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Mechanism and Caloric Effects of the Thermal Dehydration of $GdCl_3 \cdot 6H_2O$ Crystalline Hydrate

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Abstract—The thermal dehydration of $GdCl_3 \cdot 6H_2O$ crystalline hydrate is studied by synchronous thermal analysis and mass spectrometry using certified samples. The mechanism and the caloric effects of the chemical reactions are determined. The thermal decomposition of $GdCl_3 \cdot 6H_2O$ crystalline hydrate is accompanied by hydrolysis, leading to the formation of oxychloride GdOCl.

Keywords: dehydration, crystalline hydrate, gadolinium chloride, synchronous thermal analysis, mass spectrometry

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INTRODUCTION

Rare-earth metals find wide use in various fields of industry, science, and technology. In particular, gadolinium and its compounds are actively used in nuclear power engineering, electronics, and medicine [1]. Among all stable elements, gadolinium is characterized by the highest capability of neutron capturing, is used for protection from thermal neutrons, and, hence, is promising for controlling nuclear reactors. Enamels, ceramics, and paints are prepared on the basis of gadolinium oxide. An alloy of gadolinium with nickel is used for manufacturing containers for burning radioactive wastes. Alloys of gadolinium with cobalt and iron possess unique magnetic properties and, therefore, are applied for manufacturing memory carriers with high recording density. Gadolinium oxides are among the basic components of superconducting ceramics and laser materials. Gadolinium salts are used as contrast substances for medicinal research in magnetic resonance tomography. The main method for the preparation of gadolinium is metallothermy, during which gadolinium is reduced in $GdCl_3$ and GdF_3 melts using calcium [1].

It is known that gadolinium chloride (as other rare-earth metal chlorides) is hygroscopic and adsorbs water vapors to form crystalline hydrates, heating of which can result in the formation of an impurity of oxychlorides [2, 3].

This can change the physicochemical properties of an electrolyte and exert a negative effect on the high-temperature chemical processes that occur and on the yield of the target components [1].

The available data [2–7] obtained during recent fifty years on the scheme of the thermal dehydration of gadolinium chloride crystalline hydrates, on the heats of phase transitions, and on the compositions of the intermediate and final phases are contradictory. The thermal decomposition of gadolinium chloride in air was studied by thermogravimetry (TG) [2]. The results showed [2] that the thermal decomposition of $GdCl_3 \cdot 6H_2O$ started at 90°C. A decrease in the sample weight on heating to 210°C was 27.1%, which is consistent with the assumption about the formation of the $GdCl_3 \cdot H_2O$ crystalline hydrate phase. An anhydrous salt with an impurity of GdOCl oxychloride is formed when temperature increases to 350°C, and the subsequent weight decrease is attributed to the formation of the GdOCl phase.

The thermal dissociation of $GdCl_3 \cdot 6H_2O$ in an inert atmosphere (N_2) was studied [4] by differential scanning calorimetry (DSC), and the enthalpies of the occurred processes were determined. The following scheme of thermal dehydration is presented on the basis of gravimetric measurements: $GdCl_3 \cdot 6H_2O \rightarrow GdCl_3 \cdot 3H_2O \rightarrow GdCl_3 \cdot 2H_2O \rightarrow GdCl_3 \cdot H_2O \rightarrow GdCl_3$. In this process, the final product (anhydrous $GdCl_3$) is formed at 260°C. The enthalpy of formation of gadolinium chloride trihydrate was 180.5 kJ/mol, but the tensimetric measurements [5] gave the heat of the same reaction of 126.3 kJ/mol.

The data on $GdCl_3 \cdot 6H_2O$ dehydration were obtained using a unique procedure and supplemented by chemical analysis results for the final product [6]. The following scheme of thermal dehydration is pre-

sented on the basis of the obtained experimental data: $GdCl_3 \cdot 6H_2O \rightarrow GdCl_3 \cdot 3H_2O \rightarrow GdCl_3 \cdot 2H_2O \rightarrow GdCl_3 \cdot H_2O$.

