Nature and Conditions of Formation of Structural Defects in Zirconium(IV) Oxide in the Course of Its Preparation from Zirconium Hydroxide

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Received February 9, 2005

Abstract—The nature of paramagnetic defects in nanosized ZrO_2 samples prepared by the sol–gel method was studied by ESR. Conditions of formation of different centers $(Zr^{3+}, F \text{ centers}, O^-, O_2^-)$ in ZrO_2 were elucidated. The Zr^{3+} and O^- centers arise in the course of thermal dehydration of $Zr(OH)_4$ under the conditions when the formation of a Zr–O–Zr bridging bond is hindered. The *F* centers are formed in ZrO_2 on heating in a reducing atmosphere or as a result of structural rearrangements accompanied by a decrease in the amount of lattice oxygen in the coordination surrounding of Zr(IV). **DOI:** 10.1134/S1070363207040056

Simulation of the ZrO_2 structure and studies of its properties are important for the development of materials for various purposes. ZrO_2 doped with CaO, Y_2O_3 , or other oxides is the most important oxygenion conductor [1–4]. In addition, it is of interest as a catalyst support [5–9] and as a component of complex oxide catalytic systems based on CeO₂ [10, 11]. It is also known as an active additive to some glass-forming oxides (SiO₂, GeO₂), strongly affecting the optical and mechanical properties of glasses [12–15], and as a matrix for rare-earth elements, affecting the luminescence properties of the system [16–18].

The properties of materials containing ZrO_2 differ essentially depending on the structural and phase state of the material [19]. It is known that, depending on the conditions of synthesis and heat treatment of ZrO_2 , various structural modifications can be obtained: stable (monoclinic) and metastable (amorphous, tetragonal, cubic) [20]. The formation and stabilization of nonequilibrium phases in ZO_2 in a wide temperature range are primarily favored by the high dispersity of $Zr(OH)_4$ and ZrO_2 particles, and also by the nonstoichiometry in the ZrO_2 structure caused by formation of oxygen vacancies [21, 22].

A promising procedure for preparing finely dispersed ZrO_2 is the sol-gel method based on the use of inorganic precursors [23, 24]. It was shown [24–27] that additives introduced for the stabilization of metal hydroxide sols (HNO₃, C-containing compounds), when decomposing on heating, promote formation of structural defects in oxides $(SnO_2, In_2O_3, ZrO_2, MoO_3)$, primarily of anionic vacancies and of metal ions in a lower (compared to the main substance) oxidation state. However, structural defects caused by the oxygen deficiency in the crystal lattice of some oxides (MoO_3, ZrO_2) are also formed in the course of thermal dehydration of metal hydroxides without N-and C-containing additives [27, 28].

In most cases, ZrO_2 obtained by thermal dehydration of $Zr(OH)_4$ xerogels is nanosized and nonstoichiometric. Data of [29–37] show that, depending on the formation conditions, ZrO_2 and oxide systems based on it can contain paramagnetic defects of the following types: Zr^{3+} , *F* centers (color centers V_0^-), hole centers O^- , and adsorbed radical anions O_2^- . At significant disturbance of the stoichiometry in the course of mechanochemical activation, formation of crystallographic shear structures containing Zr^{3+} with ordering of $[Zr^{4+}-Zr^{3+}]$ pairs is assumed; such structures are not detected by ESR [37].

However, it is unclear from the available data what factors favor formation of various kinds of structural defects in ZrO_2 . For example, it is unclear under what conditions the nonstoichiometry of ZrO_2 , caused by formation of oxygen vacancies in the course of thermal dehydration of $Zr(OH)_4$, leads to the formation of Zr^{3+} defects and under what conditions it causes the formation of color centers (*F* centers), i.e., of electrons localized in oxygen vacancies. Data on this matter are contradictory. Furthermore, no data are available on the formation of hole centers O^- in ZrO_2 .

Thus, the nature of defects prevailing in ZrO_2 depending on the conditions of synthesis and heat treatment remains a matter of discussion.

