

# Effect of ZrO<sub>2</sub> Nanocrystals on the Stabilization of the Amorphous State of Alumina and Silica in the ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>–SiO<sub>2</sub> Systems

O. V. Almjashaeva and V. V. Gusarov

*Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences,  
ul. Odoevskogo 24/2, St. Petersburg, 199155 Russia*

Received November 25, 2005

**Abstract**—Structural and chemical transformations in the ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>–SiO<sub>2</sub> systems containing ZrO<sub>2</sub> nanocrystals are examined. It is shown that the presence of zirconia nanoparticles in the oxide mixture retards the processes of crystallization and phase formation. The revealed effect is explained by the space blocking of nucleation in the systems under consideration.

**DOI:** 10.1134/S1087659606020064

## INTRODUCTION

The mutual influence of components on the rate of chemical and structural transformations in heterogeneous mixtures of oxides with different dispersions has been studied by many researchers [1–3]. It has been found that an increase in the surface area of contact between different oxides can lead to both an increase and a decrease in the rate of chemical and structural transformations [4–7]. In [8], the possible factors responsible for the opposite effects of an increase in the surface area of contact between components in heterogeneous systems on the rate of transformations were analyzed as functions of the chemical composition and the structure of the studied oxides. However, up to now, this question remains open. The investigation of the systems in which one or several components are nanocrystals is of particular interest because nanocrystals, as a rule, have a structure not typical of macrocrystals under the same conditions [9]. Furthermore, in this case, it can be expected that the surface area of contact between the components in the heterogeneous system will be maximum and, hence, the mutual influence of the oxides on the structural and chemical transformations will also be maximum.

The purpose of this work is to investigate how the nanocrystalline state of components affects the structural and chemical transformations in heterogeneous systems, in particular, the ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> (SiO<sub>2</sub>) systems in which zirconia has the form of nanocrystals.

## SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Zirconia-based nanocrystals were prepared under hydrothermal conditions according to the procedure described in detail in [9].

A heterogeneous mixture of zirconia and alumina was prepared through precipitation of aluminum hydroxide from a solution of AlCl<sub>3</sub> (analytical grade) in a suspension of ZrO<sub>2</sub> nanoparticles, followed by dehydration of the precipitate under hydrothermal treatment at temperatures of 350, 400, and 470°C.

Mixtures of zirconia and silica were prepared by mechanical mixing of macrocrystalline or nanocrystalline ZrO<sub>2</sub> with SiO<sub>2</sub> in the form of Aerosil A-300. Then, the mixtures were treated under “annealing–quenching” conditions at temperatures of 1300 and 1500°C.

The thermal and thermogravimetric effects in the course of heating of the samples in the ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> system were measured using complex thermal analysis on a Q-1500 C derivatograph (Hungary).

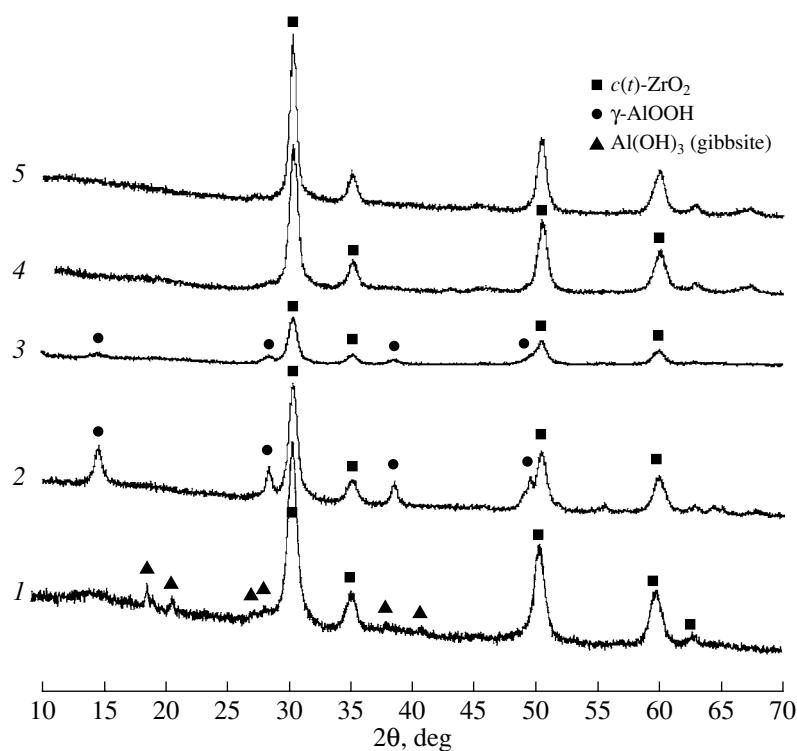
The phase transformations were determined by X-ray powder diffraction analysis on a DRON-3 diffractometer (CuK<sub>α</sub> radiation).

