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Research article
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Heterophase synthesis of rare-earth zirconates

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Abstract: This study focuses on developing a heterophase process for synthesizing rare-earth zirconates, specifically $R_2Zr_2O_7/R_2O_3{\cdot}2ZrO_2$ (R = La, Sm, Gd, Dy). We investigated the sorption properties of low-hydrated zirconium hydroxide, a precursor for complex-oxide phases, towards rare-earth elements' ions (La, Sm, Gd, Dy). The results indicate that sorption by low-hydrated zirconium hydroxide is a multifaceted process, involving the incorporation of rare-earth cations into the pores of low-hydrated hydroxide and ion exchange. The paper details the synthesis of $R_2Zr_2O_7/R_2O_3{\cdot}2ZrO_2$ (R = La, Sm, Gd, Dy), considering both "light" and "heavy" elements. The process involves the interaction between $Zr(OH)_{3\div1}O_{0.5\div1.5}{\cdot}(1.6\div2.6)H_2O$, low-hydrated zirconium hydroxide, and an aqueous solution of rare-earth acetate ($C(La^{3+}) = 0.155$ mol/L, $C(Sm^{3+}) = 0.136$ mol/L, $C(Gd^{3+}) = 0.141$ mol/L, $C(Dy^{3+}) =$ $= 0.120$ mol/L) followed by heat treatment. The resulting phases and their thermolysis products were analyzed using differential thermal analysis and *X*-ray phase analysis. Single-phase rare-earth zirconates $R_2Zr_2O_7$ (R = La, Sm, Gd) and the $Dy_2O_3{\cdot}2ZrO_2$ solid solution were only obtained at 800 °C. The lattice parameters are calculated for each phase. Lanthanum, samarium, and gadolinium zirconates exibited a cubic pyrochlore structure ($Fd\bar{3}m$), while dysprosium displayed a fluorite structure ($Fm\bar{3}m$). The average particle size of all zirconates was 1.14 ± 0.02 μm.

Key words: zirconium, lanthanum, samarium, gadolinium, dysprosium, zirconate, oxide, low-hydrated hydroxide, sorption properties, heterophase synthesis.

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Гетерофазный синтез цирконатов редкоземельных элементов

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Аннотация: Представлены результаты разработки гетерофазного метода синтеза цирконатов редкоземельных элементов (РЗЭ) состава $R_2Zr_2O_7/R_2O_3{\cdot}2ZrO_2$ (R = La, Sm, Gd, Dy). Предварительно изучены сорбционные свойства маловодного гидроксида циркония (предшественника для получения сложнооксидных фаз) по отношению к ионам редкоземельных элементов (La, Sm, Gd, Dy). Результаты исследований показали, что сорбция маловодным гидроксидом циркония является сложным процессом, включающим вхождение катионов РЗЭ в поры маловодного гидроксида и ионный обмен. Проведен синтез цирконатов РЗЭ состава $R_2Zr_2O_7$ /$R_2O_3 \cdot 2ZrO_2$ (R = La, Sm, Gd, Dy; выбор РЗЭ определялся вовлечением в рассмотрение «легких» и «тяжелых» элементов). Он заключался во взаимодействии маловодного гидроксида циркония $Zr(OH)_{3\div1}O_{0,5\div1,5}\cdot(1,6\div2,6)H_2O$ с водным раствором ацетата РЗЭ ($C(La^{3+})$ = 0,155 моль/л, $C(Sm^{3+})$ = 0,136 моль/л, $C(Gd^{3+})$ = 0,141 моль/л, $C(Dy^{3+})$ = 0,120 моль/л) и последующей термической обработке. Методами дифференциально-термического и рентгенофазового анализов охарактеризованы синтезированные фазы и продукты их термолиза. Только при температуре 800 °C удалось получить однофазные цирконаты РЗЭ состава $R_2Zr_2O_7$ (R = La, Sm, Gd) и твердый раствор $Dy_2O_3 \cdot 2ZrO_2$. Для каждой фазы рассчитаны параметры решетки. Цирконаты лантана, самария и гадолиния имеют кубическую структуру пирохлора ($Fd\bar{3}m$), а диспрозия – структуру флюорита ($Fm\bar{3}m$). Средний размер частиц у всех цирконатов составляет 1,14 ± 0,02 мкм.

