

PHYSICAL METHODS
OF INVESTIGATION

Isolation of Rare-Earth Elements from Mixtures of Calcium and Lanthanide Oxalates

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Abstract—The temperature regions for separate crystallization of rare-earth element (REE) oxides of the cerium group in the presence of CaCO_3 have been determined using X-ray diffraction, differential thermogravimetric analysis, inductively coupled plasma mass spectroscopy, and X-ray fluorescence. The possibility to separate REE oxides from CaCO_3 in H_2SO_4 solutions after heat treatment ($450\text{--}600^\circ\text{C}$) has been studied. The solid phase of the precipitate is represented by slightly soluble calcium sulfate, whereas the REE oxides pass into the liquid phase in the form of highly soluble sulfates. After heat treatment of the test mixture of REE oxalates and calcium oxalate at a temperature higher than 750°C , calcium compounds pass into 1–2% HNO_3 liquid phase in the form of nitrates, whereas lanthanide oxides remain in the insoluble phase of REE oxide solid solution having CeO_2 structure.

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Calcium compounds are widely used to isolate and concentrate REE in chemical production. Calcium sulfate hemihydrate is advisable to use for the associated isolation of REEs from extraction phosphoric acid (EPA) [1]. The isomorphous substitution in systems $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} - \text{LnPO}_4 \cdot 0.5\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} - \text{NaLn}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, where $\text{Ln} = \text{La, Ce, Pr, Nd, and Sm}$, enables one to concentrate REE impurities containing in EPA in the form of precipitates based on $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ [2]. Calcium oxalate was proposed as an adsorbent for the coprecipitation of REE oxalates from dilute aqueous solutions [3, 4]; the optimal solution acidity parameters and the effect of basic and secondary reactants ratio on the rate and completeness of lanthanide oxalates concentration in the solid phase of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ were also determined.

Features of the combined thermal decomposition of calcium oxalate and REE oxalates have been studied earlier; the effect of impurities of the cerium group REEs on dehydration, air oxidation, and decarboxylation of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ was determined [5]. However, in [5] the effect of CaCO_3 on the phase formation of REE oxides in the temperature range $442\text{--}600^\circ\text{C}$ was not studied and the causes resulted in a significant decrease in CaCO_3 decomposition temperature (from 883 to 736°C) in the presence of phases of cerium-group lanthanide oxides were not determined. In addition, possible methods of separating calcium compounds and compounds of rare-earth elements were not considered.

The separation of calcium and lanthanides is a rather complex chemical task. In this work we study the possibility to prepare concentrates of the cerium group REEs using the heat treatment of a mixture of calcium oxalates and lanthanides oxalates with subsequent phase separation.

EXPERIMENTAL

The quantitative content of REE and Ca in the samples under discussion was determined by inductively coupled plasma mass spectrometry using an XSeries2 ICP-MS spectrometer. As a preliminary analysis of the samples prepared, X-ray fluorescence (XRF) studies were performed on a SkyRay EDXRF 3600 device. The La–Sm content was determined according to the procedure reported in [6].

The X-ray powder diffraction studies of samples were performed using a G670 focusing chamber monochromator ($\text{CuK}_{\alpha 1}$ radiation). Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were performed on a Netzsch STA 409 PC synchronous thermal analyzer (sample weight, 10 mg; heating rate, 10 K/min).

A calcium oxalate sample containing 16 wt % of REE oxalates was obtained as a result of oxalate conversion of the calcium sulfate precipitate isolated from technical-grade extraction phosphoric acid containing rare earth elements [7, 8]. The chemical composition of the initial sample is shown in Table 1. The oxalate precipitate sample contained the following rare-earth

Table 1. Contents of Ca and REE in the starting sample of the oxalate precipitate, % wt

Element	Content	Element	Content	Element	Content
Ca	24	Y	0.10	Er	0.007
La	0.96	Eu	0.042	Tm	0.0004
Ce	2.4	Gd	0.11	Yb	0.0013
Pr	0.30	Tb	0.011	Lu	0.0001
Nd	1.1	Dy	0.039		
Sm	0.16	Ho	0.0048	Ln + Y	5.24

