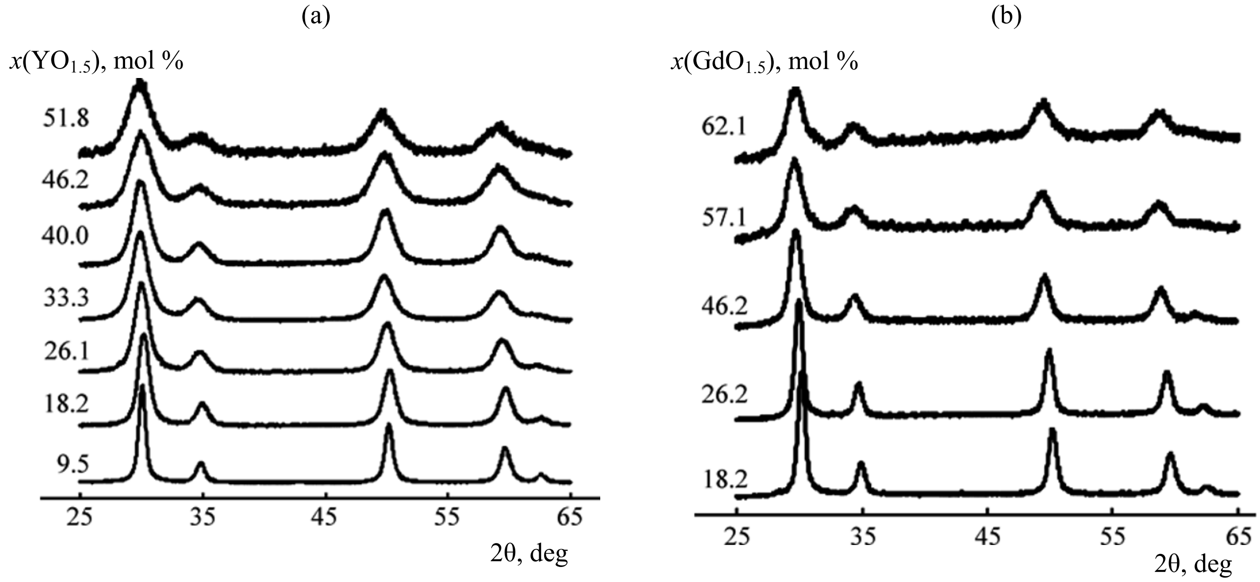

Fig. 1. X-ray diffraction patterns of the products of dehydration of ZrO_2–$YO_{1.5}$ (a) and ZrO_2–$GdO_{1.5}$ (b) mixtures under hydrothermal conditions. Molar fraction of $YO_{1.5}$ (a) and $GdO_{1.5}$ (b) is shown near the corresponding curves.

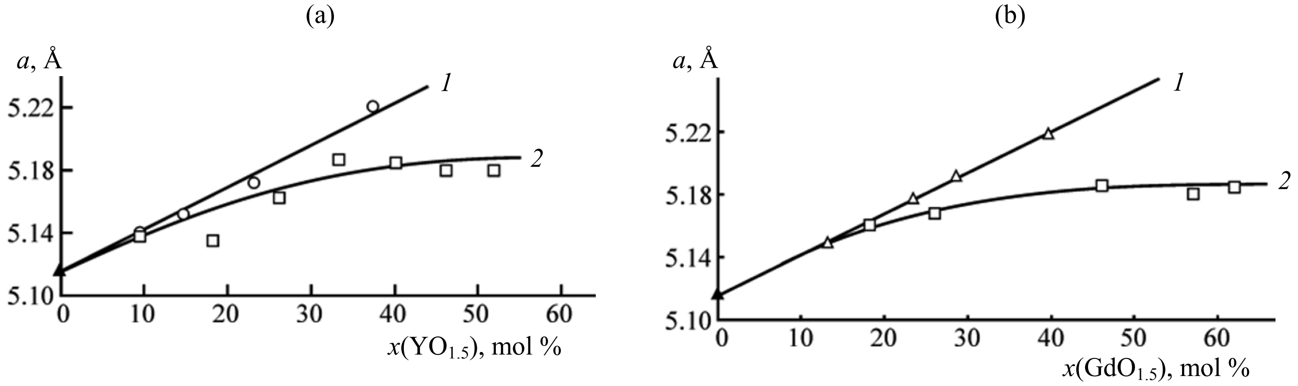

Fig. 2. Parameter of the elementary unit cell of ZrO_2 with fluorite-type structure as function of $YO_{1.5}$ content (a) {from [10, 16] (*1*) and from results of this work (*2*)} and of $GdO_{1.5}$ content (b) {from [12, 16] (*1*) and from results of this work (*2*)}.