Ключевые слова: цирконий, лантан, самарий, гадолиний, диспрозий, цирконат, оксид, маловодный гидроксид, сорбционные свойства, гетерофазный синтез.

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Introduction

$R_2Zr_2O_7$ rare-earth zirconates find extensive applications as thermal barrier coatings, catalysts, sensors, oxygen-ion conducting solid electrolytes, and matrices for the immobilization of radioactive waste [1—10]. These compositions possess unique physical and chemical properties, including a high melting point, absence of phase transitions over a wide temperature range, high coefficient of thermal expansion, and low thermal conductivity. Additionally, they demonstrate dielectric, piezo- or ferroelectric, fluorescent, and phosphorescent properties, along with chemical and radiation resistance, and a high capacity for radionuclide absorption [1; 4; 10—12].

The primary space groups for $R_2Zr_2O_7$ rare-earth zirconates are cubic pyrochlore ($Fd\bar{3}m$) and defective fluorite ($Fm\bar{3}m$) (Fig. 1) [2].

If the ratio of cation radii $r(R^{3+})/r(Zr^{4+})$ is less than 1.46, the resulting substance is classified under a defective fluorite space group; otherwise, it falls into a pyrochlore space group [9]. Based on the cation radii, La—Gd zirconates exhibit a pyrochlore space group, whereas Tb—Lu zirconates belong to a defective fluorite space group. The coordination number of zirconium ranges from 4 to 6. Additionally, a decrease in the cation radius ratio corresponds to an increase in disorder. To achieve a more ordered structure, one could replace the rare-earth element cation with a larger-radius cation or replace the zirconium cation with a smaller-radius cation. [9; 13—15].

The phase diagrams reveal that within the La_2O_3—ZrO_2 systems, $La_2Zr_2O_7$ present, maintaining a pyrochlore space group up to the melting point. In the case of Sm_2O_3—ZrO_2, $Sm_2Zr_2O_7$ exhibits a pyrochlore space group up to 2080 °C, transitioning to a defective fluorite space group above this temperature. Within the Gd_2O_3—ZrO_2 system, $Gd_2Zr_2O_7$ solidifies with a pyrochlore structure below 1550 °C, subsequently transforming into a disordered fluorite structure (F-$Gd_2Zr_2O_7$). Notavly, the Gd_2O_3—ZrO_2 system encompasses a broad region featuring the $R_2O_3 \cdot 2ZrO_2$ homogeneous solid solution with a fluorite crystal structure [15—19].

Other researchers have outlined various processes for the preparation of $R_2Zr_2O_7$ rare-earth zirconates [1; 4; 12; 14; 15; 20—26]. Notably, papers [4; 20; 21] detail the solid-phase reparation of rare-earth zirconates through the mechanical mixing of zirconium and rare-earth element oxides, followed by calcination at high temperatures (exceeding 1100 °C). However, this process is notably time-consuming. To expedite solid-phase reactions, mechanochemical synthesis offers two approaches:

1. Mechanochemical synthesis involves the direct formation of the compound through the mechanical processing of reactants in an activator mill.
2. A two-stage process incorporates mechanical activation of the initial mixture, followed by subsequent heat treatment [14; 19].

In the co-precipitation method, hydroxides are simultaneously precipitated from precursor solutions, and the resulting sediments are subsequently calcinated to obtain $R_2Zr_2O_7$ [4; 23; 24]. A known process for producing $R_2Zr_2O_7$ rare-earth zirconates (R = Gd, Tb,