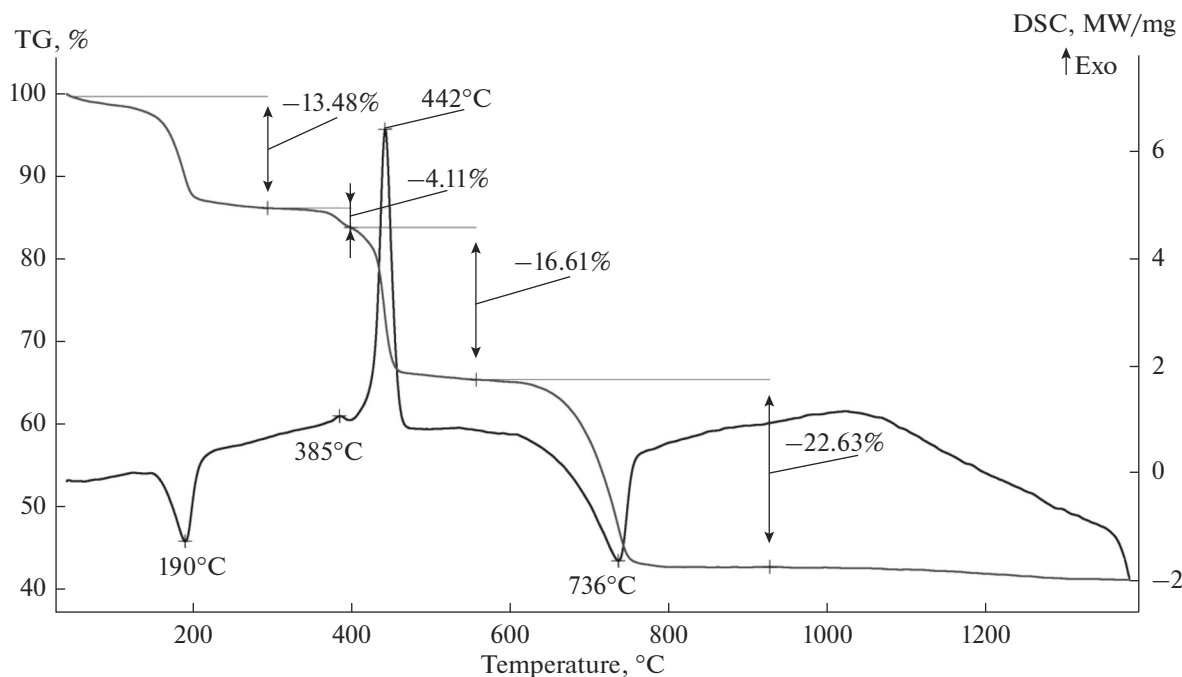
elements: Ce, Nd, La, Pr, and Sm. The starting sample contained $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, $\text{CaC}_2\text{O}_4 \cdot 2.25\text{H}_2\text{O}$, and $\text{Ln}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ phases in the ratio of 76 : 8 : 16 wt %, respectively. The quantitative contents of phases were determined by the method of corundum numbers according to the program for calculating X-ray powder diffraction patterns using a Bruker D8 Advance diffractometer (Bruker, Germany).

RESULTS AND DISCUSSION

Figure 1 shows the results of thermogravimetric analysis (TG-DSC) of the combined decomposition of calcium oxalate and REE oxalates. The endotherm at 190°C is accompanied by 13.48% weight loss and corresponds to the theoretically calculated total loss of hydrate water from all three initial oxalate species (calcd., 14.40%). The next small exotherm at 385°C corresponds to the decomposition of REE oxalates to

the oxides and is accompanied by 4.11% weight loss (calcd., 3.89%). The exotherm at 442°C corresponds to the decomposition of calcium oxalate to form calcium carbonate and is accompanied by 16.61% weight loss (calcd., 15.71%). The total weight loss upon the decomposition of REE and calcium oxalates is 20.72% and is close to the calculated value of 19.6%. The decomposition of CaCO_3 at 736°C is accompanied by 22.63% weight loss and is in satisfactory agreement with the calculated value (24.45%). The insignificant differences between the experimental and the corresponding calculated values of weight loss can be explained by experimental conditions, in particular, a sufficiently high (10 K/min) heating rate of the sample under study.

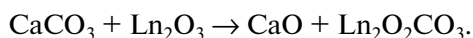
When studying the phase transformations of the oxalate precipitate within a narrow temperature range of 385–442°C, we noticed that dehydrated oxalates $\text{Ln}_2(\text{C}_2\text{O}_4)_3$ and CaC_2O_4 successively decomposed in air in the temperature range mentioned to give a small exotherm at 385°C and an exotherm at 442°C on the DSC curve, respectively. Unfortunately, X-ray powder diffraction data for samples annealed in the temperature range 385–442°C did not allow us to determine accurately the presence of phases of REE oxides. At a given annealing temperature, lanthanide oxides are in an X-ray amorphous state. The REE oxides became more crystallized with an increase in the annealing temperature of the oxalate precipitate (>442°C), especially after CaC_2O_4 was decomposed and CaCO_3 was formed.

**Fig. 1.** Thermal curves for the combined decomposition of calcium and REE oxalates.

We determined earlier [9] that a single-phase solid solution of lanthanide oxides based on the CeO_2 structure was formed after the decomposition of pure oxalates $\text{Ln}_2(\text{C}_2\text{O}_4)_3$ at a temperature higher than 374°C . Lanthanide (Ln) is represented by an isomorphous mixture of cerium-group REEs (La, Ce, Pr, Nd, and Sm) containing no calcium compounds. It was noted [5] that the simultaneous decomposition of $\text{Ln}_2(\text{C}_2\text{O}_4)_3$ mixed with CaC_2O_4 afforded individual phases of lanthanide oxides La_2O_3 , CeO_2 , Pr_6O_{11} , and Nd_2O_3 and CaCO_3 at 550°C with no formation of the mentioned phase of the REE oxide solid solution based on the cerium(IV) oxide structure.

