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Features of the Sol–Gel Process of Formation of Nanostructured Gadolinium Oxide

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Abstract—The process of dehydration of $Gd(OH)_3 \cdot nH_2O$ obtained by the sol–gel method from a solution of $Gd(NO_3)_3$, to Gd_2O_3 in the temperature range of 50–700°C was explored. The hydrogel and Gd_2O_3 structurization is shown to depend on the additives (AF-12 and 2-propanol). The final average particle size of Gd_2O_3 after annealing at 700°C is 20±2 nm, depending on the conditions of the synthesis. The resulting oxide particles are larger than the particles of yttrium oxide Y_2O_3 (17±2) obtained under the same conditions of the process due to the higher basicity of gadolinium and its higher coordination number with respect to the OH groups. This promotes the formation of crystalline phases of $Gd(OH)_3$ at lower temperature, 50–250°C, while maintaining a favorable structural short-range order in passing through an amorphous state to a crystalline Gd_2O_3.

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Europium-activated gadolinium oxide is one of the most stable and efficient luminophores used as a detector of soft X-ray and hard γ-radiation [1] in flat panel displays [2, 3] etc. In addition, gadolinium oxide is a promising material for the formation of optical fibers [4].

Today the obtaining of luminescent materials in nanostructured state is relevant. This is due to economic considerations in rare earth elements (REE) application. However, a problem exists of forming mini-displays with the pixel size in ultrafine range. Obviously, this requires the development of the processes of materials formation with a particle size of about 1 μm or less. The most appropriate in this regard is the sol–gel method, which allows a control of the forming particles size from nanometers to microns by changing the temperature and time of hydroxide dehydration and by annealing the produced REE oxides [5]. In this paper the regularities were found of changes in particle size of Y_2O_3 while changing the conditions of the hydroxide precipitation and dehydration.

As is known, gadolinium hydroxides are highly resistant to dehydration [6] compared to yttrium hydroxides due to higher basicity of gadolinium [7]. Usually the sol–gel method of a REE hydroxide precipitation in air is accompanied by the formation of a number of hydrated carbonates, therewith the hydration numbers of the carbonates of various REE are different [8]. These features of REE should be reflected in the change in the ultraporosity of the xerogels and ultradispersity of the gadolinium hydroxides and oxides in comparison with the known parameters obtained for similar yttrium compounds [5].

The purpose of this paper is to examine the patterns of dehydration and dehydroxylation of hydrogels $Gd(OH)_3 \cdot nH_2O$ obtained by the sol–gel method from nitrate solutions as the basis of gadolinium oxide with a specified particle size.

In this work a series of samples obtained using a specific set of reagents and procedures is presented in Table 1.

Figure 1 shows the results of thermal analysis in oxygen of hydrogels $Gd(OH)_3 \cdot nH_2O$, obtained by the sol–gel method using NaOH as a precipitant. Points *1* and *2* are marked on the TG curves correspond to the theoretical composition $Gd(OH)_3$ and GdOOH with respect to the sample of Gd_2O_3 formed as a result of the dehydroxylation. This suggests that the peaks at

310°C and 450°C correspond to the maximum development of the processes of decomposition of gadolinium trihydrate and monohydroxide, respectively. The obtained values of the transition temperature of the phases of the indicated composition differ from the corresponding equilibrium transitions at 210 and 310°C given in [6]. This means that in a dynamic mode of heating gadolinium hydrogels (thermal analysis) the dehydroxylation processes of gadolinium trihydrate and monohydrate may proceed in parallel and end at higher temperatures. For comparison, the maximum temperature for these transformations of yttrium trihydrate and monohydroxide is considerably lower, at 180 and 300°C, respectively [5].

Figure 2 shows the mass loss during the static annealing at appropriate temperatures. As can be seen from Fig. 2, the presence of 2-propanol in the mother liquor leads to a monotonic weight loss during the annealing of the sample in the temperature range 50–200°C, and in the absence of 2-propanol (Fig. 2b), the mass of the sample is stabilized by heating to 200°C. These features can be explained by the intense evaporation of 2-propanol in the initil stage of heating in the first case. This is observed also in the case of dynamic heating in thermogravimetry samples (Fig. 1). The above effect is also consistent with the increase of the first DTG peak in the derivatograms (Fig. 1b) after washing gel with the alcohol. The slight slowing of weight loss samples of series 3 (ammonia deposition) under static heating to 230°C (Fig. 2a) is due to the presence and decomposition of ammoniates and double nitrate of the type $(NH_4)_2Me(NO_3)_5$, where Me is Y or Gd [7]. Figure 2b shows that the presence or absence of surfactant AF-12 has no effect on the character of samples dehydroxylation in the static mode. The comparison of the data in Fig. 2a and 2b leads to the conclusion that the presence of the 2-propanol results in a marked increase in the weight loss of samples as a whole, which is associated with the removal of the 2-propanol and its degradation products.

