Effect of Carbonization and Mechanical Activation of Coprecipitated Gadolinium and Zirconium Hydroxides on the Synthesis of Gd₂Zr₂O₇

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Abstract. The processes occurring during carbonization and subsequent mechanical activation of coprecipitated gadolinium and zirconium hydroxides, as well as their effect on the synthesis of $Gd_2Zr_2O_7$ during thermal and autoclave treatment of the obtained precursors have been investigated. It has been revealed that when the coprecipitated hydroxides of Gd and Zr are saturated with carbon dioxide, crystalline hydrated gadolinium carbonate is formed. It has been shown that carbonization reduces the yield of gadolinium zirconate upon subsequent calcination of the precursor. As a result of autoclave treatment of the initial and carbonized precursor at 250 °C for 4 h, zirconium and gadolinium-containing phases crystallize separately, and $Gd_2Zr_2O_7$ is not formed. After thermal treatment of the mechanically activated carbonized precursor at 900 °C for 3 h nanocrystalline fluorite-type $Gd_2Zr_2O_7$ is formed with a yield of 100 %.

Keywords: hydroxides, gadolinium zirconate, mechanical activation, carbonization, thermal and autoclave treatment.

Влияние карбонизации и механоактивации совместно осажденных гидроксидов гадолиния и циркония на синтез $Gd_2Zr_2O_7$

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Аннотация. Исследованы процессы, протекающие при карбонизации и последующей механоактивации совместно осажденных гидроксидов гадолиния и циркония, а также их влияние на синтез $Gd_2Zr_2O_7$ при термической и автоклавной обработке полученных прекурсоров. Установлено, что при насыщении совместно осажденных гидроксидов Gd и Zr углекислым газом образуется кристаллический гидратированный карбонат гадолиния. Показано, что карбонизация снижает выход цирконата гадолиния при последующем прокаливании прекурсора. В результате автоклавной обработки исходного и карбонизированного прекурсора при 250 °C в течение 4 ч отдельно кристаллизуются цирконий- и гадолинийсодержащие фазы, $Gd_2Zr_2O_7$ не образуется. После прокаливания механоактивированного карбонизированного прекурсора при 900 °C в течение 3 ч образуется нанокристаллический $Gd_2Zr_2O_7$ со структурой флюорита с выходом 100 %.

Ключевые слова: гидроксиды, цирконат гадолиния, механоактивация, карбонизация, термическая и автоклавная обработка.

Introduction

Deposits of rare metal minerals such as loparite, baddeleyite, eudialyte and others containing zirconium and rare earth elements (REE) are concentrated on the Kola Peninsula. During the chemical-technological processing of such deposits, it is possible to obtain a variety of compounds, for example, REE zirconates, which are widely used in many high-tech applications. Compounds with the general formula $Ln_2Zr_2O_7$ (Ln - REE) have a number of unique properties. In particular, $Gd_2Zr_2O_7$ has a high melting point (2500 °C), low thermal conductivity (1.28 W/(m·K) at 1000 °C), and is characterized by high radiation, chemical, and thermal stability [1–3]. In this regard, REE zirconates, including $Gd_2Zr_2O_7$, have been intensively studied in recent years as promising components of thermal barrier coatings, catalysts, solid electrolytes, and matrices for immobilizing radioactive waste [1–5].

Previously, we studied the synthesis of $Gd_2Zr_2O_7$ from a precursor obtained by coprecipitation of Zr and Gd hydroxides using mechanical activation (MA) [6]. It was shown that MA of a hydroxide precursor followed by calcination resulted in formation of nanocrystalline fluorite-type gadolinium

zirconate (polycrystalline sample, in which the average crystallite size is in the nanorange). The specific surface area of the synthesized $Gd_2Zr_2O_7$ was 4–9 times greater than that of a similar sample synthesized without the application of the MA. It was noted that, according to IR spectroscopy and thermal analysis (TA), Gd and Zr hydroxides interacted with each other at the molecular scale during coprecipitation, forming mixed hydroxides, and also reacted with the atmospheric carbon dioxide. In particular, it was revealed that the IR spectrum of coprecipitated gadolinium and zirconium hydroxides is not a superposition of the spectra corresponding to the separately precipitated hydroxides. In addition, coprecipitated gadolinium and zirconium hydroxides displayed different thermal decomposition behavior as compared to that of the mixture of the separately precipitated hydroxides. TA showed that the release of CO_2 from the carbonate groups of the precursor occurred at noticeably higher temperatures compared to the thermolysis of carbonate groups formed due to the absorption of carbon dioxide from the air by the separately precipitated hydroxides of Gd and Zr. It was found also that the MA of the precursor lead to mechanochemical interaction with atmospheric CO_2 [6]. The aim of this work is to elucidate the effect of CO_2 on the synthesis of $Gd_2Zr_2O_7$. We have studied the phase formation during carbonization of coprecipitated gadolinium and zirconium hydroxides. The carbonization was carried out using bubbling CO_2 through an aqueous suspension of Gd and Zr hydroxides. In addition, the processes occurring during MA as well as the thermal and autoclave treatment of the prepared precursor have been studied.