The results of synchronous thermal analysis (STA) including parallel measurements of the sample weight on heating and accompanying thermal effects of gadolinium trichloride crystalline hydrate are presented in one of the recent studies in this field [7]. To prevent hydrolysis, a sample was heated in argon to 230°C. The conclusions made on the basis of the obtained data differed substantially from the earlier conclusions [2–6], and the authors of [7] proposed the following scheme of thermal dehydration: $GdCl_3 \cdot 7H_2O \rightarrow GdCl_3 \cdot 4.4H_2O \rightarrow GdCl_3 \cdot 2.4H_2O \rightarrow GdCl_3 \cdot 0.3H_2O$. It should be mentioned that the temperatures of the marked thermogravimetric and caloric effects do not agree with those in the dehydration scheme.

In our opinion, substantial drawbacks of all studies considered are lacking data on the certification of the initial samples, limited data obtained by thermal analysis methods, and the absence of a combined approach to the investigation of the dehydration process using additional methods of research to establish the type of chemical reactions and the accompanying caloric effects.

The purpose of this work is to obtain data on the mechanism and thermal effects of the dehydration of $GdCl_3 \cdot 6H_2O$ crystalline hydrate using STA, mass spectrometry, X-ray diffraction (XRD) analysis, Raman spectroscopy, IR spectroscopy, and calculations of the thermodynamic parameters of the chemical reactions.

EXPERIMENTAL

Experimental Techniques

The temperatures of phase transitions and the accompanying thermal effects were measured and mass spectrometric measurements of the evolved gases were conducted on an STA 449C Jupiter synchronous thermal analyzer equipped with an Aëolos quadrupole mass spectrometer (NETZSCH, Germany). The instrument was calibrated using reference samples of $RbNO_3$, $KClO_4$, Ag_2SO_4, CsCl, K_2CrO_4, and biphenyl $C_{10}H_{12}$ (NETZSCH). The initial sample weight was 10–13 mg, the heating rate was 5°C/min, and the temperature range was 25–500°C. The measurements were carried out in an atmosphere of high-purity (99.998%) argon, and a Pt–Rh alloy crucible served as a container for a sample. According to the technical characteristics of the device, the error of determining the temperature was less than 1°C and the error of measuring the mass was 10^{-6} g. The experimental data were processed with the licensed Proteus software package.

The synthesized samples of $GdCl_3 \cdot 6H_2O$ crystalline hydrate and final products of its thermal decomposition were certified using XRD analysis, Raman spectroscopy, and IR spectroscopy. The phase compositions of the samples were determined on a Rigaku D/MAX-2200VL/PC automated X-ray diffractometer (Japan), a TENSOR 27 FT-IR spectrometer (Bruker, Germany), and an Ava-Raman fiber-optic spectrometric complex (Avantes, Netherlands).

The thermodynamic parameters of the possible chemical reactions in the temperature range 200–500°C were calculated using the HSC 7 Chemistry 8 program package.

Synthesis and Certification of $GdCl_3 \cdot 6H_2O$ Crystalline Hydrate

Crystalline hydrate $GdCl_3 \cdot 6H_2O$ was synthesized by the reaction

$$Cd_2O_3 + HCl_{conc.(exc.)} \rightarrow CdCl_3 \cdot 6H_2O + H_2O\uparrow. \quad (1)$$

Oxide Gd_2O_3 (TU 48-4-524-90v) was transferred into a glassy carbon cup and dissolved in an excess of concentrated HCl (reagent grade).

