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## Local Structure of Amorphous and Highly Dispersed Zirconium Hydroxides and Oxides

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**Abstract**—The local structure of amorphous and highly dispersed hydroxide and oxide zirconium compounds prepared from zirconyl nitrate solutions by precipitation was studied by an X-ray diffraction technique of radial electron distribution. It was found that X-ray amorphous precipitates were formed at 383 K. These precipitates were polynuclear hydroxo complexes, whose short-range ordering was similar to the structure of a cubic  $ZrO_2$  phase. A special feature of these formations, compared with the cubic oxide phase, is that the closest Zr–Zr distance in them is shortened by 0.2 Å,  $NO_3$  and OH groups are the constituents of an anionic sublattice, and the coordination number of Zr–anion distances is increased. Calcination at 653 K followed by cooling to room temperature resulted in the appearance of a monoclinic  $ZrO_2$  phase with a crystallite size of ~60 Å along with the cubic phase. The amount of the former phase depended on the pH of precipitation and on the presence of residual  $NO_3$  and OH groups in precipitates.

### INTRODUCTION

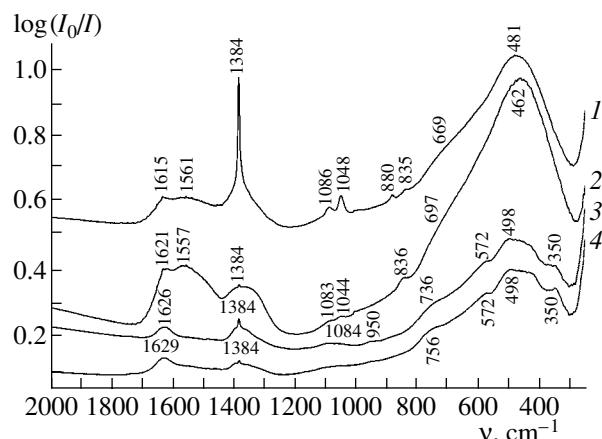
The considerable interest in low-temperature zirconium oxide compounds is due to the extended areas of application of these materials, not only as starting components for the production of high-temperature electrolytes and refractories but also as catalysts and supports. Catalysts based on  $ZrO_2$  are used in redox reactions, hydrocarbon isomerization, various organic syntheses, and selective oxidation reactions. Zirconium oxides are the main components of three-way catalysts (TWCs), which are used for the removal of  $CO$ ,  $NO_x$ , and hydrocarbons from automotive exhaust emissions.

Low-temperature metastable phases, which are characterized by a certain structure and a developed specific surface area, are of particular interest in catalysis. Various procedures for the preparation of hydrated zirconium dioxide were considered in sufficient detail in [1]. Strekalovskii *et al.* [2] concentrated most of their attention on the properties and preparation of highly dispersed zirconium dioxide and considered the mechanism of its dehydration and the nature of metastable zirconium dioxide modifications. Domnina and Filatov [3] studied phase transitions in zirconium dioxide using high-temperature diffractometry. They found that, over a wide temperature range (673–1123 K), a metastable tetragonal modification was detected, with a variable  $c/a$  ratio depending on temperature. According to Domnina and Filatov [3], it was unambiguously demonstrated that only a single phase was formed in the above temperature range. An increase in the calcination temperature to 1123 K was favorable for the conversion of this phase into a stable tetragonal phase of  $ZrO_2$ . Upon cooling, this stable phase transformed to a monoclinic phase. Domnina and Filatov [3] believed that the metastable tetragonal modification was formed by

the continuous stretching (diffusionless martensite transition) of a cubic structure along a coordinate axis. The extrapolation of the  $c/a$  ratio to unity gave a cubic unit-cell parameter equal to 5.09 Å at 523 K; however, this cubic phase was not directly observed in experiments. On the other hand, Sukharevskii *et al.* [4] found that the metastable tetragonal phase transformed to a monoclinic phase upon cooling; however, this transition can be partially or even completely blocked by tetragonal structure defects. In the best case, to characterize the structures of test compounds, Sukharevskii *et al.* [4] cited diffraction patterns for individual polycrystalline phases and used the term *X-ray amorphous* for highly dispersed samples.

According to Goldschmidt, the cubic modification of a fluorite structure is usually crystallized under conditions where  $R_c/R_a > 0.723$ , where  $R_c$  and  $R_a$  are the ionic radii of the cation and the anion, respectively. This ratio is equal to 0.66 for  $ZrO_2$ ; therefore, a cubic phase can be stabilized by increasing the distance between anionic positions. This is achieved either by the replacement of cations or by a modification of the anionic sublattice. Boganov *et al.* [5] used another stabilization mechanism, namely, lattice expansion by a temperature effect, to prepare cubic  $ZrO_2$  with  $a = 5.256$  Å by heating it to 2603 K in a vacuum. Garvie [6] obtained a cubic modification of  $ZrO_2$  with  $a = 5.09$  Å; he believed that the stabilization of this phase was related to a small size of crystallites.