Table 1. Special features of the preparation of nanostructured gadolinium oxide samples of various series

Series no.	Additive	Precipitant	Solvent for washing the precipitate of gadolinium oxide
1	2-Propanol	NaOH	Water
2	"	NaOH	2-Propanol
3	"	NH_4OH	Water
4	Surfactant AF-12	NaOH	2-Propanol
5	"	"	Water
6	–	"	Water
7	–	"	2-Propanol

In Fig. 3 are presented the diffractograms of samples of series 1 suggesting that in the initial dehydroxylation stage at 50–300°C the gadolinium hydroxide is nanosruktured with a manifestation of crystallinity, in contrast to the $Y(OH)_3$, which is amorphous up to 500°C [5]. Peaks of crystalline $Gd(OH)_3$ are identified according to [8].

Structural transformations of the samples obtained with 2-propanol (Fig. 3a) and without (Fig. 3b), including the use of surfactant AF-12 retain the temperature sequence of phase transitions, however, in the series 5 the degree of crystallinity in the temperature range 200–250°C is much higher. Indeed, for the series 1 the acquisition time of the acceptable

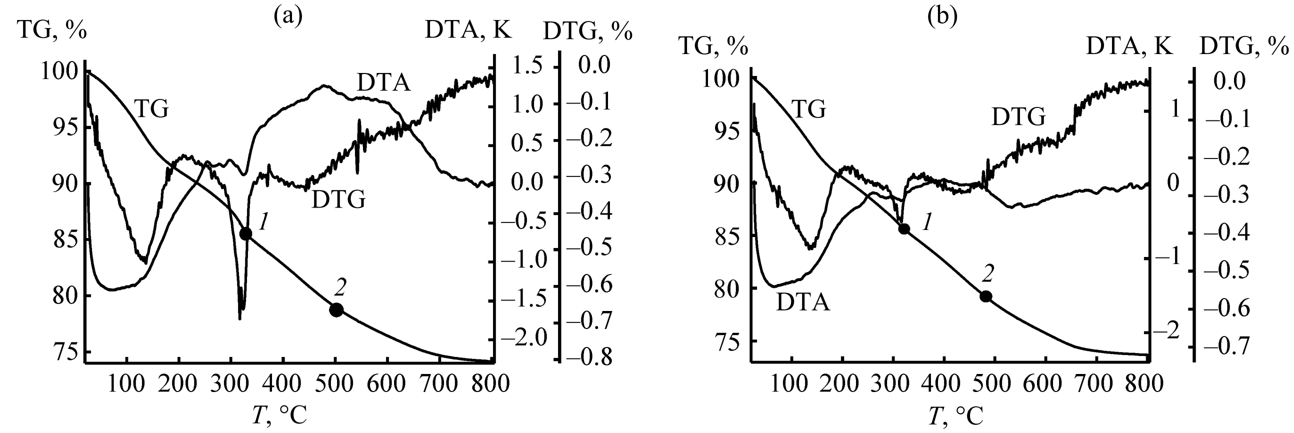

Fig. 1. Thermal analysis curves of the samples after drying at 50°C washed with water (series 1, a) and 2-propanol (series 2, b). Heating rate 10 deg min^{-1}, O_2 flow rate 10 mL min^{-1}.