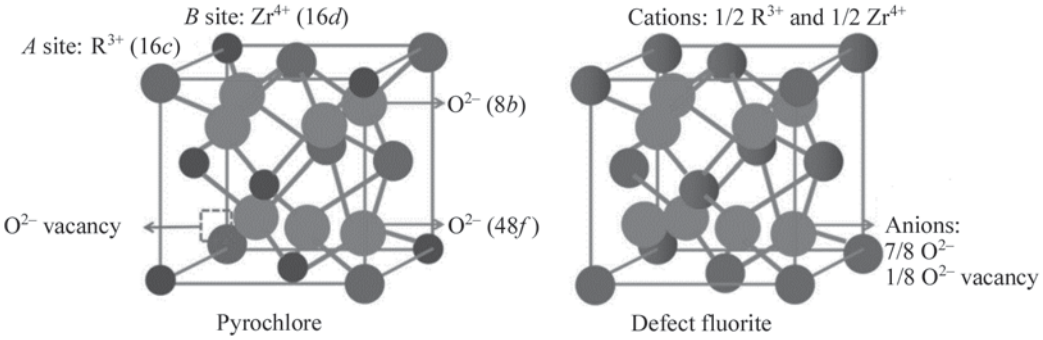

Fig. 1. Crystal structures of $R_2Zr_2O_7$ rare-earth zirconates [2]

Рис. 1. Структуры цирконатов редкоземельных элементов $R_2Zr_2O_7$ [2]

Dy) through co-precipitation involves using rare-earth nitrate and zirconium oxychloride as starting materials. These are mixed and treated with an aqueous ammonia solution. The zirconate powders are obtained by calcination of the washed and dried sediment at temperatures ranging from 1000 to 1500 °C for 3 to 6 h in the presence of air [24].

However, a disadvantage of this method is that the co-precipitation product forms a gel, making it challenging to remove impurities through washing. Consequently, the resulting gel contains a significant amount of wash water.

In the hydrothermal process, the complex oxide phase precipitates from solutions in an autoclave, forming through nucleation and growth at specific temperatures and pressures. This method is convenient, straightforward, and easily controllable. Water serves as the solvent, offering affordability and wide availability [4; 12].

The sol-gel method involves thermally treating gels derived from the hydrolysis and subsequent polycondensation of initial metal alcoholates [4; 12; 22; 25; 26].

It’s worth noting that in all the mentioned processes, the initial reagents consist of oxides, salts, or complex compounds of zirconium.

The objective of this study is to establish a heterophase method for synthesizing $R_2Zr_2O_7/R_2O_3{\cdot}2ZrO_2$ (R = La, Sm, Gd, Dy) rare-earth zirconates using low-hydrated zirconium hydroxide (referred to as “low-hydrated hydroxide” or LHH) as the precursor. This approach aims to lower the synthesis temperature while achieving the production of single-phase complex oxides.

Materials and methods

We used zirconium oxochloride (reagent-grade, TU 6-09-3677-74 Spec., Reakhim, Moscow) and an aqueous ammonia solution (ASC, GOST 24147-80, Khimmed, Moscow) in this study. Acetates of rare-earth elements (lanthanum, dysprosium, samarium, gadolinium) were obtained by dissolving the oxide precursors (La_2O_3 — reagent-grade, TU 48-4-523-90 Spec.; Dy_2O_3 (reagent-grade) — TU 48-4-524-90 Spec.; Sm_2O_3 (reagent-grade) — TU 48-4-523-89 Spec.; Gd_2O_3 (reagent-grade), TU 48-4-200-72 Spec.) from Lankhit, Moscow, in glacial acetic acid (ASC grade, GOST 61-75, Khimmed). The resulting solution was solidified, filtered, and air-dried to obtain crystallohydrates, such as $La(CH_3COO)_3{\cdot}1.6H_2O$, $Gd(CH_3COO)_3{\cdot}4.2H_2O$, $La(CH_3COO)_3{\cdot}1.8H_2O$, $Dy(CH_3COO)_3{\cdot}4.1H_2O$. Acetate salts were chosen for their water solubility and the ease with which volatile products (CO and CO_2) could be removed from the substance.

The zirconium dioxide content in the low-hydrated hydroxide was determined by calcination at 800 to 900 °C to form ZrO_2.

The chloride ion content in LHH was assessed using argentometry (the Folgard method).

To evaluate the sorption capacity of low-hydrated zirconium hydroxide under static conditions at room temperature, we employed aqueous solutions of rare-earth acetates.