Gadolinium trichloride crystalline hydrate $GdCl_3 \cdot 6H_2O$ was prepared by the evaporation of the solution on slow heating to the temperatures not higher than 100°C. XRD analysis of the obtained sample showed the formation of crystalline hydrate $GdCl_3 \cdot 6H_2O$ (Fig. 1). The IR and Raman spectra of the synthesized crystalline hydrate contain vibrational bands of medium intensity in a range of 200–400 cm^{-1} assigned to the Gd–Cl bond, intense vibrational bands attributed to bending symmetric and stretching antisymmetric vibrations of crystallization water molecules in the ranges 1620–1650 and 3100–3500 cm^{-1}, and low-intensity bands in a range of 500–700 cm^{-1} characteristic of libration vibrations of the metal–OH_2 bond (Fig. 2) [8]. The results of XRD certification of the synthesized crystalline hydrate $GdCl_3 \cdot 6H_2O$ confirmed its single-phase character, and the IR and Raman spectroscopy data showed the absence of an impurity of adsorbed water, the presence of which in a sample can result in additional caloric and thermogravimetric effects during STA.

RESULTS AND DISCUSSION

The data of STA and mass spectrometry of the evolved gases obtained by heating crystalline hydrate $GdCl_3 \cdot 6H_2O$ in a temperature range of 25–500°C are presented in Fig. 3. The TG curve in a temperature range of 20–200°C exhibits three weak steps of the sample weight decrement accompanied by caloric effects in the DSC curve at 133, 152, and 170°C, and H_2O molecules are detected in the gas phase. The TG curve in a temperature range of 200–275°C contains one step of the weight decrement corresponding to the caloric effect in the DSC curve with the peak maximum at 238°C accompanied by the detection of H_2O and HCl molecules in the gas phase. The further heat-