The goal of this study was to elucidate the nature of structural defects in finely dispersed samples of ZrO_2 depending on the heat treatment conditions. To this end, we varied the conditions of synthesis and heat treatment to an extent ensuring significant effect on the structure of primary $Zr(OH)_4$ particles and on the process of their dehydration and crystallization in the course of heat treatment.

Structural features of ZrO₂ in relation to synthesis conditions. Samples were prepared at high concentrations of ammonia or NaOH. These conditions ensure formation of the product from which, in the course of heating, an amorphous ZrO₂ phase is formed initially; with increasing temperature, it gradually transforms into tetragonal and then into stable monoclinic phase of ZrO₂. The formation and stabilization of the amorphous and tetragonal phases of ZrO₂ are favored by high concentration of OH groups in the course of the synthesis (pH 9.5-10.0). The OH groups present in a large amount on the surface of primary particles and the bonds between them prevent the polymerization and condensation. Crystallization processes in such samples are observed at higher temperatures than in samples prepared at lower pH values (pH 8.0-9.0). An increase in the crystallization temperature favors formation of tetragonal, and not monoclinic, ZrO₂ phase in a wider temperature range. Transformation of the precipitate into a sol leads to further inhibition of the crystallization of the amorphous phase and to higher temperature of formation of the tetragonal and/or monoclinic phase. It is presumed that xerogels of such samples have a developed surface layer consisting of polymeric cationic zirconium species, which provides high content of water in the sols dried at 100°C; the water molecules stabilize the nondissociated OH groups on the surface. The monoclinic ZrO_2 phase can be formed directly from the amorphous xerogel, without intermediate formation of the tetragonal phase, if zirconium hydroxide was precipitated at pH 8.3-8.5.

Hydrolysis in an acidic $ZrO(NO_3)_2$ solution (pH 4.2–4.5) leads to the formation of the monoclinic phase at low temperatrue. It is noted [19] that the monoclinic structure is formed under such conditions even in solution in the course of precipitation (without formation of the amorphous phase). The phase composition of the main examined samples of ZrO_2 in relation to the pH of precipitation and calcination temperature is given in Table 1.

All the samples synthesized in an alkaline solution (pH 8–10), dried at 100°C, and calcined at 300°C are

Table 1. Phase composition of ZrO_2 samples obtained at different precipitant concentrations and calcination temperatures ($^{\circ}C)^{a}$

	<i>T</i> , °C				
Precipitant and concentration	300	500	700	950	
NaOH, 2.8 M	XA	Т	Т	Т	
NH ₄ OH, 5.5 M	XA	XA	Т	Т	
NH_4OH , 3.0 M	XA	Т	Т	T + M	
NH_4OH , 1.5 M	XA	M + T	M + T	Μ	
$NH_4OH, 0.5$ M	XA	Μ	Μ	Μ	
	М	М	М	М	
	Precipitant and concentration NaOH, 2.8 M NH ₄ OH, 5.5 M NH ₄ OH, 3.0 M NH ₄ OH, 1.5 M NH ₄ OH, 0.5 M	$\begin{array}{c} \mbox{Precipitant and concentration} \\ \mbox{NaOH, 2.8 M} & XA \\ \mbox{NH}_4OH, 5.5 M & XA \\ \mbox{NH}_4OH, 3.0 M & XA \\ \mbox{NH}_4OH, 1.5 M & XA \\ \mbox{NH}_4OH, 0.5 M & XA \\ \mbox{-} & M \end{array}$	$\begin{array}{c c} & T, \\ \hline T, \\ \hline Precipitant and concentration \\ \hline 300 \\ \hline 500 \\ \hline \\ NaOH, 2.8 \\ NH_4OH, 5.5 \\ NH_4OH, 5.5 \\ NH_4OH, 3.0 \\ M \\ NH_4OH, 1.5 \\ M \\ NH_4OH, 0.5 \\ M \\ - \\ M \\ M \\ \hline \end{array}$	$\begin{array}{c c} T, \ ^{\circ}C \\ \hline T, \ ^{\circ}C \\ \hline Precipitant and concentration \\ 300 \\ 500 \\ 500 \\ 500 \\ 700 \\ \hline \\ 7$	

^a (XA) X-ray amorphous, (M) monoclinic, and (T) tetragonal phase.