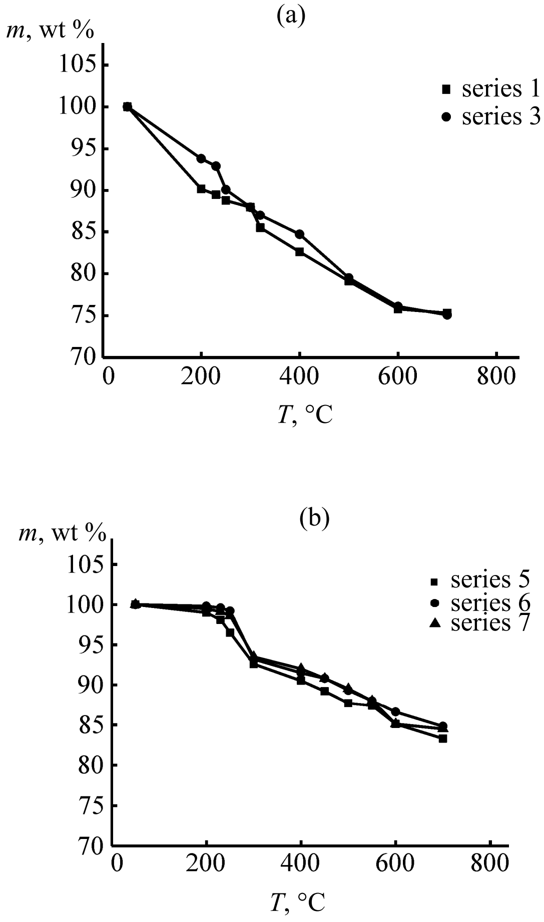

Fig. 2. Mass loss during the heating of samples sequentially at different temperatures: series 1 and 3 with the 2-propanol in the mother liquor (a) and the series 5, 6, 7 without the use of 2-propanol (b).

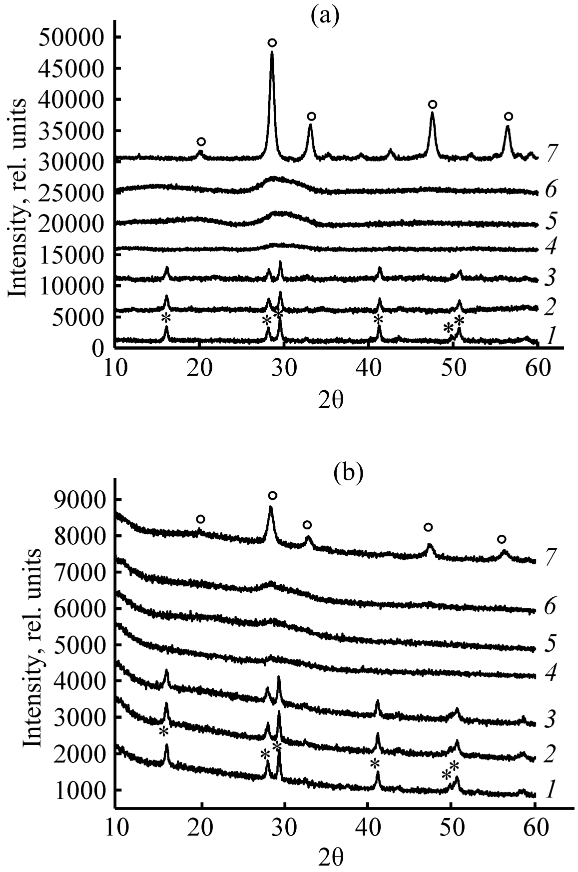

Fig. 3. X-ray phase analysis of sample series 1 (with 2-propanol) (a) and series 5 (without 2-propanol, but with surfactant AF-12) (b) at temperatures (*1*) 50, (*2*) 200, (*3*) 250, (*4*) 300, (*5*) 400, (*6*) 500, and (*7*) 700°C. The symbols "*" and "°" denote the main peaks of $Gd(OH)_3$ and Gd_2O_3, respectively.

signal was 20 times longer. This indicates that the concentration of the crystallites in the samples of series 1 (obtained with 2-propanol) in this temperature range is much smaller than in the series 5 (obtained without 2-propanol). Higher crystallinity of the samples of series 5 is probably another reason of the delay of dehydration in static heating (Fig. 2b). Table 2 shows the results of the calculation of the region of the coheret scattering by the Scherrer equation. These data suggest that the $Gd(OH)_3$ crystallites have a size of 30–60 nm, and they are stretched in one of the crystallographic x directions. For samples of series 1 (2-propanol without surfactant) and Series 5 (without the 2-propanol, but with surfactant) this is the direction <201>, and the samples obtained without 2-propanol and surfactant (series 6) the direction of the accelerated growth is <101>. Apparently, the organic molecules 2-propanol and AF-12 block the growth of crystallites in the <101> direction. After the destruction of the crystallinity of $Gd(OH)_3$ in the region of 300–500°C the formation of the crystalline phase is characterized by the formation of Gd_2O_3 crystallites of the size of 12–18 nm for all the above series.