The elemental composition of the samples was determined by energy-dispersive X-ray microanalysis with the use of an Oxford Link microprobe attachment to a scanning electron microscope. The error in the determination of the element content was equal, on average, to ±0.3 wt %.

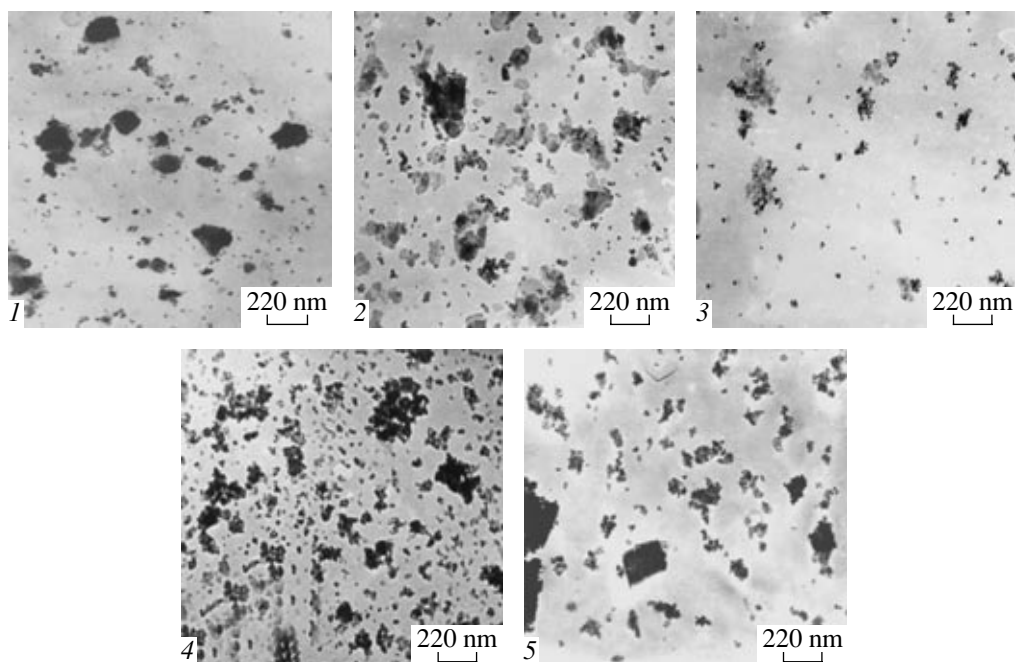
The particle sizes were determined from the broadening of lines in the X-ray diffraction patterns of the samples according to the Scherrer formula and by transmission electron microscopy (EM-125 microscope,  $U_{acc} = 75$  kV).