X-ray amorphous. Calcination at 500°C leads to the formation of crystalline phases: tetragonal, monoclinic, or their mixture with different extents of crystallization depending on the synthesis conditions. It should be noted, however, that calcination at 500°C, as a rule, does not eliminate the amorphous phase completely, and the other phases are poorly crystallized. Formation of fragments of crystalline structures starts long before the phase becomes detectable by X-ray phase analysis and DTA.

 Zr^{3+} centers. The Zr^{3+} signal is observed in the ESR spectra of samples synthesized in alkaline solutions and containing both amorphous and crystalline (tetragonal, monoclinic) phases of ZrO2. Figure 1 shows the spectra of ZrO₂ samples differing (according to X-ray phase analysis) in the phase composition. The Zr³⁺ signal has an axial shape with a weakly pronounced g_{\parallel} component, which is particularly characteristic of samples having an amorphous structure (Fig. 1, spectrum 1). It is known that such a shape (broadened signal with a weakly pronounced parallel component) is caused by the facts that the coordination surrounding of Zr³⁺ is nonuniform and the structure as a whole is amorphous. The parameters of the ESR spectra of the ZrO_2 samples meet the condition $g_{\parallel}, g_{\perp} < g_{\rm e} (d^{\rm l} \text{ state of } Zr^{3+})$ and, depending on the sample history, can be somewhat different $(g_{\perp} 1.977 -$ 1.979, g_{\parallel} 1.958–1.963). With an increase in the degree of crystallinity of the samples in going from amorphous to tetragonal and then monoclinic structure, the anisotropy of the Zr^{3+} spectrum $(\Delta g = g_{\perp} - g_{\parallel})$ decreases from 0.020 to 0.016.

The Zr^{3+} signal appears in the ESR spectra of ZrO_2 samples prepared by low-temperature calcina-

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 77 No. 4 2007



Fig. 1. ESR spectra of ZrO_2 samples of various phase compositions (300 K): (1) amorphous, (2) monoclinic, and (3) tetragonal.

tion of both the precipitates prepared at high pH values (9.0-10.0) and of xerogels (air-dry sols prepared by converting the precipitates into a colloid state). In the case of xerogels, Zr^{3+} appears in ZrO_2 at a lower temperature (150°C) than in heat treatment of the precipitates (200°C). With increasing calcination temperature, the concentration of Zr^{3+} in ZrO_2 passes through a maximum (500°C, Fig. 2). Under similar conditions of heat treatment, the Zr³⁺ concentration in the samples prepared from sols is higher than in the samples prepared from the $Zr(OH)_4$ precipitate. Calculation shows that the Zr^{3+} : Zr^{4+} ratio in the ZrO_2 sample with the highest content of Zr^{3+} $(\sim 10^{18} \text{ g}^{=1})$ is about 1 : 4000. This content of Zr^{3+} is sufficiently high for affecting the adsorption and catalytic properties of ZrO_2 , taking into account the arrangement of the Zr^{3+} centers on the surface.



Fig. 2. Logarithm of the Zr^{3+} concentration in ZrO_2 (*c*) as a function of the calcination temperature: (*1*) xerogel and (*2*) precipitate.

The sample synthesized using ammonia and calcined at 700°C gives two signals from Zr^{3+} centers. These signals have the same shape and somewhat differ in the *g*-factors, suggesting a certain difference in the coordination surrounding of Zr^{3+} (Fig. 3). The spectrum of the sample calcined at a lower temperature (500°C) contains only the signal with the larger anisotropy, and that of the sample calcined at 950°C, only the signal with a smaller anisotropy (Table 2).