Figures 4a and 4b show the temperature dependence of the specific surface of the samples obtained with the 2-propanol and without 2-propanol, respectively. Here is also shown for comparison the temperature dependence of the specific surface of samples of hydroxides and oxides of yttrium subjected to dehydration under the conditions of the series 1 (series 1Y). As can be seen, the samples of $Y(OH)_3$–Y_2O_3 have a much larger specific surface [curves Series 1 (Gd) and (Y)]. The presence of surfactant AF-12 in the system (Fig. 4b, series 4 and 5) increases the surface area of the samples. However for systems

Table 2. The results of phase analysis and calculations of OCD of samples of $Gd(OH)_3$ and Gd_2O_3 with 2-propanol (series 1), without 2-propanol with surfactant (series 5), and without surfactant and 2-propanol (series 6)

Sample, *T*(annealing), °C	Phase	OCD, nm						
		(100)	(110)	(101)	(201)	(222)	(004)	(044)
Series 1								
50	$Gd(OH)_3$	43(8)	32(4)	41(8)	54(14)	–	–	–
200	$Gd(OH)_3$	31(5)	25(4)	33(4)	45(8)	–	–	–
250	$Gd(OH)_3$	34(6)	31(4)	36(6)	44(8)	–	–	–
300	Amorphous.	–	–	–	–	–	–	–
400	Amorphous.	–	–	–	–	–	–	–
500	Amorphous.	–	–	–	–	–	–	–
700	Gd_2O_3					18(2)	15(2)	–
Series 5								
50	$Gd(OH)_3$	34(4)	36(9)	46(8)	55(14)	–	–	–
200	$Gd(OH)_3$	29(6)	30(6)	46(10)	63(18)	–	–	–
250	$Gd(OH)_3$	28(6)	26(5)	48(8)	59(16)	–	–	–
300	Amorphous.	–	–	–	–	–	–	–
400	Amorphous.	–	–	–	–	–	–	–
500	Amorphous.	–	–	–	–	–	–	–
700	Gd_2O_3	–	–	–	–	14.0(6)	14.4(1.6)	12(1)
Series 6								
50	$Gd(OH)_3$	37(7)	29(6)	57(11)	39(6)	–	–	–
200	$Gd(OH)_3$	40(11)	29(6)	57(9)	38(5)	–	–	–
250	$Gd(OH)_3$	27(5)	28(6)	51(7)	35(6)	–	–	–
300	Amorphous.	–	–	–	–	–	–	–
400	Amorphous.	–	–	–	–	–	–	–
500	Amorphous.	–	–	–	–	–	–	–
700	Gd_2O_3	–	–	–	–	17(2)		

washed with alcohol the presence of surfactant AF-12 results in a significant increase in the specific surface of the sample below the annealing temperature 400°C (series 4). Above 400°C, these parameters for the samples obtained with surfactant and without surfactant, washed with water, and washed with alcohol are identical in pairs, but for the former pair the specific surface is 3–4 times larger.

The findings suggest that the combination of the presence of surfactant AF-12 and rinsing with alcohol contribute to a significant increase in S_{sp}, i.e. promote the formation of a hydrogel and an openwork net of hydrogel and alcogel. In the range of the xerogel formation (200–420°C, Fig. 4b, series 4) this combination is characterized by a rapid decrease in the specific surface area due to the burning of organic material. Figure 4 indicates that the deposition of gadolinium hydroxide with ammonia (series 3) reduces the surface area relative to the samples obtained by the deposition with sodium hydroxide (series 1). Under the same conditions in the system $Y(OH)_3$–Y_2O_3 the specific surface of samples is 2-fold larger, and for the annealing temperature of 400–700°C, this parameter is up to 3 times larger (series 3Y). As shown previously [5] for the yttrium system the cause of the anomaly at 500°C was the amorphization of the samples at the decomposition of double hydrocarbonates $NH_4[Y(CO_3)_2]\cdot nH_2O$. For a system with gadolinium, this anomaly is expressed significantly weaker.