The aim of this work was to study the local structure of amorphous and dispersed zirconium hydroxide and oxide compounds by the direct X-ray diffraction technique of constructing electron radial distribution func-



**Fig. 1.** IR absorption spectra of samples prepared at different pH of precipitation and treated at various temperatures: (1) pH 7,  $T = 383$  K; (2) pH 9,  $T = 383$  K; (3) pH 7,  $T = 653$  K; and (4) pH 9,  $T = 653$  K.

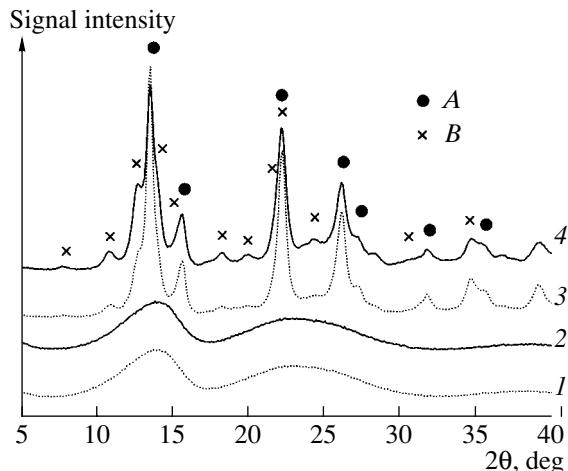
tions (RDFs), which provides information on interatomic distances and coordination numbers.

## EXPERIMENTAL

The samples were prepared by the precipitation of an aqueous zirconyl nitrate solution with an aqueous ammonia solution (1 : 1) at pH 7 (samples 1 and 3) or 9 (samples 2 and 4) and  $343 \pm 2$  K followed by filtration and precipitate washing with distilled water until the absence of nitrates from the filtrate. The precipitates were dried in air and then in a drying oven at 383 K for 12–14 h (samples 1 and 2). Thermal treatment was performed in a flow of dry air at 653 K for 4 h (samples 3 and 4). Samples 1 and 2 had a specific surface area of  $430 \text{ m}^2/\text{g}$ ; samples 3 and 4 had specific surface areas of 150 and  $190 \text{ m}^2/\text{g}$ , respectively.

The IR absorption spectra were measured on a BOMEM-102 spectrometer.

The X-ray diffraction patterns were obtained on a high-resolution diffractometer at the Synchrotron Radiation Station of the Siberian Center (Budker Institute of Nuclear Physics, Siberian Division, Russian Academy of Sciences) with the use of a Si(1.1.1) monochromator crystal, which separated radiation with  $\lambda = 0.695 \text{ \AA}$  and provided a degree of monochromatization of  $\Delta\lambda/\lambda \sim 10^{-4}$ . Scanning was performed over an angle range from  $5^\circ$  to  $135^\circ$  ( $2\theta$ ). According to a published procedure [7], the radial electron distribution (RED) curves, which have the form  $4\pi r^2 \rho(r)$ , where  $r$  is the interatomic distance in  $\text{\AA}$ , and  $4\pi r^2 \rho$  is the radial electron distance in  $(\text{electron})^2/\text{\AA}$ , were calculated from measured X-ray scattering intensities.



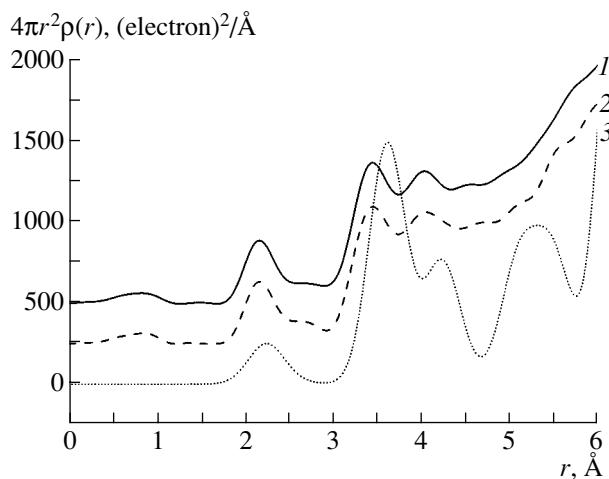
**Fig. 2.** Diffraction patterns of samples prepared at different pH of precipitation and treated at various temperatures: (1) pH 7,  $T = 383$  K; (2) pH 9,  $T = 383$  K; (3) pH 7,  $T = 653$  K; and (4) pH 9,  $T = 653$  K. A and B indicate the diffraction peaks of cubic and monoclinic  $\text{ZrO}_2$  phases, respectively.