The procedure involved adding 8.0 mL of aqueous solutions of rare-earth element acetates with varying concentrations (ranging from 0.044 to 0.155 mol/L) to 0.4 g of LHH samples. The filled tubes underwent shaking on an AVU-6S shaker for durations spanning from 20 to 160 min, with 10-minute pauses. Following settling, samples were extracted from the solutions to determine the concentrations of rare-earth elements.

For assessing the concentrations of rare-earth elements in the initial acetous solutions, determining the residual concentrations of rare-earth elements in the mother solutions, and investigating the sorption capacity of low-hydrated zirconium hydroxide, we employed direct titration with Trilon B solution (0.05 mol/L). Xylenol orange indicator (0.1 % solution) was utilized, and titration proceeded until the wine-red color of the solution transitioned to yellow.

The absorption degree (α, %) of rare-earth element cations by the solid phase of low-hydrated zirconium hydroxide was calculated using the following formulas:

$$\alpha = \Delta / C_{\text{init}}, \tag{1}$$

$$\Delta = C_{\text{init}} - C_{\text{aft//sorp.}}, \tag{2}$$

where C_{init} is the initial concentration of the rare-earth element solution before sorption, mol/L; $C_{\text{aft//sorp.}}$ is the concentration of the rare-earth element solution after sorption, mol/L.

The sorption capacity (G, mmol/g) for low-hydrated zirconium hydroxide is determined by:

$$G = \Delta \cdot V / m, \tag{3}$$

where V is the volume of the solution, mL; m is the sorbent weight, g.

We conducted differential thermal analysis (DTA) in the 20—1000 °C temperature range with a heating rate of 10 °C/min (±5 °C error) using a Q-1500 D derivatograph (F. Paulik, J. Paulik, L. Erdey; MOM, Hungary) and a platinum-rhodium (type S) thermocouple.

X-ray diffraction (XRD) was employed to identify final and intermediate products with a Rigaku D/max-C *X*-ray diffractometer (CuK_α radiation, Ni filter, Si monochromator) in the $10° \le 2\theta \le 80°$ angle range, with a 0.02° scanning step.

Powder granulometry was determined using the DelsaNano laser particle analyzer (Beckman Coulter Inc., USA) applying dynamic light scattering to estimate particle size distribution in the 0.6 nm to 10 μm range.

Results and discussion

The low-hydrated $Zr(OH)_{3÷1}O_{0,5÷1.5}\cdot(1.6÷2.6)H_2O$ was synthesized through heterophase interaction between zirconium oxychloride and a 6.0 mol/L aqueous solution of ammonia hydrate. Detailed information on the method, as well as the physical and chemical properties of zirconium LHH and its thermolysis products, can be found in [27; 28].

Upon filtration and air drying, we obtained a well-filtered, crumbly white powder with a low content of chloride ion impurities (less than 0.05 %). The zirconium dioxide content in the low-hydrated hydroxide is 68.8 ± 0.1 wt.%, and the average particle size of zirconium LHH is 2.2 μm.

Our DTA and XRD studies of the low-hydrated zirconium hydroxide thermolysis indicated that the LLH is an *X*-ray amorphous phase. The dehydration process halts at $t = 400 \pm 5$ °C, resulting in the formation of monoclinic zirconium dioxide ($a = 0.514 \pm 0.001$ nm, $b = 0.521 \pm 0.002$ nm, $c = 0.531 \pm 0.001$ nm, $\beta = 99.10 \pm \pm 0.01°$). Most particles have a size of 2.0—4.0 μm, with an average particle size of 2.8 μm.

We proposed a thermal decomposition process for low-hydrated zirconium hydroxide as follows:

$$Zr(OH)_{3÷1}O_{0.5÷1.5}(1.6÷2.6)H_2O \xrightarrow[-H_2O]{200±5\ °C} \xrightarrow[-H_2O]{200±5\ °C} ZrO_2(0.1÷0.2)H_2O \xrightarrow{400±5\ °C} ZrO_2. \tag{4}$$

The low-hydrated zirconium hydroxide, classified as oxyhydrates, exhibits the presence of hydroxo- and aqua groups alongside oxo groups, all of which can serve as sorption sites. Our investigations have identified macro-, nano-, and ultra nanopores in the zirconium LHH samples, rendering this class of compounds suitable for application as a sorbent in the synthesis of complex oxide phases [27; 28].