Figure 5 shows the change in density of the samples with increasing annealing temperature. It should be noted that up to ~500°C the density of the samples of series 1, 3 with 2-propanol is of close values, but the sample obtained by precipitation with ammonium

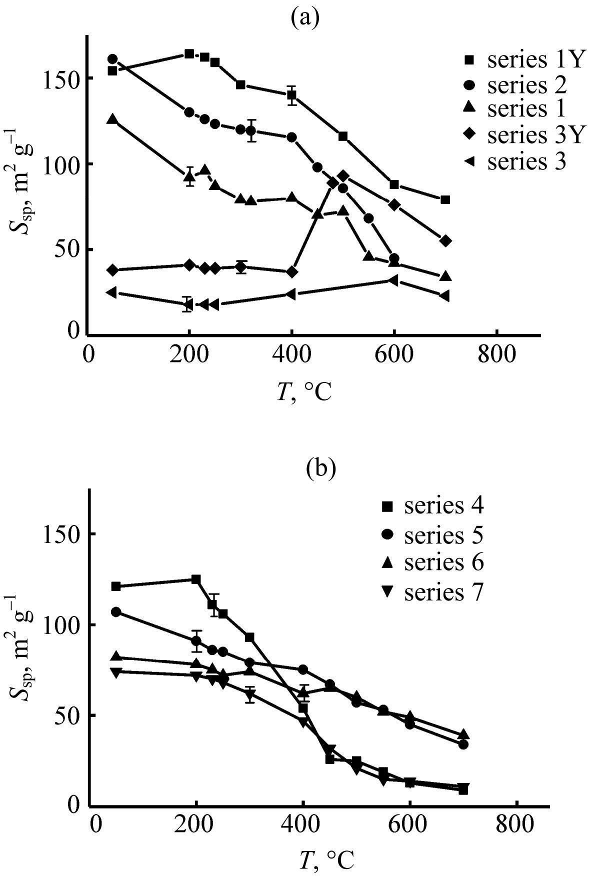

Fig. 4. Specific surface area of samples obtained with 2-propanol (a) and without 2-propanol (b) depending on the temperature.

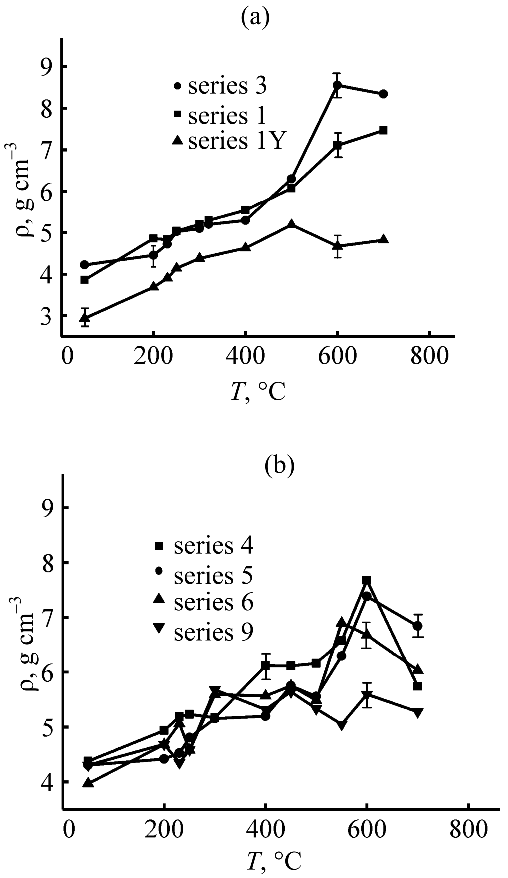

Fig. 5. Dependence of sample density on the annealing temperature of samples obtained with the addition of 2-propanol (a) and without the addition of 2-propanol (b).

hydroxide (series 3) at a temperature of 600°C has the highest density. As follows from Fig. 5b, the density of all the samples without the addition of 2-propanol has abnormal dependence not only at the above temperatures (230–250°C and 400–500°C), but also at 550–600°C, and in the latter temperature range the samples of series 4−7 have an anomalous surge of ρ values. However, at 700°C, a sharp decrease in the density is observed, the largest case corresponding to the sample with surfactant AF-12 washed with alcohol.