The observed difference in the anisotropy of the Zr^{3+} ESR signals may be due to the fact that one of them (with a smaller anisotropy) belongs to bulk Zr^{3+} centers, and the other (with a larger anisotropy), to surface Zr^{3+} centers. Morterra et al. [33] also assigned the two observed signals to the surface and bulk Zr^{3+} centers. In this case, an increase in the concentration

Precipitant $(T, °C)$	Zr ³⁺		Zr ³⁺ concentration,	0-		0 <u>-</u>		
	g_{\perp}	g	$\times 10^{-16}, g^{-1}$	g_{\perp}	g_{\parallel}	<i>g</i> ₁	<i>g</i> ₂	<i>g</i> ₃
NH ₄ OH (500)	1.979	1.958	100	2.055	2.044		2.033	
NH ₄ OH (700)	1.979	1.958	20	2.055	2.044	2.033	2.008	2.003
	1.977	1.965						
NH ₄ OH (950)	1.978	1.964	4	2.045		2.033	2.008	2.003
NaOH (500)	1.977	1.963	40	_		2.033	_	2.003
NaOH (700)	1.976	1.961	3	2.055	2.044	2.033	2.008	2.003

Table 2. Parameters of the ESR spectra of some ZrO_2 samples differing in the conditions of the synthesis and heat treatment



Fig. 3. ESR spectra of ZrO_2 (77 K) synthesized with NH₄OH and calcined at (1) 500, (2) 700, and (3) 950°C. Insert: fragments of ESR spectra of Zr^{3+} centers in ZrO_2 samples 1 and 2.

of bulk centers with increasing calcination temperature is attributable to coalescence of the primary particles; in the process, the initially surface centers become bulk centers. However, it is not improbable that the change in the anisotropy is due to the fact that the crystalline structure of ZrO₂ becomes more perfect. In the spectra of samples containing the better crystallized monoclinic phase, Δg is lower than in the spectra of the amorphous and tetragonal samples. However, the interpretation based on the surface and bulk centers seems preferable, because structural rearrangements occurring in the course of formation of the monoclinic ZrO₂ structure lead to a considerable decrase in the surface area of the dioxide compared to the samples having amorphous or tetragonal structure. Under similar conditions of heat treatment, the Zr^{3+} concentration and signal anisotropy are lower for the sample prepared using NaOH, compared to the sample prepared with ammonia (Table 2). In this case, the Zr³⁺ formation can be affected by the presence of Na⁺ ions in the ZrO₂ structure. The sample prepared in acidic solution and calcined at 500°C (optimal temperature for the formation of Zr^{3+} gives no Zr^{3+} signal in the ESR spectrum.

These data show that the Zr^{3+} centers were formed in ZrO_2 samples obtained by thermal dehydration at 200–950°C of both xerogels and precipitates prepared in a strongly alkaline solution. No Zr^{3+} was detected upon dehydration of the precipitate prepared in acidic solution.

Color centers (F centers). In the ESR spectra of ZrO₂ samples prepared in strongly alkaline solutions and calcined in air at 300-950°C, in which the amorphous and/or tetragonal phase is formed and Zr³⁺ signals are observed, the signal of F centers is absent. A weak signal of F centers is observed only in the ESR spectra of the samples containing the monoclinic phase. Calcination in H₂ (350°C, 0.5 h) of ZrO₂ samples calcined in air (500°C) leads to appearance of a strong signal of F centers at g 2.003 and to a decrease in the Zr^{3+} signal (Fig. 4). A decrease in the intensity of the Zr³⁺ signal is accompanied by an increase in its anisotropy due to a decrease in g_{\parallel} (g_{\perp} 1.979, g_{\parallel} 1.956). Also, weak ill-resolved lines of the hyperfine structure of the signal of F centers are observed in the ESR spectrum of the ZrO_2 sample reduced in H_2 (Fig. 4, spectrum 2). The hyperfine structure of this signal probably originates from partial delocalization of the electron density of the unpaired electron between the orbitals of adjacent zirconium cations with 11.2 at. % abundance of the 91 Zr isotope (nuclear spin J 5/2).