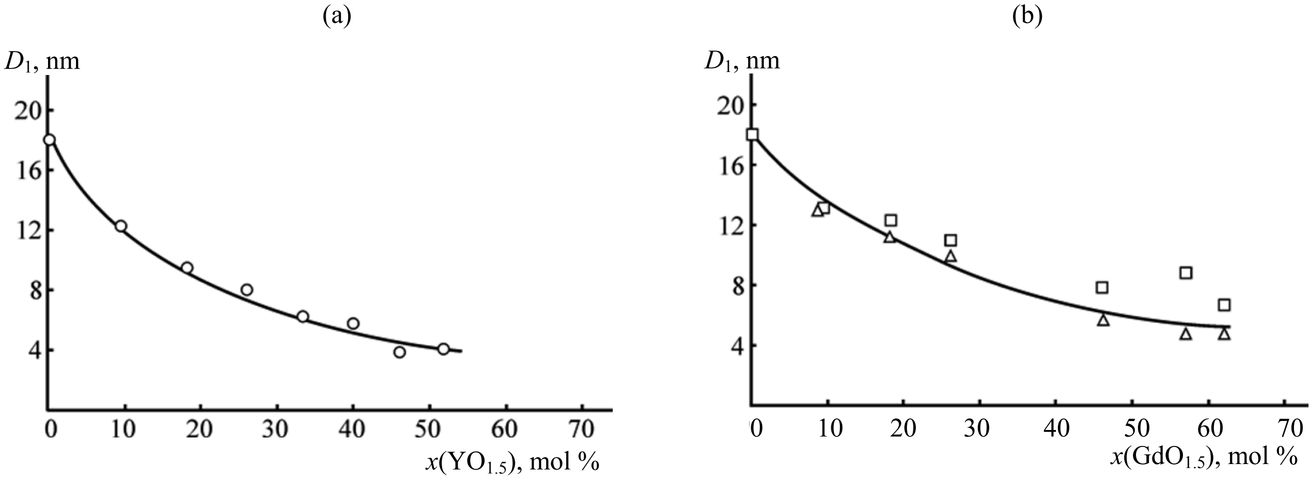

Fig. 3. The ZrO_2-based crystallite (nanoparticles core) size as function of content of $YO_{1.5}$ (a) and $GdO_{1.5}$ (b) as derived from widening of X-ray diffraction bands (circles and squares) and from small-angle X-ray scattering (triangles).

Noteworthily, systematic differences were revealed between dependences of the ZrO_2 elementary cell parameter on the components (ZrO_2 and Y_2O_3) ratio in the cases of nanoparticles (13–19 nm) prepared under hydrothermal conditions, nanoparticles (7–10 nm) prepared via decomposition of the co-precipitated hydroxides in air at 400°C [13], and the macroscopic particles [10, 11, 14]. When nanoparticles of varied composition prepared under hydrothermal conditions were thermally treated in air, their elementary cell parameter approached that typical of macroscopic crystals and of nanoparticles initially prepared in air [10]. Hence, the unit cell parameter as function of the system composition was majorly dependent on the preparation method rather than on the crystal size.

It should be considered that hydrothermal synthesis of nanoparticles in the ZrO_2–Y_2O_3–H_2O system was carried out under conditions of stability of $Y(OH)_3$. Therefore, the above-described differences in the unit cell parameters could be due to type of charge compensation upon substitution of Zr^{4+} with Y^{3+}. In particular, when the phase of variable composition was formed via thermal treatment in air, Y_2O_3 oxide was dissolved in the ZrO_2 lattice, and charge compensation occurred via formation of holes in the oxygen sublattice [34]. Formation of the similar nanoparticles under hydrothermal conditions {coexistence of ZrO_2 and $Y(OH)_3$ [35]} led to charge compensation via substitution of O^{2-} with $(OH)^-$. In the latter case, larger unit cell parameter could be expected at a given ratio of Zr^{4+} : Y^{3+}. Indeed, in the presence of oxygen vacancies Y^{3+} ion should be coordinated with seven oxygen atoms, whereas in the absence of oxygen vacancies the Y^{3+} coordination number is eight, and its ionic radius is higher [36]. Hydrothermal synthesis of compounds of variable composition in the ZrO_2–Gd_2O_3–H_2O system was carried out under conditions (temperature and pressure) of $Gd(OH)_3$ instability [35]; therefore, in that case no differences between the elementary unit parameter was expected in the cases of hydrothermal conditions and thermal treatment in air, Zr : Gd ratio being the same.