The calculation results of the size of particles using the experimental values of S_{sp} and ρ are presented in Figs. 6a and 6b. These figures show the dependence of particle size on the annealing temperature of samples obtained with and without 2-propanol, respectively. *D* parameters for gel up to 250°C are effective values that characterize a relative degree of nanostructuring. Samples with 2-propanol deposited with NaOH consist of particles with average sizes (15–20) ± 2 nm at increasing annealing temperature from 200 to 700°C. Characteristically, the yttrium system contains noticeably smaller particle sizes (Series 1Y), therewith with respect to the gadolinium system the values of S_{sp} are much larger, and the values of ρ are much smaller. These features of parameters are associated with a higher basicity of Gd and his large coordination number due to the large size of Gd^{3+} ion. This, in turn, results in the increased likelihood of crystalline $Gd(OH)_3$ formation, and therefore denser and less opemwork gel and xerogel.

Samples with 2-propanol IRS deposited by NH_4OH, have the largest particle size [Fig. 6a and series 3 for gadolinium and yttrium oxides (series 3Y)], but annealed at 600 and 700°C they become comparable in size to the samples deposited with NaOH (series 1) For samples without 2-propanol (Fig. 6b), the largest size have samples washed with alcohol (series 4 and 7) and annealed at temperatures >400°C. Up to this temperature the effective size of the nanostructure of all the samples are almost identical

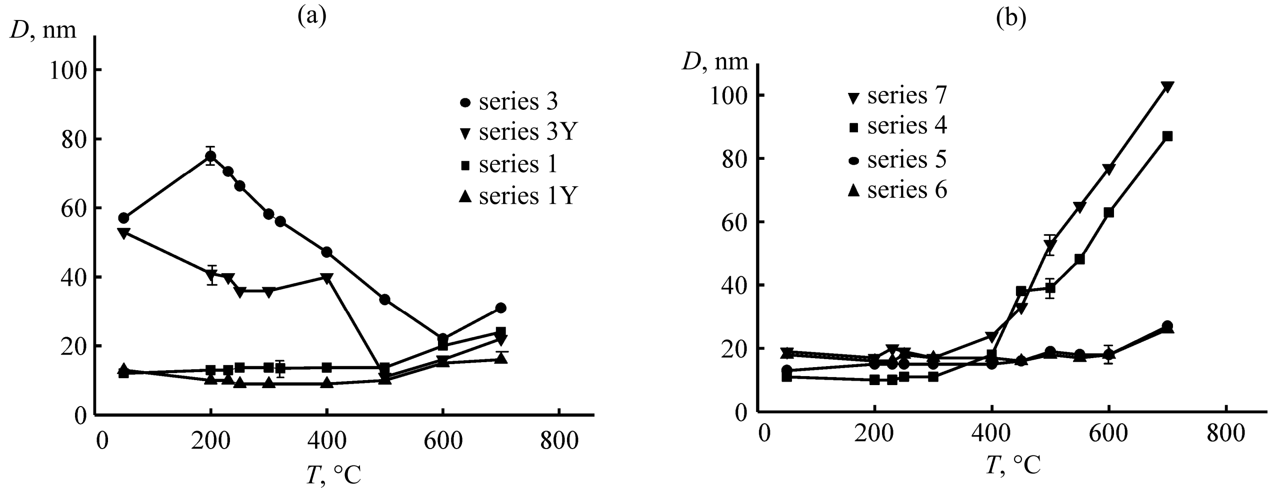

Fig. 6. The dependence of the particle size on the annealing temperature of samples of gadolinium oxide films deposited with the use of 2-propanol (a), and without 2-propanol (b).

[(10–20) ± 2 nm]. Samples, washed with water and precipitated without 2-propanol and the surfactant (series 6) and using only the surfactant (series 5) have almost the same size (18–24) ± 2 nm for Gd_2O_3. These values are close to the previously mentioned dimensions of the crystallites.