Reoxidation of the samples in air (500°C, 1 h) leads to disappearance of signals of F centers and restoration of the Zr^{3+} signal of the initial shape (Fig. 4). Thus, in ZrO₂ prepared by the sol-gel method, the main defects (Zr^{3+} , F centers) undergo reversible transformations depending on the conditions of redox treatment. Free electrons are stabilized either on zirconium cations or on oxygen vacancies. The spec-

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 77 No. 4 2007



Fig. 4. ESR spectra (300 K) of ZrO_2 samples heattreated under various conditions: (1) 500°C, 1 h; (2) 350°C, 1 h; and (3) 350°C, 1 h + 500°C.



Fig. 5. ESR spectra (300 K) of ZrO_2 samples prepared using (1) NaOH and (2) NH₄OH and calcined at 700°C.

trum of the sample prepared in acidic solution exhibits a broad and strong signal at g_{iso} 2.003 assignable to the *F* centers, with no Zr³⁺ signal as mentioned above.

Oxygen paramagnetic centers. Along with the wellresolved Zr^{3+} signal, the ESR spectra of the samples prepared in alkaline solutions and calcined at 500– 950°C contain broadened signals at $g > g_e$ (Figs. 1, 3, 4), which can be assigned, taking into account the signal shapes and parameters, to oxygen paramagnetic centers. In the room-temperature ESR spectra of some samples calcined at 700–950°C, the structure of the broadened signal becomes well-resolved, which allows us to distinguish two signals of paramagnetic oxygen centers (Fig. 5): a signal with triaxial anisotropy of the g-factor $(g_1 \ 2.033, g_2 \ 2.008, g_3 \ 2.003)$ and an axial signal (g_{\parallel} 2.055, g_{\parallel} 2.044). The first of them prevails in the ESR spectrum of ZrO₂ prepared using ammonia, and the second, in the spectrum of ZrO_2 prepared with NaOH. The triplet signal is undoubtedly due to the presence of adsorbed oxygen species (O_2^-) on the ZrO_2 surface. Such paramagnetic centers on the surface of ZrO₂ and other oxides (TiO₂, ZnO, SnO₂, Al_2O_3) are well known; they are formed on the partially reduced surface of metal oxides upon oxygen adsorption [38]. In most cases, oxygen adsorption gives rise to several forms of O_2^- differing in the coordination and effective charge of the cation near which O_2^- is stabilized. For the π coordination of O_2^- , the Δg value depends on the cation charge. The g_1 value we obtained from the ESR spectra (2.033) suggests the stabilization of O_2^- on Zr^{4+} , which is consistent with the data of [32, 35] on fixation of O_2^- on ZrO_2 with the same parameters. Formation of such centers is due to adsorption of O_2 on Zr^{3+} : $Zr^{3+} + O_2 \rightarrow Zr^{4+} - O_2^-$.

The broadened signal of the pseudoaxial shape with the above-indicated (or very close) *g*-factors was observed in the spectra of TiO_2 , SnO_2 , and MoO_3 and was attributed to thermo- and photostimulated formation of hole centers O⁻ [38–41].

Mechanism of formation of paramagnetic centers in ZrO_2 . It is common knowledge that thermal dehydration of hydroxides inevitably disturbs the oxide stoichiometry [22, 42]. The results agree with the concept that ZrO_2 prepared from $Zr(OH)_4$ is oxygen-deficient. Some authors gave for amorphous ZrO_2 the composition $ZrO_{1.95}$ [34].