Materials and methods

The initial hydroxide precursor (IP) was prepared by adding a mixed solution of gadolinium nitrate and zirconium oxychloride (molar ratio Zr: Gd = 1: 1) to the ammonia solution, followed by washing the precipitate from nitrate and chlorine ions. The method for obtaining the precursor is described in detail in [6]. Carbonization was carried out by bubbling CO_2 from a cylinder at atmospheric pressure at a rate of 30 L/min through an aqueous suspension of IP for up to 60 h with continuous stirring using a magnetic stirrer. Samples were taken by filtration, and then they were dried at 100 °C for 12 h and analyzed for carbon content using a CS-2000 analyzer. Autoclave treatment of the precursors was carried out using a nickel-metal autoclave at 250 °C for 4 h with a load of 1 g sample + 40 ml distilled H_2O.

X-ray phase analysis was carried out using a Shimadzu XRD 6000 diffractometer (CuK_α-radiation). The X-ray diffraction patterns were taken with a step of 0.02° (2θ), the dwell time was 1 s. Thermal analysis was performed on a NETZSCH STA 409 PC/PG unit in the range 20–1300 °C. The results were obtained in the mode of heating the sample at a rate of 10 °C/min in an alumina crucible in an argon atmosphere. IR spectra were recorded with a Nicolet 6700 FT-IR spectrometer in potassium bromide tablets.

The MA of the precursor carbonized for 60 h was carried out in an AGO-2 laboratory centrifugal-planetary mill for 30 minutes at a centrifugal factor of 20 g in steel vials lined with zirconia using 150 g of 8 mm balls also made of zirconium dioxide. The ratio of balls: loading was 20: 1. The mechanically activated carbonated precursor is designated as MCP.

Results and discussion

The dependence of the CO_2 content of the precursor on the time of carbon dioxide bubbling is shown in Table 1. From the data presented in Table 1 it follows that almost complete saturation with

Table 1. The CO_2 content of the precursor versus CO_2 bubbling time

CO_2, wt.%	CO_2 bubbling time, h
6.31	0
12.2	10
12.3	17
13.2	40
13.4	60

carbon dioxide takes about 40 hours. The CO_2 content in the carbonated precursor after 60 hours of bubbling (hereinafter referred to as CP) was 13.4 %, which is more than 2 times higher than in the initial hydroxide precursor (IP).

According to the XRD data, the IP is X-ray amorphous (Fig. 1, curve 1), while in the precursor, after 17 h of bubbling CO_2 (Fig. 1, curve 2), the formation of gadolinium carbonate $Gd_2(CO_3)_3 \cdot nH_2O$ (n = 2–3) is observed. With an increase in the bubbling time to 60 h (Fig. 1, curve 3), the intensities of the peaks of gadolinium carbonate increase, and the amorphous background decreases. This indicates a greater carbonization of Gd hydroxide. Mechanical activation leads to complete amorphization of $Gd_2(CO_3)_3 \cdot nH_2O$ formed during carbonization (Fig. 1, curve 4).

Fig. 2 shows the IR spectra of the precursors. The IP spectrum (Fig. 2, curve 1) differs markedly from the spectra of carbonated precursors (Fig. 2, curves 2 and 3). At the same time, in agreement with the XRD data (Fig. 1), the position and shape of the absorption bands in the spectrum of the completely carbonized precursor (CP) (Fig. 2, curve 3) are very close to those in the spectrum of $Gd_2(CO_3)_3 \cdot nH_2O$ [7].