## RESULTS AND DISCUSSION

Figure 1 demonstrates the IR absorption spectra of the test samples. The samples treated at 383 K contained absorption bands due to the vibrations of the  $\text{NO}_3$  group ( $835$  and  $1384 \text{ cm}^{-1}$ ), along with absorption bands characteristic of the  $\text{Zr}-\text{O}$  bond ( $481$  and  $669 \text{ cm}^{-1}$ ). The former bands were most pronounced in a sample prepared at pH 7. The intensity of these bands decreased upon thermal treatment. Moreover, broad absorption bands due to the vibrations of the  $\text{Zr}-\text{O}$  bond were split. A number of absorption bands ( $880$ ,  $1048$ ,  $1086$ , and  $1561 \text{ cm}^{-1}$ ) due to the vibrations of  $\text{CO}_3$  groups and a band at  $1615 \text{ cm}^{-1}$  due to the deformation vibration of  $\text{H}_2\text{O}$  were observed in the spectra of all of the samples. The appearance of these bands was related to the carbonization of the samples and to the sorption of water, which usually occurred if powders with high specific surface areas were removed into air.

Figure 2 demonstrates the diffraction patterns of samples synthesized at various temperatures and pH of precipitation. It can be seen in Fig. 2 that the samples dried at 383 K (1, 2) were X-ray amorphous; the size of crystallites was  $\sim 10 \text{ \AA}$ , as estimated from 1.1.1 diffraction peak broadening (on the assumption of the formation of a cubic phase). After heating to 653 K and cooling to room temperature, two zirconium oxide phases, cubic and monoclinic, with a crystallite size of  $\sim 60 \text{ \AA}$ , were formed in these samples. The amounts of the monoclinic phase were estimated using the external standard technique to be 40 and 60% for samples 3 and 4, which were prepared at pH 7 and 9, respectively.

Figure 3 demonstrates the RED curves calculated from experimental data for samples 1 and 2 and a model curve for cubic  $\text{ZrO}_2$  ( $a = 5.09 \text{ \AA}$ ). The experimental curves practically do not differ from each other and significantly differ from the model curve. First,

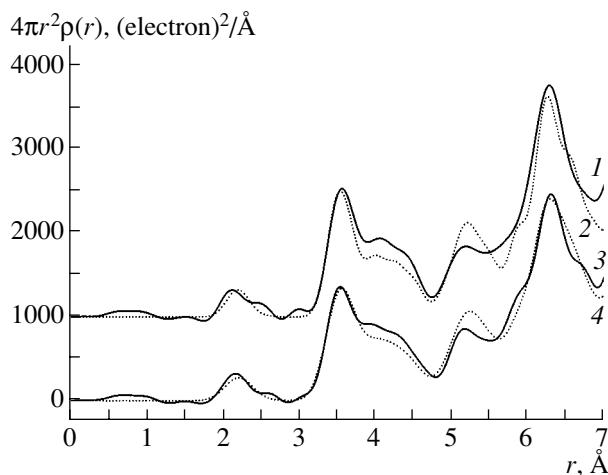


**Fig. 3.** RED curves for samples prepared at pH (1) 7 and (2) 9 and thermally treated at 383 K and (3) a model RED curve for the cubic  $\text{ZrO}_2$  phase of a fluorite structure.

these differences concern a shift of the coordination peak that corresponds to the  $\text{Zr-Zr}$  distance toward smaller values of  $r$  (see table). Moreover, the experimental curves exhibit an additional peak at 2.63 Å, different ratios between the intensities of peaks related to  $\text{Zr-Zr}$  and  $\text{Zr-O}$  distances, and a practically complete disappearance of peaks at  $r$  values greater than 4.5 Å. This circumstance lends support to the validity of crystallite size calculations from X-ray diffraction data.

Figure 4 illustrates the simulation of the phase composition of two samples prepared at different pH values and thermally treated at 653 K. The model curves were calculated based on structure data (interatomic distances and coordination numbers) for a cubic fluorite-like phase ( $a = 5.09$  Å) and a monoclinic phase ( $a = 5.15$  Å,  $b = 5.21$  Å, and  $c = 5.31$  Å;  $\beta = 99.2^\circ$ ). The main differences between the experimental and model curves are the occurrence of a peak at 2.63 Å, which is characteristic of the  $\text{Zr-NO}_3$  bond in the structure of  $\text{ZrO}(\text{NO}_3)_2$ , and a peak at 3.05 Å, which is characteristic of the  $\text{Zr-OH}$  bond, in the experimental curves of both of the two samples, as well as an inconsistency between the peak areas in the range from 4.0 to 5.8 Å. Coordination peaks that correspond to  $\text{Zr-O}$  and  $\text{Zr-Zr}$  distances occur in the regions 4.0–4.5 and 5.1–5.3 Å, respectively.