Another special feature of the nanoparticles of variable composition prepared under hydrothermal conditions was systematic deviation from the Vegard's law with increasing concentration of either Y^{3+} or Gd^{3+} (Fig. 2). The deviation could be explained [17, 20] if the nanoparticles were represented as core-shell structures, the shell being formed of the yttrium- or gadolinium-containing component. Therefore, the fraction of Y^{3+} or Gd^{3+} in the core based of cubic zirconium dioxide was lowered, and the elementary unit cell parameter was no longer proportional to the overall yttrium (or gadolinium) fraction in the system.

From the content of Y^{3+} and Gd^{3+} in the nanoparticles based on zirconium dioxide (elucidated from the elementary unit cell parameter), the overall Zr : Y(Gd) ratio in the system, and the crystalline core size, we estimated the shell thickness H of the nanoparticles (Fig. 4).

Alternatively, the shell thickness was derived from results of small-angle X-ray scattering. In particular, the diameters D_1 and D_2 were calculated from the experimentally determined radius of inertia R_g (see Experimental) for all the studied gadolinium fractions. Noteworthily, in the case of the ZrO_2–Gd_2O_3 system, the crystalline core size as determined from widening of the X-ray diffraction lines strongly correlated with those derived from the small-angle X-ray scattering data (Fig. 3). Similarly, the X-ray amorphous shell thickness values as deduced from those methods were in good agreement (Fig. 4). From Figs. 3 and 4 it follows that with increasing shell thickness the crystalline core size decreased. Likely, the crystallite growth rate was suppressed due to impeded transport of zirconium ions across the thicker shell. Furthermore, decrease of the variable-composition nanocrystals size with increasing the fraction of minor component was noted in [37, 38]. The explanation of those experimental facts suggested in this work (impediment of the ions transfer) seems more natural than that developed in [39] (slowing down of the nanoparticles growth due to enhancement of the strains in the crystal lattice arising from the solid solution formation).

EXPERIMENTAL

Nanoparticles based on the ZrO_2–Y_2O_3 and ZrO_2–Gd_2O_3 systems were prepared via dehydration of co-precipitated hydroxides under hydrothermal conditions [40], the components ratio being varied. The hydroxides were precipitated from mixtures of aqueous solutions of zirconium oxychloride and either yttrium chloride or gadolinium chloride with aqueous ammonia (12 mol/L). The so prepared precipitates were washed with distilled water and dried at 100°C. Hydrothermal treatment of the product was carried out at 250–450°C and 70 MPa during 3–6 h in distilled water.