Intense double absorption bands in the range of 1550–1300 cm^{-1} in the spectra of all samples (Fig. 2) correspond to stretching vibrations of the CO_3^{2-} group [8]. The appearance of this band is due to the carbonization of the precursor as a result of interaction with atmospheric carbon dioxide
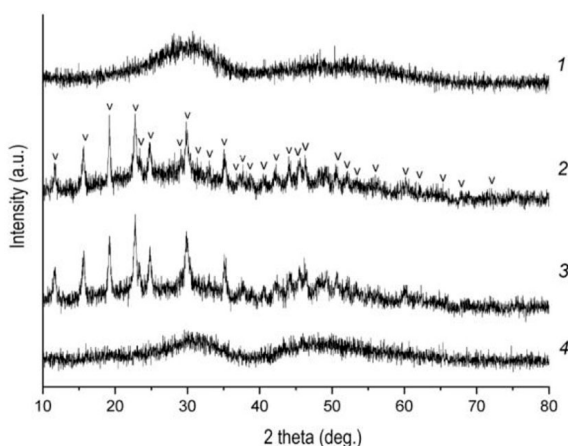

Fig. 1. XRD patterns: 1 – initial precursor (IP); 2 – precursor after 17 hours of bubbling CO_2; 3 – precursor after 60 h of bubbling CO_2(CP); 4 – mechanically activated carbonated precursor (MCP). Solid phase: v – $Gd_2(CO_3)_3 \cdot nH_2O$ (PDF 37–0559)
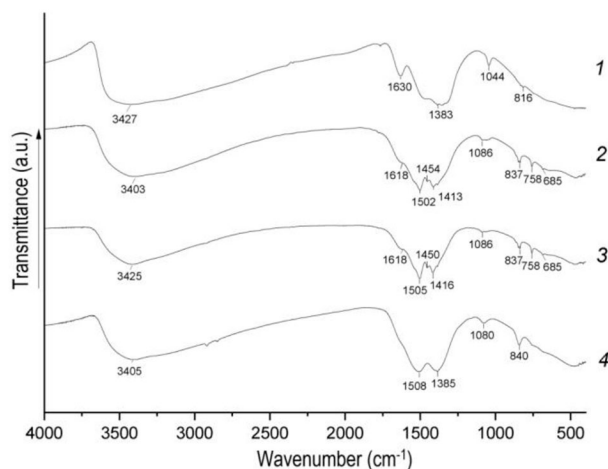
Fig. 2. FT-IR spectra: 1 – initial precursor (IP); 2 – precursor after 17 hours of bubbling CO_2; 3 – fully carbonated precursor (CP); 4 – mechanically activated carbonated precursor (MCP)

(in the case of IP), as well as due to the bubbling CO_2 (for the carbonated precursors). It is noteworthy that in the MCP spectrum (Fig. 2, curve 4), the shape of the stretching vibration band of the CO_3^{2-} group and the positions of the corresponding absorption maxima differ significantly from those in the CP spectrum (Fig. 2, curve 3). This reflects a significant change in the environment of carbonate groups in the MCP under the influence of intense mechanical treatment, apparently associated with the interaction of CO_3^{2-} with metal ions.

For carbonized precursors, in comparison to IP, the intensity of the OH-group stretching vibration band in the range of 3700–3300 cm^{-1} decreases relative to the intensity of the CO_3^{2-} group band in the 1550–1300 cm^{-1} region, which indicates an increase in the content of carbonate ions and, possibly, dehydration. It can also be noted that the IP spectrum (Fig. 2, curve 1) contains a band at 1630 cm^{-1}, which corresponds to the bending vibrations of OH groups [8]. In the spectra of carbonated precursors (Fig. 2, curves 2 and 3) and especially in the MPC spectrum (Fig. 2, curve 4), the intensity of the similar band is much lower. This indicates that the modified precursors (CP and MCP) contain a noticeably smaller amount of molecular water, in contrast to IP.

According to XRD data, annealing at 900 °C of IP (Fig. 3, curve 1) and MCP (Fig. 3, curve 3) results in formation of 100 % fluorite-type $Gd_2Zr_2O_7$. The crystallite size in these samples was calculated using the Scherrer formula