In an effort to exploit the sorption properties of low-hydrated zirconium hydroxide for intensifying the formation of rare-earth element zirconates, we aimed to obtain a suitable intermediate product during the sorption stage. This approach ultimately lowers the synthesis temperature and facilitates the creation of a single-phase product. To achieve this, we studied the sorption of rare-earth cations by low-hydrated zirconium hydroxide under static conditions at room temperature. Adopting a volume ratio of the aqueous solution of rare-earth element acetate to the zirconium LHH sample as S : L = = 1 : 20, the latter demonstrated robust sorption of R^{3+} cations (R = La, Sm, Gd, Dy) from acetate solutions. Saturation was observed within 30—40 min. Consequently, 40 min of phase contact during the rare-earth zirconate synthesis was considered sufficient to achieve equilibrium in this specific system at the defined S : L ratio. The table below outlines the properties of rare-earth element sorption by low-hydrated zirconium hydroxide.

The rare-earth cations in the aqueous solution exist in the form of hydrates: $R(H_2O)_n]^{3+}$ ($n = 9.0$ for La^{3+}, 8.94 for Sm^{3+}, 8.27 for Gd^{3+}, 8.01 for Dy^{3+}) [29; 30]. We observed no correlation between the size of the rare-earth cation and its sorption capacity. The interaction between rare-earth element hydrates and low-hydrated zirconium hydroxide occurs primarily through cation exchange. The rare-earth cations are bound to the hydroxo- and aqua groups in the LHH, leading to the release of H_3O^+ hydroxonium ions into the solution. This interaction is further confirmed by the acidification of the initial solution, resulting in a change in pH from 6 to 5. Sorption by oxyhydrates represents a complex process involving both ion exchange and the entry of cations into the pores.

The heterophase synthesis of rare-earth zirconates was conducted using amorphous low-hydrated zirconium hydroxide containing 68.8 ± 0.1 wt.% of ZrO_2 zirconium dioxide and aqueous solutions of acetates of lanthanum, samarium, gadolinium, and dysprosium ($C(La^{3+})$ = 0.155 mol/L, $C(Sm^{3+})$ = 0.136 mol/L, $C(Gd^{3+})$ = 0.141 mol/L, $C(Dy^{3+})$ = 0.120 mol/L). The S : L ratio was maintained at 1 : (36÷46). Adequate amounts of acetate solutions were used to achieve the required $R_2O_3 : ZrO_2$ molar ratio. The synthesis procedure for rare-earth element zirconates involved adding an acetate solution of the respective rare-earth element to zirconium LHH and stirring the mixture on a shaker at room temperature for 1—2 h. The resulting suspension was then evaporated to dryness for 24 h at t = 120 °C.

Subsequently, a stepwise heat treatment was carried out in the 600—900 °C temperature range with a 100 °C increment. Each step lasted for 2 h. The choice of 600 °C as the initial temperature was based on the differential thermal analysis results, where at this temperature and higher, no observable effects were noted, and the sample weight remained constant. Fig. 2 illustrates the results of the thermal analysis of the intermediate product obtained through the interaction of low-hydrated zirconi-

Sorption of R^{3+} (R = La, Sm, Gd, Dy) by low-hydrated zirconium hydroxide, 68.8 ± 0.1 wt.% ZrO_2 content, 40 min phase contact period

Сорбция R^{3+} (R = La, Sm, Gd, Dy) маловодным гидроксидом циркония при содержании ZrO_2 68,8 ± 0,1 мас.% и продолжительности контактирования фаз 40 мин