The block of observations presented allows the following generalization. The use of 2-propanol in the synthesis of gadolinium hydroxide affects a number of features of the process. The weight loss of the samples during annealing is significantly greater than for samples without 2-propanol (Fig. 2). In this case, at the stage of gel $Gd(OH)_3 \cdot nH_2O$ an amorphous phase with a low content of the crystallites forms, then the sample is completely converted to an amorphous state and subsequently to phase Gd_2O_3 (Fig. 3a). These facts suggest that amorphous state of the hydroxide favors a rapid dehydration of the sample. As Fig. 2b shows, the hydroxide synthesis in the absence of 2-propanol results in a slow loss of water during dehydration, regardless of the other terms of the process: the addition of surfactant AF-12 or flushing with 2-propanol instead of washing with water, or with surfactants and rinsing with 2-propanol. Therewith the temperature range of the amorphization is large enough, 300–500°C, but the hydroxide precipitate already at room temperature and above has a significant degree of crystallinity. This means that the hydroxide crystallization provides a lower rate of dehydration due to the compactness of the crystallite particles. The mentioned phases are characterized by two intense diffraction reflexes of gadolinium hydroxide {011}/{020}–(200 093 ICSD) and gadolinium oxide {222}/{004}–(152 449 ICSD), which correspond to the interplanar distances of similar values 3.0270/2.7405 and 3.1230/2.7046 Å in these phases, respectively. This contributes to the easy reconstruction of the lattice of hydroxide while maintaining short-range order in the amorphous phase into the lattice of gadolinium oxide.

The addition of 2-propanol or surfactant AF-12 to the system causes a change in the morphology of crystals (see Table 2): they become elongated in the direction <201>. Perhaps this is due to the peculiarities of the adsorption of AF-12 and 2-propanol, which is also a surfactant, on the faces of the crystallites, so that these surfactants block the growth of faces in the <101> direction (the fastest growing without AF-12 and IPS) and are almost "neutral" for the {100} and {110}, but can accelerate the growth of crystallites in the <201> direction.

The characteristic increase in the S_{sp} of samples synthesized with 2-propanol or with the addition of surfactant AF-12 and washed with alcohol, and a substantially smaller S_{sp} for samples synthesized without 2-propanol and surfactant suggest that looser gel structure is formed by forming alcogel during washing the samples. Moreover, this process contributes to the presence of adsorbed surfactant 2-propanol or AF-12 on the surface of sol $Gd(OH)_3$ formed at the initial stage of deposition. However pycnometrical density and temperature changes for all samples of all the series are almost identical. This means that the alcogel openwork exists not at the molecular level but at the level of the formation of alcohol bridges between particles whose degree of contact with each other is minimal. The destruction of the alcohol bridges at 400°C in the absence of adsorbed 2-propanol causes intense coagulation of xerogel particles (Fig. 6b).

The deposition of gadolinium hydrogels with ammonia leads to the formation of the precipitate with significantly lower S_{sp} at about the same pycnometric density. This, in accordance with the used to calculate D the ratio $D = 6/(\rho S_{sp})$ [9], provides a large value for the particle size of the sol precipitation. However, the sol particles and then hydrogel contain significant amounts of ammoniates, similar to the yttrium system [5]. Complete decomposition of these by-products at temperatures up to 500°C leads to a particle size of oxide 20 nm.

The most stable process of creating nanostructured powders of Gd_2O_3 is a simple version of the synthesis of hydrogel $Gd(OH)_3{\cdot}nH_2O$ by deposition NaOH and washing with water. These samples are characterized by monotonic temperature dependence of parameters S_{sp} and ρ and virtually unchanged particle size of 20 nm in the whole range of annealing temperatures up to 700°C. A similar process for yttrium hydrogels leads to a somewhat smaller particle size of 15 nm [5], which is the result of stable amorphization of hydrogels $Y(OH)_3{\cdot}nN_2O$ during annealing at low temperatures. The appearance of crystallinity of the gadolinium hydrogel at the stage of synthesis may be associated with the large diameter of ion Gd^{3+}, which increases the coordination environment of hydroxide ions. This removes the difficulty of kinetic nucleation of $Gd(OH)_3$ crystals.

EXPERIMENTAL

In this work we used gadolinium nitrate $Gd(NO_3)_3{\cdot}6H_2O$ with the content of the main component no less than 99.9%, precipitants NaOH of grade pure for analysis and NH_4OH of grade especially pure, nonionic surfactants: 2-propanol brand especially pure, alkyl phenyl ether and polyethylene oxide (AP-12). For the preparation of gadolinium hydroxide the concentrations of the stock solutions of nitrate gadolinium for different experiments ranged within 0.20–0.25 M concentration of solutions of NaOH = 1.20–1.49 M, and the solution of NH_4OH = 1.16 M. The procedures used are described in [5]. Distinctive features of the synthesis of hydroxides and oxides of gadolinium are presented in Table 1.

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