$$D = \lambda/(B \cdot \cos\theta),$$

where λ is the radiation wavelength, B is the integrated width of a reflection, θ is the diffraction angle of a line maximum. For IP and MCP the D value was 10 and 18 nm, respectively. The CP sample after heat treatment at 900 °C is a mixture of Gd_2O_3 and a solid solution $Gd_xZr_{1-x}O_{2-x/2}$ (0.18≤x≤0.45 [9]) with the fluorite-type structure (Fig. 3, curve 2). Consequently, carbonization of co-precipitated hydroxides prevents the complete synthesis of $Gd_2Zr_2O_7$ during subsequent calcination. The reason is probably an increase in the degree of heterogeneity of the precursor after bubbling CO_2 due to the crystallization of $Gd_2(CO_3)_3 \cdot nH_2O$. MA of CP results not only in amorphization of gadolinium carbonate and increasing
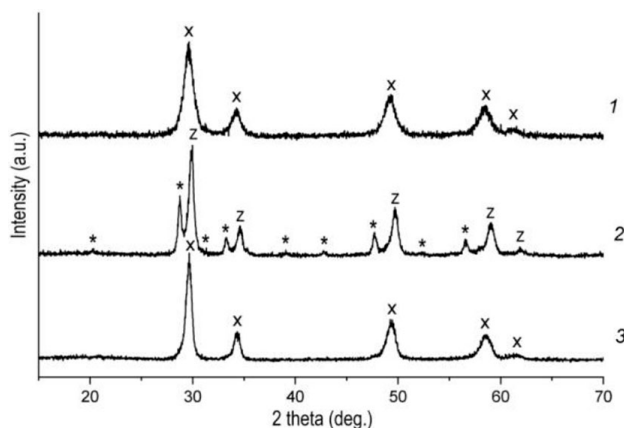
Fig. 3. XRD patterns of precursors calcined at 900 °C for 3 h: 1 – initial precursor (IP); 2 – completely carbonated precursor (CP); 3 – mechanically activated carbonated precursor (MCP). Solid phases: x – fluorite-type $Gd_2Zr_2O_7$ (PDF 80–0471); z – $Gd_xZr_{1-x}O_{2-x/2}$ solid solution with the fluorite-type structure [9]; * – Gd_2O_3 (cubic) (PDF No. 12–0797).

the degree of homogeneity of the precursor, but also, according to IR spectroscopy data (Fig. 2), leads to interaction of zirconium, gadolinium, and CO_3^{2-} ions, which contributes to the complete synthesis of $Gd_2Zr_2O_7$ (Fig. 3, curve 3).

The results of thermal analysis of the CP and MCP are shown in Figs. 4 and 5, respectively. In the DTA curves, the endothermic peaks at 110 °C (Fig. 4) and 115 °C (Fig. 5), associated with the DTG peaks, correspond to the removal of adsorbed water. The exothermic DTA peaks of the CP in the range of 500–700 °C (Fig. 4) probably correspond to the crystallization of both the $Gd_xZr_{1-x}O_{2-x/2}$ solid solution with the fluorite-type structure and Gd_2O_3 in agreement with the XRD data (Fig. 3, curve 2). It should be noted that the complete decomposition of gadolinium carbonate with the formation of Gd_2O_3 occurs at temperatures not exceeding 520–580 °C [7]. The exothermic DTA peak of the MCP at 662 °C (Fig. 5) is likely related to the crystallization of $Gd_2Zr_2O_7$.
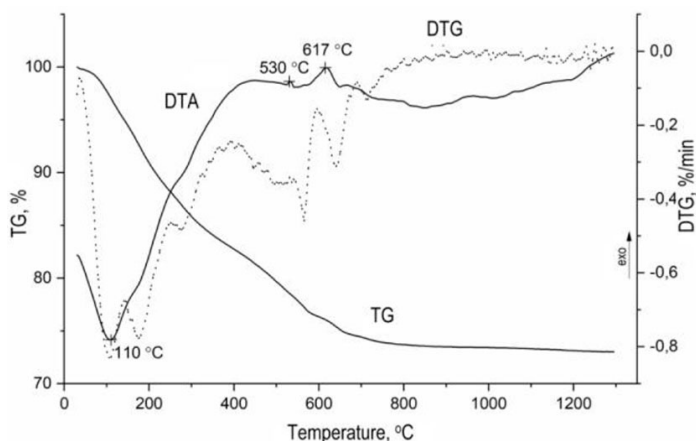

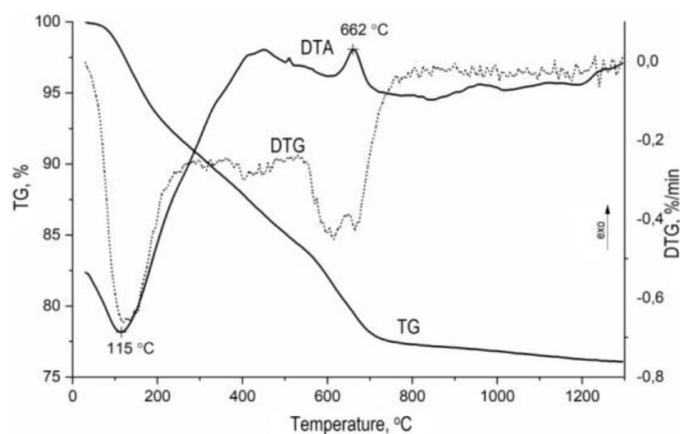Fig. 4. DTA, TG, and DTG curves for the carbonated precursor after 60 hours of bubbling CO_2 (CP)