Concentration of the $R(CH_3COO)_2$ solution, mol/L		Concentration change after sorption Δ, mol/L	Efficiency of Zr sorption by LHH, %	Sorption capacity G, mmol/g
Initial C_{init}	After sorption $C_{aft/sorp}$			
		R = La^{3+}		
0.053	0.045	0.008	15.1	0.16
0.102	0.072	0.030	29.4	0.60
0.155	0.110	0.045	29.0	0.90
		R = Sm^{3+}		
0.044	0.038	0.006	13.6	0.12
0.100	0.073	0.027	27.0	0.54
0.136	0.100	0.036	26.5	0.72
		R = Gd^{3+}		
0.060	0.049	0.011	18.3	0.22
0.103	0.071	0.032	31.1	0.64
0.141	0.096	0.045	31.9	0.90
		R = Dy^{3+}		
0.055	0.045	0.010	18.2	0.20
0.105	0.075	0.030	28.6	0.60
0.120	0.086	0.034	28.3	0.68

um hydroxide with an aqueous solution of dysprosium acetate, followed by the evaporation of the resulting mixture.

The DTA curve reveals two endothermic and two exothermic effects. The first endothermic effect (80—260 °C) corresponds to dehydration. The thermal effects observed in the 310—405 °C range are attributed to the decomposition of the organic component, accompanied by the release of CO and CO_2. The exothermic effect at 500—550 °C can be associated with the formation of the final substance. This is substantiated by the absence of an exothermic effect on the DTA curve at $t = 400 \pm 5$ °C, indicating the solidification of zirconium dioxide.

The stepwise heat treatment produced finely dispersed powders, which were subjected to XRD analysis. It was observed that the formation of $R_2Zr_2O_7$ / $R_2O_3 \cdot 2ZrO_2$ (R = La, Sm, Gd, Dy) commenced at $t = 600$ °C. However, the samples were not single-phase at this stage; they contained not only zirconate but also unreacted oxides of zirconium and the rare-earth element. In Fig. 3, the XRD pattern of lanthanum zirconate obtained at 600 °C for 2 h is presented. Apart from the $La_2Zr_2O_7$ peaks, the XRD pattern exhibits peaks corresponding to zirconium dioxide and lanthanum hydroxide.

Single-phase products were successfully obtained at 800 °C. Using this method, $R_2Zr_2O_7$ (R = La, Sm, Gd) rare-earth zirconates and the $Dy_2O_3 \cdot 2ZrO_2$ solid solution were synthesized. Lanthanum, samarium, and gadolinium zirconates belong to the cubic pyrochlore ($Fd\bar{3}m$) space group:

$$La_2Zr_2O_7\text{:}\quad a = 10.85 \pm 0.01\ \text{Å},$$

$$Sm_2Zr_2O_7\text{:}\quad a = 10.59 \pm 0.02\ \text{Å},$$

$$Gd_2Zr_2O_7\text{:}\quad a = 10.50 \pm 0.01\ \text{Å},$$

while dysprosium zirconate belongs to the fluorite space group ($Fm\bar{3}m$), with a = 5.212 ± 0.002 Å.

Figure 4 displays the XRD patterns of $Sm_2Zr_2O_7$ and the $Dy_2O_3 \cdot 2ZrO_2$ solid solution.

Figure 5 illustrates the particle size distribution of the synthesized zirconates. In all samples, a distinct peak is evident on the curves, indicating the maximum content of powder particles in the range of 0.8—1.8 μm. The average particle size for all zirconates is approximately the same, with differences in hundredths of microns, μm: $La_2Zr_2O_7$ — 1.12, $Sm_2Zr_2O_7$ — 1.10, $Gd_2Zr_2O_7$ — 1.18, $Dy_2O_3 \cdot 2ZrO_2$ — 1.12.

The disparity in particle sizes observed between the synthesized zirconates and low-hydrated zirconium hydroxide can be attributed to the agglomeration of zirconium LHH particles..