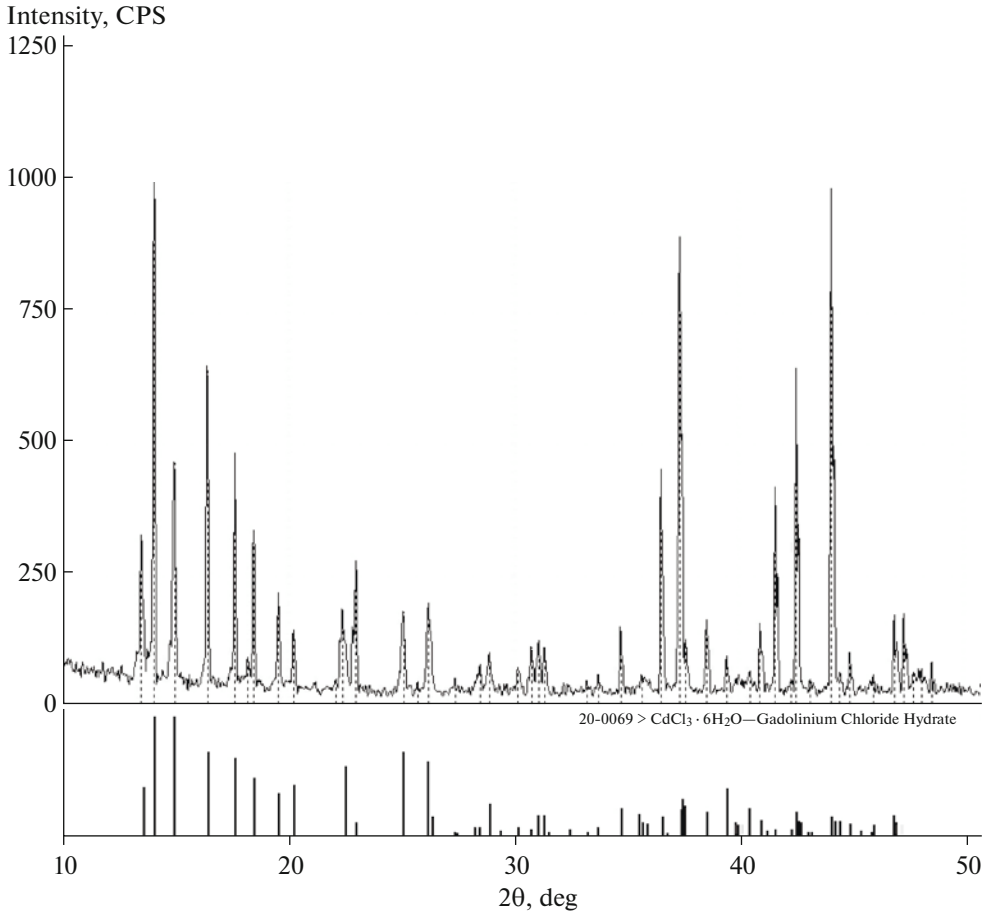

Fig. 1. Results of XRD analysis of synthesized $GdCl_3 \cdot 6H_2O$.

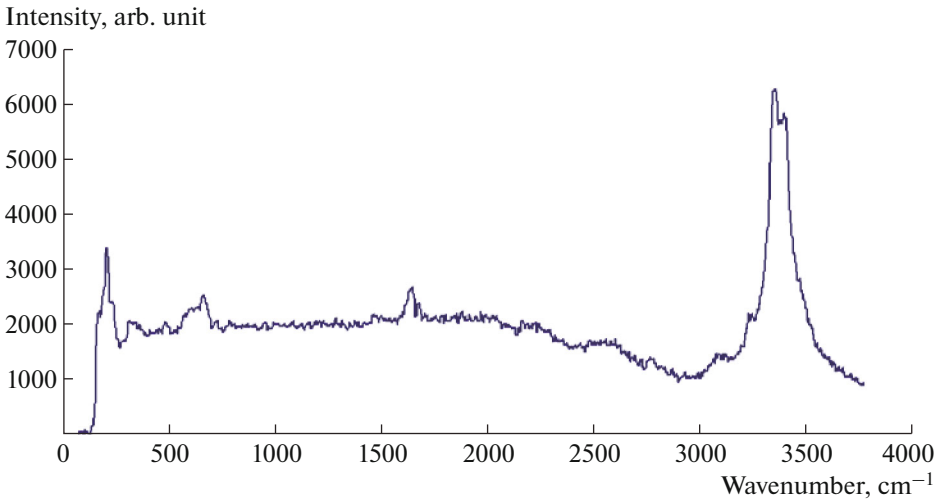

Fig. 2. Raman spectrum of synthesized $GdCl_3 \cdot 6H_2O$.

ing of the sample in a temperature range of 300–375°C results in the detection of a stepwise decrease in the sample weight accompanied by the heat uptake with a maximum of the effect at 358°C, and hydrogen chloride molecules appear in the gas phase. The reproducibility of the TG and DSC signals was confirmed in a series of experiments.

A general analysis of the obtained experimental data enables us to propose the following scheme of the thermal dehydration of crystalline hydrate $GdCl_3 \cdot 6H_2O$:

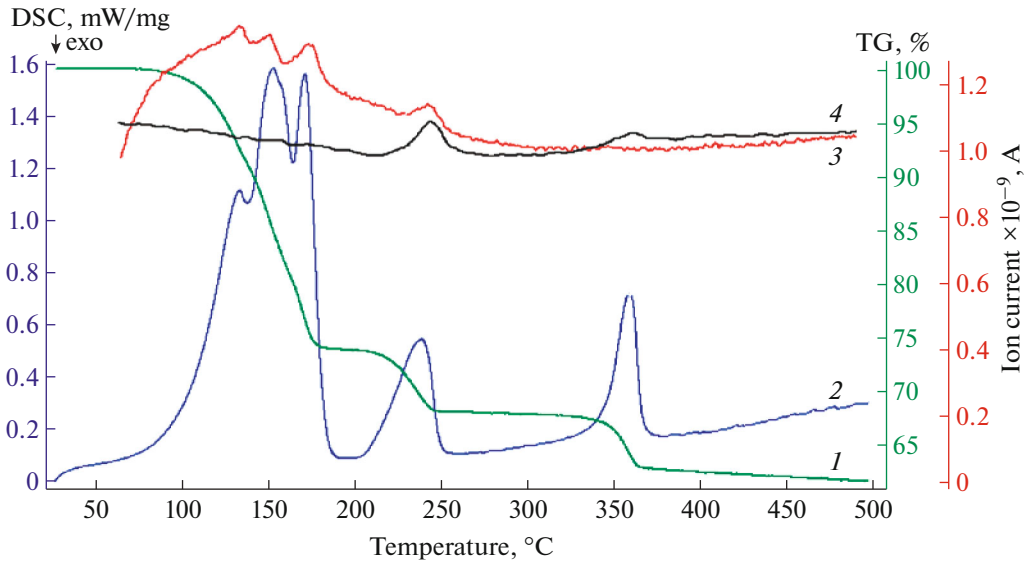

Fig. 3. (*1*) Sample weight, (*2*) thermal flow, and ionic current of (*3*) water and (*4*) HCl molecules during STA and mass spectrometric analyses of $GdCl_3 \cdot 6H_2O$ crystalline hydrate.

stepwise separation of water molecules occurs in a temperature range of 25–200°C according to the reactions

$$CdCl_3 \cdot 6H_2O \rightarrow CdCl_3 \cdot 3H_2O + 3H_2O\uparrow, \quad (2)$$

$$CdCl_3 \cdot 3H_2O \rightarrow CdCl_3 \cdot 2H_2O + H_2O\uparrow, \quad (3)$$

$$CdCl_3 \cdot 2H_2O \rightarrow CdCl_3 \cdot H_2O + H_2O\uparrow. \quad (4)$$

The change in the sample weight calculated by Eqs. (2)–(4) is consistent with the weight change detected experimentally (25.9%).

Hydrolysis occurs upon further heating of the sample in the temperature range 200–275°C along with anhydrous salt formation. The hydrolysis affords gadolinium oxychloride according to the following reactions:

$$CdCl_3 \cdot H_2O \rightarrow CdCl_3 + H_2O\uparrow, \quad (5)$$

$$CdCl_3 \cdot H_2O \rightarrow CdOCl + HCl\uparrow. \quad (6)$$

The heating of anhydrous gadolinium chloride in the closed space of the working chamber of the instrument in the presence of water vapors leads to its hydrolysis at temperatures of 300–375°C via the reaction

$$CdCl_3 + H_2O \rightarrow CdOCl + HCl\uparrow. \quad (7)$$

Thus, the overall equation of the thermal dehydration of gadolinium chloride crystalline hydrate can be written as follows:

$$CdCl_3 \cdot 6H_2O \rightarrow CdOCl + 2HCl\uparrow + 5H_2O\uparrow. \quad (8)$$

This conclusion is confirmed by a comparison of the results of the sample weight change (turned out to be 43.8%) calculated by Eq. (8) and the data of thermogravimetric measurements in a temperature range of 25–500°C (weight decrease 38.3%). It should be mentioned that the experimentally observed trend of a sample weight decrease is not finished at 500°C (maximum experimental temperature).

The XRD data for the reaction product confirmed the formation of the GdOCl phase (Fig. 4).

The IR and Raman spectra of the final product exhibit vibrational bands at 535 and 400 and 182, 235, 383, and 508 cm^{-1}, respectively, which is consistent with the data for the vibrational spectra of GdOCl [9, 10].

The peaks of the DSC curve were separated and the thermal effects accompanying the occurred chemical reactions were estimated by the results of caloric measurements of the dehydration of crystalline hydrate $GdCl_3 \cdot 6H_2O$ using the PEAK SEPARATION software. The data obtained are presented in Fig. 5 and Table 1.

The thermodynamic parameters of reaction (8) were additionally calculated using the HSC 7 Chemistry 8 program package, and the results are presented in Table 2.