Fig. 5. DTA, TG, and DTG curves for the carbonated precursor after 60 hours of bubbling CO_2 and 30 minutes of MA (MCP)

Using the CO_2 content of the CP (13.4 %) and the TG data on total weight loss (26.98 %) we have calculated the molar ratio of CO_2/Gd_2O_3=2.46 of the CP. This value is 18 % less than the corresponding value equal to 3 for $Gd_2(CO_3)_3 \cdot nH_2O$. The reduced value of the degree of carbonization of the CP in comparison to the stoichiometric one indicates an incomplete transformation of gadolinium from the hydroxide form to the carbonate, that is apparently due to the interaction of Gd and Zr at the molecular level during coprecipitation of hydroxides [6].

According to the TG data (Figs. 4 and 5), the weight loss in the range 600–1300 °C, which can be attributed to the removal of carbon dioxide as a result of the decomposition of CO_3^{2-} groups, is 3.32 % for CP, and 5.99 % for MCP. The CO_2 content of the CP (13.4 %) and the MCP (14.2 %) differs only by 0.8 %. Hence, it can be concluded that the carbonate groups in MCP are thermally more stable than in CP. Indirectly, this agrees with the IR spectroscopic data indicating the nonequivalence of carbonate ions in these precursors (Fig. 2).

Fig. 6 shows the XRD data for CP and MCP after autoclave treatment. Both samples contain tetragonal ZrO_2 and basic Gd carbonates, and for the mechanically activated precursor, the relative content of the latter is noticeably higher. It should be noted that autoclave treatment at 250 °C leads to the crystallization of separately zirconium and gadolinium-containing phases, while no $Gd_2Zr_2O_7$ is formed.

Conclusions

Thus, our studies have shown that Gd hydroxide, upon carbonization of the hydroxide precursor of gadolinium zirconate, is converted by about 82 % into $Gd_2(CO_3)_3 \cdot nH_2O$. Some amount of the gadolinium probably remains associated with zirconium. Besides gadolinium carbonate, no additional crystalline phases have been found in the carbonization product according to the XRD data. MA of the carbonized precursor results in its homogenization and formation of a metastable amorphous phase, in which metal ions and CO_3^{2-} interact according to IR spectroscopy and thermal analysis data. To clarify the nature of this phase, additional studies are required. The separation of Gd and Zr in the course of carbonization of the precursor leads to the incomplete synthesis of $Gd_2Zr_2O_7$ upon calcination. Autoclave treatment of the initial and carbonized precursor at 250 °C for 4 h results in
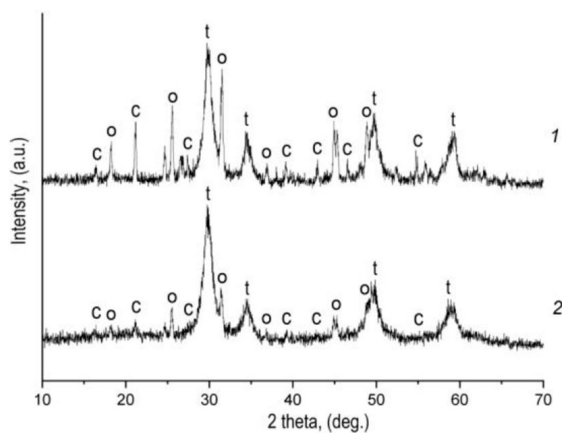
Fig. 6. XRD patterns of MCP (1) and CP (2) after autoclave treatment at 250 °C. Solid phases: o – $GdOHCO_3$ (PDF 24–0421); c – $Gd_2O(CO_3)_2 \cdot H_2O$ (PDF 43–0604); t – ZrO_2 (tetrag.) (PDF 73–1441)

formation of tetragonal zirconium dioxide and basic gadolinium carbonates. Calcination of the initial and mechanically activated carbonized precursors at 900 °C for 3 h allows one to prepare 100 % nanocrystalline fluorite-type gadolinium zirconate.

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