Through these investigations, we successfully deve-

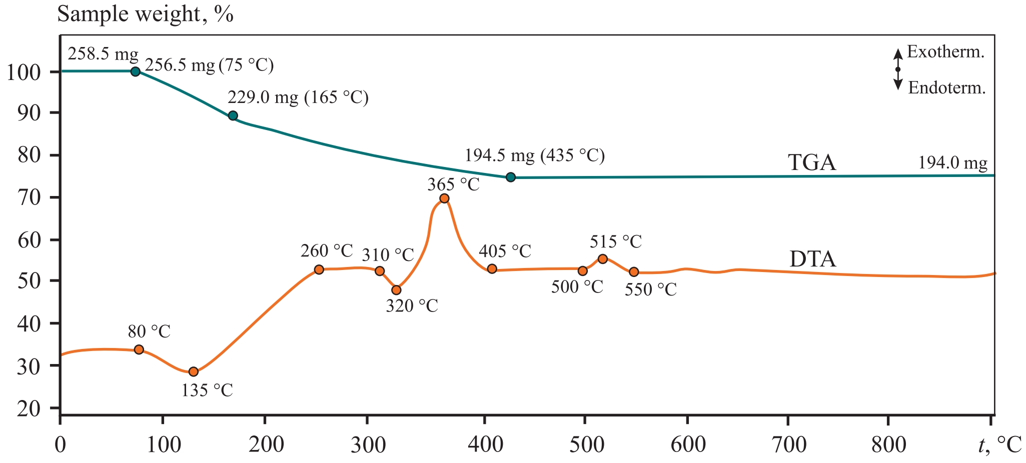

Fig. 2. Thermal analysis curves for the sample obtained by interacting low-hydrated zirconium hydroxide (68.8 ± 0.1 wt.% ZrO_2) with an aqueous solution of dysprosium acetate ($C(Dy^{3+}) = 0.120$ mol/L) followed by evaporation at $t = 120$ °C

TGA – weight change curve; DTA – differential thermal analysis curve

Рис. 2. Кривые термического анализа образца, полученного при взаимодействии маловодного гидроксида циркония (68,8±0,1 мас.% ZrO_2) с водным раствором ацетата диспрозия ($C(Dy^{3+}) = 0{,}120$ моль/л) и последующем выпаривании полученной смеси при $t = 120$ °C

ТГ – кривая изменения массы; ДТА – дифференциальная кривая нагревания

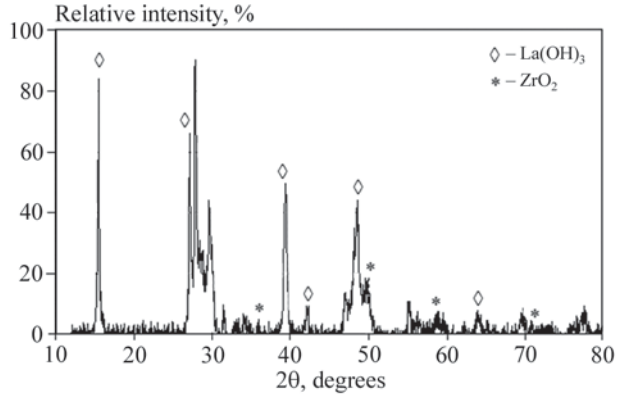

Fig. 3. XRD pattern of $La_2Zr_2O_7$ obtained at $t = 600$ °C, $\tau = 2$ h

Рис. 3. Дифрактограмма цирконата лантана $La_2Zr_2O_7$, полученного при $t = 600$ °С, $\tau = 2$ ч

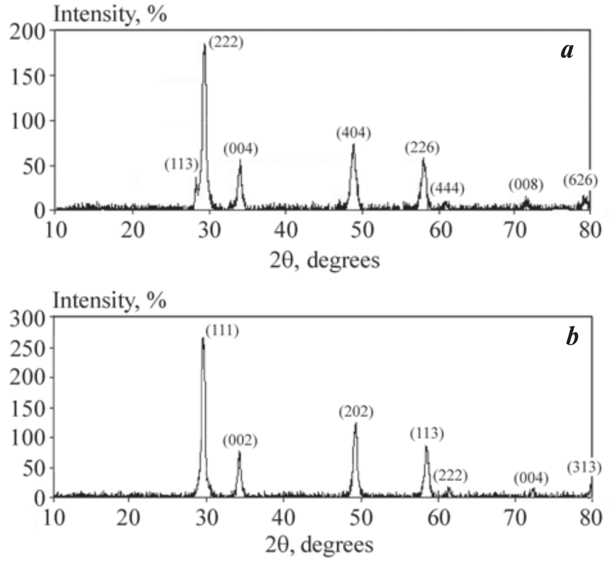

Fig. 4. XRD patterns of $Sm_2Zr_2O_7$ (***a***) and $Dy_2O_3 \cdot 2ZrO_2$ (***b***) obtained at $t = 800$ °C, $\tau = 6$ h