It turned out that the specific amount of heat absorbed by the system during this reaction was about 474 kJ/mol at 500°C (Table 2), which is comparable with the total thermal effect of reactions (2)–(4) (423 kJ/mol) determined by DSC measurements. Interestingly, according to the calculation results (Table 2), the hydrolysis of crystalline hydrate $GdCl_3 \cdot 6H_2O$ begins in

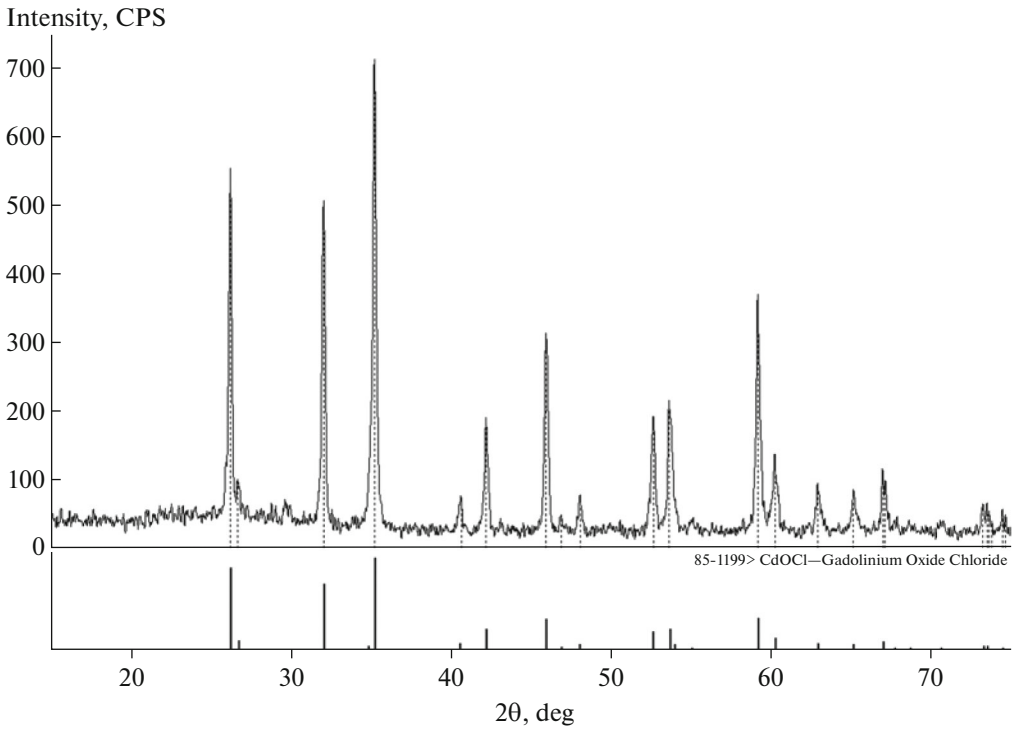

Fig. 4. XRD analysis results for the product of the thermal dehydration of $GdCl_3 \cdot 6H_2O$: GdOCl.