## RESULTS AND DISCUSSION

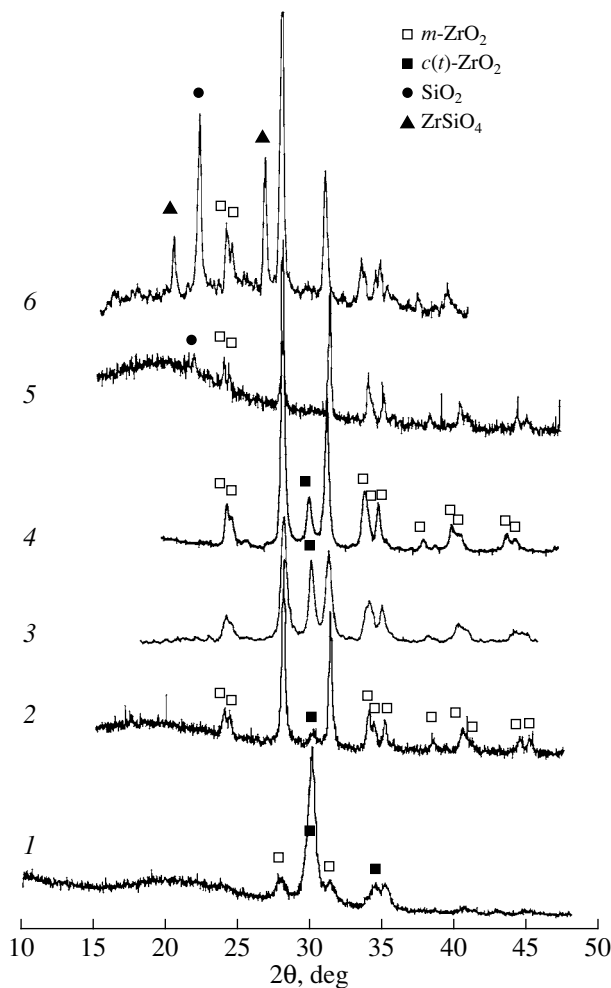
The cubic structure of zirconia (*c*-ZrO<sub>2</sub>) nanocrystals used for preparing the powdered samples in the ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> system was stabilized by introducing



**Fig. 1.** X-ray diffraction patterns of samples in the ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O system: (1) the initial sample; (2-4) the samples after hydrothermal treatment at (2) 350, (3) 400, and (4) 470°C; and (5) the sample after hydrothermal treatment at 400°C and subsequent annealing at 1000°C.



**Fig. 2.** Micrographs of samples in the ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O system. Preparation conditions for (1-5) samples are given in caption of Fig. 1.



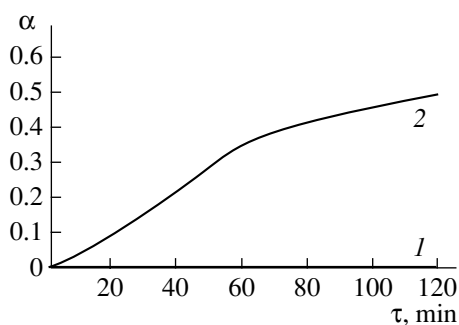
**Fig. 3.** X-ray diffraction patterns of the samples in the  $\text{ZrO}_2$ - $\text{SiO}_2$  system: (1) nanocrystals and (2) macrocrystals of the initial mixture of  $\text{ZrO}_2$  and  $\text{SiO}_2$  (A-300), (3, 4) the mixture of  $\text{ZrO}_2$  and  $\text{SiO}_2$  (A-300) nanocrystals heat treated at  $1300^\circ\text{C}$  for (3) 30 min and (4) 1 h, and (5) nanocrystals and (6) macrocrystals of the  $\text{ZrO}_2$  and  $\text{SiO}_2$  (A-300) mixture heat treated at  $1500^\circ\text{C}$  for 1 h.

3 mol %  $\text{Y}_2\text{O}_3$ . According to energy-dispersive X-ray microanalysis, the Al : Zr ratio in the samples under investigation corresponds to the eutectic ratio of alumina and zirconia in the phase diagram [10]. The analysis of the X-ray diffraction patterns demonstrated that the precipitate contains  $c$ - $\text{ZrO}_2$  nanocrystals 15–20 nm in size and trace amounts of monoclinic  $\text{Al}(\text{OH})_3$  (gibbsite) (Fig. 1, diffraction pattern 1).