Рис. 4. Дифрактограммы цирконатов $Sm_2Zr_2O_7$ (***a***) и $Dy_2O_3 \cdot 2ZrO_2$ (***b***), полученных при $t = 800$ °С, $\tau = 6$ ч

loped a heterophase process for synthesizing the $R_2Zr_2O_7$ (R = La, Sm, Gd) and $Dy_2O_3 \cdot 2ZrO_2$ complex oxide phases. The use of low-hydrated zirconium hydroxide as a precursor proved effective in lowering the synthesis temperature and achieving single-phase products.

Conclusions

1. The low-hydrated zirconium hydroxide with a composition of $Zr(OH)_{3\div1}O_{0,5\div1.5} \cdot (1.6\div2.6)H_2O$ was produced through a heterophase process, yielding a dioxide content of 68.8 ± 0.1 wt.%.

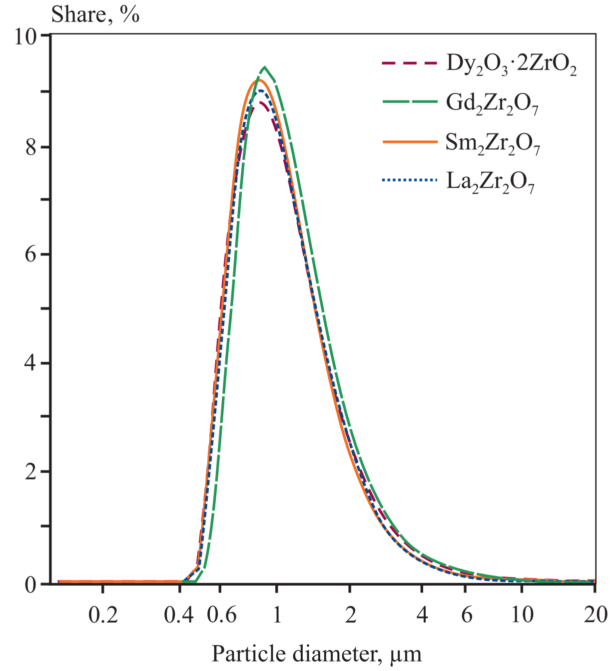

Fig. 5. Particle size distribution in $R_2Zr_2O_7$ (R = La, Sm, Gd) and $Dy_2O_3 \cdot 2ZrO_2$

Рис. 5. Распределение частиц синтезированных цирконатов состава $R_2Zr_2O_7$ (R = La, Sm, Gd) и $Dy_2O_3 \cdot 2ZrO_2$ по размеру

2. The sorption capacity of zirconium LHHs for rare-earth element cations (La, Sm, Gd, Dy) was investigated. The results revealed that sorption by low-hydrated zirconium hydroxide is a multifaceted process, involving the incorporation of rare-earth cations into the pores of low-hydrated hydroxide and ion exchange.

3. Heterophase synthesis experiments were conducted to obtain $R_2Zr_2O_7$ (R = La, Sm, Gd) and $Dy_2O_3 \cdot 2ZrO_2$ rare-earth zirconates, employing low-hydrated zirconium hydroxide and aqueous solutions of rare-earth element acetates as precursors.

4. XRD analysis demonstrated that the $R_2Zr_2O_7$ (R = La, Sm, Gd) single-phase rare-earth zirconates and the $Dy_2O_3 \cdot 2ZrO_2$ solid solution form at 800 °C. Their lattice parameters were estimated through this analysis.

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