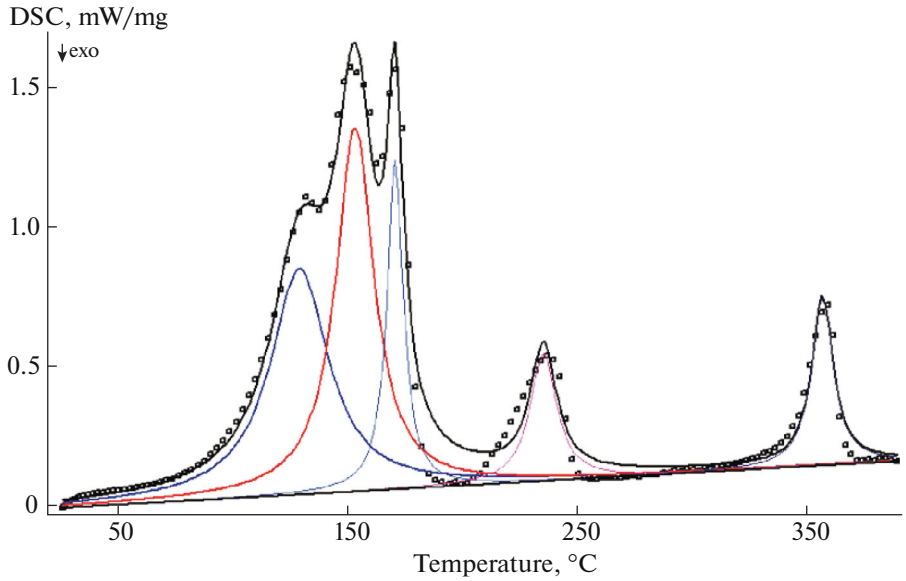

Fig. 5. Result of (smooth curves) peak separation of DSC curves using the PEAK SEPARATION software and (points) experimental data.

a temperature range of 200–250°C. This finding agrees with the experimental data obtained by the investigation of the dehydration process using a mass spectrometric study of the evolved gases (Fig. 3).

CONCLUSIONS

(1) The studies of the thermal dehydration of crystalline hydrate $GdCl_3 \cdot 6H_2O$ were carried out by STA and mass spectrometry using certified samples.

Table 1. Thermodynamic characteristics (temperature T, enthalpy ΔH) of the chemical reactions that occur during the thermal dehydration of $GdCl_3 \cdot 6H_2O$ calculated from a DSC curve using the PEAK SEPARATION software

Chemical reaction	T, °C	ΔH, kJ/mol
$GdCl_3 \cdot 6H_2O \rightarrow GdCl_3 \cdot 3H_2O + 3H_2O\uparrow$	129.0	173.78
$GdCl_3 \cdot 3H_2O \rightarrow GdCl_3 \cdot 2H_2O + H_2O\uparrow$	153.2	182.96
$GdCl_3 \cdot 2H_2O \rightarrow GdCl_3 \cdot H_2O + H_2O\uparrow$	170.7	70.92
$GdCl_3 \cdot H_2O \rightarrow GdCl_3 + H_2O\uparrow$ $GdCl_3 \cdot H_2O \rightarrow GdOCl + HCl\uparrow$	235.3	44.41
$GdCl_3 + H_2O \rightarrow GdOCl + HCl\uparrow$	356.8	46.98

Table 2. Thermodynamic parameters of reaction (8) in the temperature range 200–500°C calculated using the HSC 7 Chemistry 8 software package (ΔH is enthalpy, ΔS is entropy, ΔG is the free Gibbs energy, K is the equilibrium constant of the reaction)

T, °C	ΔH, kJ/mol	ΔS, kJ/(mol K)	ΔG, kJ/mol	$K \times 10^{-5}$	log(K)
200	482.351	1009.271	4.815	2.940E–001	–0.532
250	480.373	1005.291	–45.546	3.531E+004	4.548
300	478.603	1002.059	–95.727	5.307E+008	8.725
350	477.053	999.463	–145.762	1.657E+012	12.219
400	475.706	997.381	–195.681	1.533E+015	15.186
450	474.572	995.755	–245.508	5.433E+017	17.735
500	473.661	994.535	–295.264	8.911E+019	19.950

(2) The phase composition changes on heating crystalline hydrate $GdCl_3 \cdot 6H_2O$ according to the following scheme: $GdCl_3 \cdot 6H_2O \rightarrow GdCl_3 \cdot 3H_2O \rightarrow GdCl_3 \cdot 2H_2O \rightarrow GdCl_3 \cdot H_2O \rightarrow GdCl_3 + GdOCl \rightarrow GdOCl$. The final thermal decomposition product was certified by XRD analysis, Raman spectroscopy, and IR spectroscopy.

(3) Hydrolysis occurs along with anhydrous salt formation in a temperature range of 200–275°C to form gadolinium oxychloride.

(4) The peaks in the DSC curve were separated and the thermal effects accompanying the occurred chemical reactions were estimated using the PEAK SEPARATION software.

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