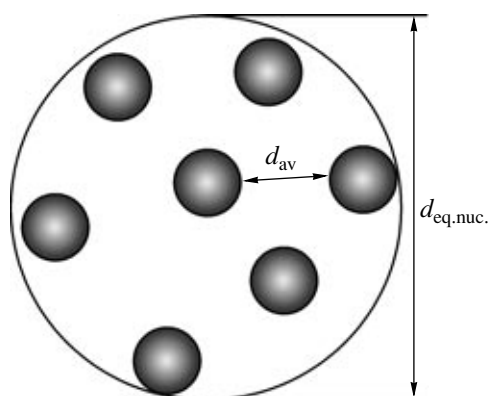
The examination under the transmission electron microscope showed that aluminum hydroxide is most likely concentrated on the surface of  $\text{ZrO}_2$  nanoparticles and in regions between them. This results in the formation of agglomerates up to 200 nm in size (Fig. 2, micrograph 1). In this case, aluminum hydroxide is apparently in the amorphous state and in the form of monoclinic  $\text{Al}(\text{OH})_3$  (gibbsite) (Fig. 1, diffraction pattern 1). After hydrothermal treatment at a temperature

of  $350^\circ\text{C}$ , the analysis of the X-ray diffraction patterns showed that the system involves the  $c$ - $\text{ZrO}_2$  phase and orthorhombic  $\gamma$ - $\text{AlOOH}$  (boehmite) crystals. The electron microscope images also revealed the presence of  $\gamma$ - $\text{AlOOH}$  in the system: in micrograph 2 in Fig. 2, the crystals with the shape typical of  $\gamma$ - $\text{AlOOH}$  (boehmite) can be seen against the background of agglomerates formed by  $c$ - $\text{ZrO}_2$  nanoparticles. An increase in the temperature of hydrothermal treatment to  $400^\circ\text{C}$  leads to a decrease in the content of  $\gamma$ - $\text{AlOOH}$  (Fig. 1, diffraction pattern 3). The shape of the diffraction peaks suggests that the fraction of relatively large  $\gamma$ - $\text{AlOOH}$  particles decreases. This effect was analyzed in our earlier work [11]. After hydrothermal treatment at  $470^\circ\text{C}$ , only one crystalline phase, i.e.,  $c$ - $\text{ZrO}_2$  nanocrystals, is identified in the system (Fig. 1, diffraction pattern 4). However, according to energy-dispersive X-ray microanalysis, the Zr : Al ratio remains approximately identical to that at the initial stage upon formation of aluminum hydroxide in the suspension of zirconia nanoparticles in agglomerates is lower than that in the system containing  $\gamma$ - $\text{AlOOH}$  crystals (compare micrographs 2 and 4 in Fig. 2). The specific features revealed in the structure of the alumina-zirconia system can be explained by the formation of a layer of amorphous alumina on the surface of zirconia nanocrystals upon dehydration of  $\gamma$ - $\text{AlOOH}$ . It should also be noted that, in the absence of  $\text{ZrO}_2$  nanocrystals, aluminum oxyhydroxide  $\gamma$ - $\text{AlOOH}$  under the same conditions of hydrothermal treatment decomposes with the formation of crystalline  $\text{Al}_2\text{O}_3$  [11]. Heat treatment of the samples at temperatures up to  $1000^\circ\text{C}$  does not result in the formation of crystalline alumina (Fig. 1, diffraction pattern 5) in distinction to heat treatment of pure alumina under the same conditions [11]. It follows from the broadening of the X-ray diffraction peaks that the size of  $c$ - $\text{ZrO}_2$  particles remains virtually unchanged. At the same time, it should be noted that denser agglomerates are formed upon heat treatment of the samples (Fig. 2, micrograph 5), most likely, due to their sintering.