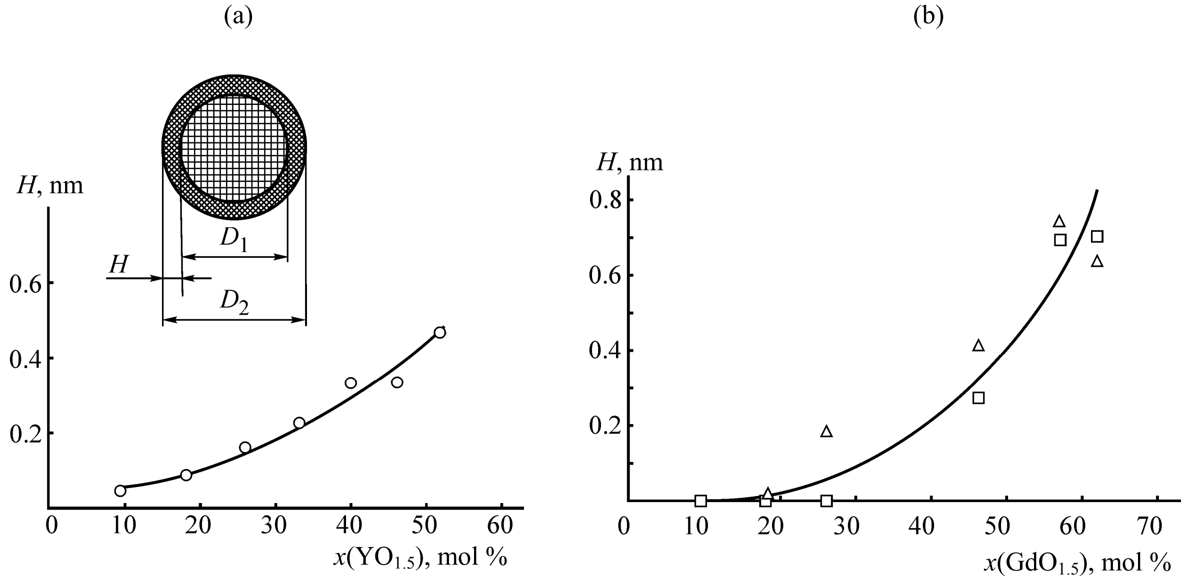

Fig. 4. The amorphous shell thickness as function of content of $YO_{1.5}$ (a) and $GdO_{1.5}$ (b) as derived from widening of X-ray diffraction bands (circles and squares) and from small-angle X-ray scattering (triangles).

Microstructure of the powder specimens and their elemental composition were determined using the Quanta 200 scanning electron microscope equipped with the EDAX X-ray microanalyzer.

Specimens structure and the elementary cell parameter were elucidated from the X-ray power diffraction data (Shimadzu XRD-7000, CuK_α, 2θ of 10° to 80°). The crystallites (coherent scattering area) size was determined from width of the diffraction lines taking advantage of the Scherrer equation.

Small-angle X-ray scattering (the Kratky compact camera, CuK_α) was used to study the powders prepared in the ZrO_2–Gd_2O_3–H_2O system. The experimental data on scattering intensity $I(q)$ ($q = 4\pi/\lambda \sin\theta/2$ with θ, scattering angle; λ, X-ray wavelength) were plotted in the Guinier coordinates, correcting for the collimation. From the linear parts of the plots, radii of inertia R_g of the nanoparticles were determined [41].

Parameters of the nanoparticles structure were derived taking advantage of the following model assumptions: the nanoparticles formed under hydrothermal conditions were uniform spheres, and the internal heterogeneity (if any) could be represented by combination of crystalline spherical core and spherical shell. Those assumptions were based on the results discussed in [20, 40, 42, 43], having revealed that the studied nanoparticles were of isometric shape and of narrow size distribution.

In the calculations, the following parameters were used: μ_1, molar mass of the core-forming compound of variable composition $Zr_{1-x}Gd_xO_{2-1.5x}$; μ_2, molar mass of $GdO_{1.5}$ forming the shell; specific gravities of the core (ρ_1) and the shell (ρ_2); electronic densities of the core ($\rho_{el,1}$) and the shell ($\rho_{el,2}$).

In the frame of the above-derived model, electronic radius of inertia R_g was associated with structural parameters and electronic densities of the core and the shell via Eqs. (1) and (2):

$$R_g = \sqrt{\frac{3}{20}\,\frac{D_1^5 + w(D_2^5 - D_1^5)}{D_1^2 + w(D_2^2 - D_1^2)}}, \qquad (1)$$

$$D_2 = D_1 \sqrt[2]{\frac{B}{A-1} - 1}\ . \qquad (2)$$

Here $A = 1/c$ (c, molar fraction of gadolinium in the shell with respect to its overall ratio in the particle); $B = (\rho_1\mu_2)/(\rho_2\mu_1)$; $w = \rho_{el,2}/\rho_{el,1}$; D_1 and D_2, diameters of the crystalline core and the particle, respectively. Combined solution of Eqs. (1) and (2) gave the values of D_1 and D_2 as well as the shell thickness $H = (D_2 - D_1)/2$.

Alternatively, the R_g value was determined via the method based on function of size distribution of geometrically similar particles [44, 45]. Radii of inertia determined by the both described methods were close in the cases of all the systems studied in this work.

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