Experimental data show that appearance of Zr^{3+} in ZrO_2 simultaneously with O⁻ is observed in the course of themal dehydration of the hydroxide, leading to the formation of the amorphous ZrO_2 phase. The temperature range of the appearance of Zr^{3+} and growth of its concentration coincides (according to DTA data) with the onset of intense elimination of OH groups. The larger the extent to which the crystallization with the formation of the monoclinic phase is inhibited, the higher the Zr^{3+} content. The factors inhibiting the crystallization are high dispersity of $Zr(OH)_4$ samples and presence of a large amount of OH groups on the surface, hindering the particle aggregation and the structural rearrangements in the course of the dehydration [22].

At low temperatures of formation of monoclinic ZrO_2 from coarsely dispersed $ZrO_2 \cdot nH_2O$ precipitates, *F* centers with a high degree of disordering are stabilized, and no Zr^{3+} centers are formed.

Heating of ZrO_2 in H₂ also leads to appearance of *F* centers and to a decrease in the content of Zr^{3+} .

These results are fully consistent with the regular trends in formation of paramagnetic centers, reported by Bobricheva et al. [43]. They showed that heating in a vacuum of ZrO_2 samples modified with H_2SO_4 leads to formation of *F* centers only. However, heat treatment in a vacuum of samples prepared by treatment of $Zr(OH)_4$ (and not ZrO_2) in H_2SO_4 gives rise to both Zr^{3+} and *F* centers simultaneously. It is known that treatment in H_2SO_4 , along with surface activation, inhibits the dehydration and crystallization of the samples.

The results obtained, in combination with published data [22, 29, 30], suggest that Zr³⁺ appears in intermediate steps of redox transformations accompanying the cleavage of the Zr-OH bonds and transformation of $Zr(OH)_4$ into ZrO_2 . According to the existing views, Zr(OH)₄ can be considered as a polymer with cubic-lattice-type ordering and significant local distortions of the structure. The polymerization and condensation processes occurring in the course of transformation of $Zr(OH)_4$ into amorphous and then tetragonal ZrO_2 are not accompanied by significant changes in the coordination surrounding of zirconium. The preservation of the surrounding characteristic of cubic symmetry in products with different degrees of dehydration is provided by high dispersity of the particles and formation from them of loose framework structures in which structural rearrangements leading to the monoclinic phase are hindered.

Garvie [21] showed in small ZrO₂ particles the formation of the tetragonal and cubic structures is more favorable than the formation of the monoclinic structure characteristic of bulk ZrO2. The stability of these structures (in the absence of admixtures) is provided by lattice defects. The stabilizing factor is the decreased number of ligands (oxygen atoms) in the coordination surrounding of zirconium atoms. Formation of oxygen vacancies (V_{O}) is necessary for increasing the volume of the free space in the surrounding of zirconium atom, in order to decrease the extent of deformation of oxygen ions relative to the eightcoordinate surrounding [44]. Thus, small crystalline and amorphous ZrO_2 particles with defects in the form of oxygen vacancies are thermodynamically stable, because high symmetry of the surrounding in them is favorable.

Formation of the monoclinic ZrO_2 structure involves major structural rearrangements with changes in the symmetry of the oxygen surrounding, decrease in the coordination number (from 8 to 7), and changes in the length and directions of Zr–O bonds. With small particles, this is energetically unfavorable.

Thus, those defects are realized (Zr^{3+} ; V_O or F centers) whose formation is the most favorable energetically depending on the dispersity and structure of ZrO_2 samples. Metal ions in the d^1 state readily change the oxidation state depending on the symmetry of the oxygen surrounding. In a tetrahedrally distorted octahedral field characteristic of amorphous and tetragonal ZrO_2 , stabilization of Zr^{3+} with an oxygen vacancy in the coordination surrounding is energetically favorable. With a decrease in the symmetry, the Zr^{3+} state is no longer stabilized, which leads to the localization of a free electron in an oxygen vacancy with the formation of an F center.