A heterogeneous equimolar mixture of zirconia and silica was prepared through mechanical mixing of  $\text{ZrO}_2$  nanocrystals (produced by the hydrothermal method [9]) with nanosized amorphous  $\text{SiO}_2$  (Aerosil A-300, the particle diameter is approximately equal to 5 nm). Moreover, for comparison, a mixture of zirconia macrocrystals (the particle size is equal to a few tens of micrometers) with Aerosil A-300 was prepared using the same procedure. The analysis of the X-ray diffraction patterns of the initial mixtures showed that  $\text{ZrO}_2$  nanocrystals predominantly have a cubic structure (Fig. 3, diffraction pattern 1), whereas macrocrystals have a monoclinic structure (Fig. 3, diffraction pattern 2). Heat treatment of the mixture of zirconia and silica nanoparticles at a temperature of  $1300^\circ\text{C}$  results in a partial transformation of the cubic zirconia modification into the monoclinic modification. It should be



**Fig. 4.** Degree of conversion upon formation of zircon at a temperature of 1500°C in the mixture of zirconia and silica (A-300) containing (1) ZrO<sub>2</sub> nanocrystals and (2) ZrO<sub>2</sub> macrocrystals.



**Fig. 5.** Schematic drawing of the heterogeneous system containing inclusions of particles of the second phase (closed circles) uniformly distributed in the first phase (white field). Designations:  $d_{av}$  is the average distance between nanoparticles, and  $d_{eq.nuc.}$  is the equilibrium-nucleus size.

noted that the size of ZrO<sub>2</sub> nanoparticles remains nearly unchanged. In this case, neither crystallization of amorphous silica nor the formation of zircon (ZrSiO<sub>4</sub>) were observed in the system (Fig. 3, diffraction patterns 3, 4). Only heat treatment of the nanoparticle mixture at a temperature of 1500°C leads to a noticeable increase in the size of ZrO<sub>2</sub> crystals and to the appearance of trace amounts of crystalline silica in the form of cristobalite (Fig. 3, diffraction pattern 5). Moreover, heat treatments for one hour or longer times do not result in the formation of ZrSiO<sub>4</sub> in the system (Fig. 4). It should also be noted that the interaction of ZrO<sub>2</sub> macrocrystals with Aerosil under the same conditions is accompanied by more intensive crystallization of amorphous silica (Fig. 3, diffraction pattern 6) and a rather active chemical interaction of the components with the formation of zircon (Fig. 3, diffraction patterns 4, 6).

Therefore, the decrease in the particle size to nanometers leads to a decrease in the rate of chemical and structural transformations in heterogeneous systems as compared to the rate of similar processes in systems containing macroparticles. This finding contradicts the traditional concepts regarding the influence of the particle size on the rate of phase and chemical transformations in systems [1]. The more stable state of heterogeneous systems composed of nanoparticles as compared to systems that have the same chemical composition but consist of macroparticles can be explained by the influence of nanoparticles on nucleation processes. For example, in the case when the size of an equilibrium nucleus is larger than the average distance between nanoparticles of another component (Fig. 5), the formation of nuclei is blocked by the second component. A new phase cannot crystallize until the sizes of these particles increase as a result of recrystallization processes so that the interparticle distance becomes larger than the equilibrium-nucleus size. This inference is strongly supported by the X-ray diffraction data (Fig. 3, diffraction pattern 5), which indicate that, only after a substantial increase in the size of ZrO<sub>2</sub> particles, there can occur crystallization of amorphous silica.

## CONCLUSIONS

Thus, the results obtained in this work have demonstrated that, in nanoheterogeneous systems, unlike macroheterogeneous systems, the rate of processes, as a rule, is determined by the nucleation rate rather than by the mass transfer rate and, hence, the rate of structural and chemical transformations in the former systems can be changed by controlling nucleation processes.

A uniform distribution of a particular number of nanoparticles in a heterogeneous system can prevent crystallization of amorphous components and phase formation in the case when the size of a nucleus of a new phase exceeds the characteristic distance between nanoparticles.

## ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 04-03-81005-Bel2004-a.

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