The formation of a local structure of low-temperature (383 K) phases can be explained based on the assumption that the formation of a hydroxide precipitate includes hydrolysis, complexation, and polymerization. In the precipitation of zirconium hydroxide, polymer aggregates (primary particles), which exhibit initial signs of an oxide phase, are formed due to hydrolysis and polymerization. The deformation of polymer particles can result in a decrease in the  $\text{Zr-Zr}$  distance ( $r = 3.4$  Å) and in an increase in the  $\text{Zr-O}$  distance ( $r \sim 3.99$  Å). The intensity ratios between these



**Fig. 4.** RED curves for samples prepared at pH (1) 7 and (3) 9 and thermally treated at 653 K and model RED curves for mixtures of the monoclinic and cubic  $\text{ZrO}_2$  phases in ratios of (2) 2 : 3 and (4) 3 : 2.

peaks for X-ray amorphous low-temperature formations and a crystalline cubic phase were  $\varepsilon_1 = 1 : 1$  and  $\varepsilon_2 = 2 : 1$ , respectively. An analogous structure was observed previously in a study of the polynuclear hydroxide complexes of palladium [8]. As the temperature was increased to 653 K, the values of  $\varepsilon_1$  and  $\varepsilon_2$  in the test samples approached each other; however, a well-crystallized cubic phase was not observed. Because of this, the simulation of RED curves for these samples, based on the well-crystallized structures of cubic and monoclinic phases, did not result in a complete fit between the model and experimental curves.

It is our opinion that the simultaneous appearance of a monoclinic phase and the stabilization of a cubic  $\text{ZrO}_2$  phase upon cooling from 653 K to room temperature depend on the sample preparation procedure. According to our data, a sample dried at 383 K contained  $\text{NO}_3^-$  groups, which are the constituents of the hydroxide structure. It is well known that the crystallization temperature of an X-ray amorphous hydroxide depends on the amount and nature of anions in it [9]. At odds with our data, Domnina and Filatov [3] observed the crystallization of a metastable tetragonal phase at 723 K; that

Experimental and calculated values of  $r$  and coordination number (CN)

Distance	Cubic $\text{ZrO}_2$ (calculated)		Sample 1 (pH 7; $T = 383$ K)		Sample 2 (pH 9; $T = 383$ K)	
	$r, \text{Å}$	CN	$r, \text{Å}$	CN	$r, \text{Å}$	CN
$\text{Zr-O}$	2.20	8	2.14	9.4	2.15	9.7
$\text{Zr-(N, O)}$	—	—	2.63	4.7	2.58	3.9
$\text{Zr-Zr}$	3.60	12	3.40	6.3	3.40	5.9
$\text{Zr-O}$	4.22	24	3.98	30.3	3.99	35

is, it is believed that the amount of impurities in their sample was greater than in our case. Upon cooling, this phase anisotropically compressed and be converted into a cubic phase. From this point of view, a metastable tetragonal phase with an inhomogeneous distribution of defects, which was due to a concentration inhomogeneity with respect to  $\text{NO}_3$  and OH groups, was directly formed in our samples at 653 K. It is likely that cooling resulted in the separation of this phase into regions with greater and smaller numbers of defects or without defects at all. As found by Sukharevskii *et al.* [4], upon cooling of a sample, these defects blocked the transition from a tetragonal to a monoclinic phase. Therefore, according to Domnina and Filatov [3], the anisotropic compression of a tetragonal cell resulted in the formation of a cubic phase, which was also stable at room temperature. The portion of a sample with a smaller number of defects was converted from a metastable tetragonal to a monoclinic phase upon cooling. Because of this, the sample containing a large number of  $\text{NO}_3$  groups was obtained with a smaller amount of a monoclinic phase upon successive heating and cooling.

The statement of Garvie [6] about cubic modification as a manifestation of the size effect seems inconsistent. The size of 300 Å is considered critical for the existence of a monoclinic phase, whereas smaller particles crystallize in tetragonal or cubic modifications. However, in our experiments, the particles of a monoclinic phase were 60 Å in size.

Thus, a study of the low-temperature (383 K) products of the precipitation of zirconyl nitrate solutions with ammonia demonstrated that X-ray amorphous polynuclear hydroxo complexes were formed, the short-range ordering of which is analogous to the cubic

phase of  $\text{ZrO}_2$ . Specific features of these structures include a Zr-Zr distance shortened by 0.2 Å, an increased coordination number of zirconium with respect to oxygen, and the incorporation of  $\text{NO}_3$  and OH groups into the structure. The thermal treatment at 653 K and cooling to room temperature resulted in the appearance of a monoclinic  $\text{ZrO}_2$  phase with a crystallite size of ~60 Å. The amount of this phase depended on the pH of precipitation and on the concentrations of residual OH and  $\text{NO}_3$  groups.

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