A decrease in the symmetry of the Zr³⁺ surrounding under the action of hydrogen, due to formation of additional oxygen vacancies, leads to disappearance of Zr^{3+} centers and appearance of F centers. This phenomenon can be accounted for as follows. Appearance of additional oxygen vacancies in the surrounding of the $[Zr^{3+}-V_{\Omega}]$ defect upon removal of lattice oxygen under the action of hydrogen promotes the migration of Zr^{3+} into the interstice, with the shift of the electron density to the oxygen vacancy. As follows from the experimental data, the transition $Zr^{3+}-V_0 \stackrel{\rightarrow}{\leftarrow} Zr^{4+} V_{\rm O}$ under the conditions of redox treatments of ZrO₂ is reversible, which is important for the preservation of the constancy of the adsorption-catalytic properties of ZrO₂ prepared by this procedure. Amorphous ZrO₂ has an enormous internal surface to which the access of atmospheric oxygen is hindered and hence oxidation of the Zr^{3+} and F centers is hindered also. Oxidation of these centers becomes possible only on heating to 700-950°C when the rate of oxygen diffusion becomes noticeable, the particles get consolidated, and their structure becomes more perfect.

It is not fully clear under what conditions the surface and bulk O⁻ centers appear in metal oxides and whether these centers are detected by ESR. Cornoz et al. [45] showed that the ESR parameters of adsorbed O⁻ radicals coincide with the parameters of O⁻_{lat} (V centers), and these centers cannot be distinguished without using oxygen isotopes. In oxide systems with the symmetry close to $C_{4\nu}$ (SnO₂), the ESR spectrum of adsorbed and photoinduced O⁻ centers is not observed, because O⁻ is a surface hole and captures an electron at a high rate: O⁻ + $e \rightarrow O^{2-}_{lat}$.

The rate of this reaction can be decreased by creating electron traps, e.g., by introducing admixtures. For example, the presence of GeO_2 in ZrO_2 enhances the intensity of the O⁻ signal in the ESR spectra [46].

In oxides with a low conductivity (MgO) and in amorphous nonconducting oxides (SiO₂, GeO₂), the ESR signal from O⁻ can be observed [47–49]. This

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 77 No. 4 2007

is, probably, the reason why the O⁻ signal is observed in the ESR spectrum of ZrO_2 whose electronic conductivity is low. High dispersity of samples, giving rise to a large number of energy barriers on intergrain boundaries, also hinders recombination of the electron and hole centers and allows these centers in ZrO_2 to be detected simultaneously by ESR.

The above facts show that the Zr^{3+} and O⁻ centers in ZrO_2 are formed by thermal dehydration of the hydroxide under the conditions when formation of a bridging oxygen bond $\equiv Zr-O-Zr\equiv$ is hindered. Such hindrance arises when surface terminal hydroxy groups $\equiv Zr-OH$ are removed from finely dispersed $Zr(OH)_4$ samples characterized by loose structure and strongly hydrated surface. Reduction of ZrO_2 and removal of lattice oxygen, and also structural rearrangements with cleavage of the Zr-O bond are accompanied by formation of *F* centers.

EXPERIMENTAL

Nanosized ZrO_2 samples were prepared by the solgel method involving precipitation of $Zr(OH)_4$, its conversion into sol (with adding a peptizing agent or without it), drying with the formation of a xerogel, and heat treatment at various temperatures (100– 950°C). For comparison, we also studied $Zr(OH)_4$ precipitates heat-treated without conversion to sol. As precipitants we used NH₃ and NaOH solutions.

The structural and phase transitions were studied by X-ray phase analysis, and the nature of defects, by ESR. X-ray diffraction patterns were recorded with an HZG 4A diffractometer (CoK_{α} radiation, MnO_2 filter). The ESR spectra were recorded at 77 and 300 K on a Varian E112 spectrometer at a frequency of 9.35 GHz. The *g*-factors and spin concentration were determined relative to references: diphenylpicrylhydrazyl (DPPH, *g* 2.0036) and lines of the hyperfine structure of Mn^{2+} in MgO.

ACKNOWLEDGMENTS

The study was financially supported by the INTAS program (project no. 2001-2162).

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