The formation of the lanthanide oxide solid solution based on the CeO_2 structure was observed only at higher temperatures ($>736^\circ\text{C}$) after the complete decomposition of calcium carbonate to calcium oxide CaO , which is chemically inert toward the solid solution of lanthanide oxides. As a result, it can be concluded that the presence of the CaCO_3 phase inhibits the formation of the REE oxide solid solution. This favors the maintenance of La_2O_3 , CeO_2 , Pr_6O_{11} , and Nd_2O_3 individual phases up to the beginning temperature of the calcium carbonate decomposition (600°C), which is completed at 736°C to form a CaO phase and the phase of lanthanide oxide solid solution. It is important that the CaCO_3 decomposition temperature was observed to decrease significantly (from 883 to 736°C).

An obstacle to the formation of REE oxide solid solution and the maintenance of individual REE oxides in the presence of CaCO_3 can be the chemical reactivity of La and Nd oxides and their tendency to form oxocarbonates $\text{Ln}_2\text{O}_2\text{CO}_3$. Oxides and hydroxides of La and Nd react actively with CO_2 to form $\text{La}_2\text{O}_2\text{CO}_3$ [10]; therefore, the presence of La_2O_3 and Nd_2O_3 contributes to the removal of carbon dioxide from calcium carbonate according to the following scheme:



It is known [11, 12] that the thermal decomposition of cerium and praseodymium oxalates in air is accompanied by the formation of CeO_2 and Pr_6O_{11} without passing through an intermediate stage of oxocarbonate formation. We have found that the presence of CeO_2 promotes the decomposition of all REE oxalates to form a mixture of Ln_2O_3 . However, cerium and praseodymium oxides take no significant part in the further decomposition of CaCO_3 , since they are incapable of absorbing CO_2 .

The intermediate phases of X-ray amorphous oxocarbonates $\text{Ln}_2\text{O}_2\text{CO}_3$ decompose to form La_2O_3 and Nd_2O_3 at 710 and 680°C , respectively, according to the scheme:



The proposed processes of formation and decomposition of lanthanide oxocarbonates and calcium carbonate proceed over a wide temperature range (600 – 736°C) and end with the endotherm of CaCO_3 decomposition observed on the DSC curve (Fig. 1). Thus, Ln_2O_3 phases are able to initiate the thermal decomposition of calcium carbonate to calcium oxide at a lower temperature. The probable mechanism of this process is due to the formation and decomposition of intermediate phases of REE oxocarbonates.

In the temperature range 442 – 600°C , the formation of lanthanum and neodymium oxocarbonates and calcium oxide was not determined by X-ray powder diffraction. At a higher annealing temperature ($>736^\circ\text{C}$), the decomposition of CaCO_3 is observed to form CaO and the solid solution of REE oxides based on the CeO_2 structure, which agrees with the results of our studies [5].

After annealing therm at 450 – 600°C the calcium and REE compounds can be separated by treating samples containing phases of CaCO_3 and REE oxides with sulfuric acid. A certain success was achieved in [13] in the separation of CaO and oxides of La, Pr, and Nd in H_2SO_4 solutions. We plotted the solubility curves of Ca, La, Ce, Pr, and Nd sulfates as functions of temperature (Fig. 2) and H_2SO_4 concentration (Fig. 3) based on earlier reported data [14, 15]. As can be seen from Fig. 2, in the temperature range 0 – 20°C REE sulfates have a higher water solubility as compared to calcium sulfate (for Pr, Ce, or Nd sulfate, 65 – 95 times; for La sulfate, 15 times). This indicates a fundamental possibility of fractional separation of REEs and calcium in the form of sulfates at room temperature.

In the presence of H_2SO_4 small excess (5 – 10 wt %), the REE sulfate solubility increases (Fig. 3). Therefore, a sample containing CaCO_3 and Ln_2O_3 was treated with a 10 wt % H_2SO_4 solution taken in excess (10 rel %) over stoichiometry. As shown in Fig. 3, the solubility of REE and calcium sulfates is significantly reduced with a higher content of free H_2SO_4 .

After the liquid and solid phases were separated, the composition of the resulting REE sulfate concentrate was determined by X-ray fluorescence (XRF) analysis. The XRF spectra of the samples studied (Fig. 4) show that the liquid phase is enriched with the cerium group REEs and contains practically no Ca impurities. The intensity of the $\text{CaK}_{\alpha 1,2}$ and $\text{CaK}_{\beta 1,3}$ analytical lines in the energy range 3.5 – 4.0 keV for the liquid phase is two orders of magnitude lower than that for the solid phase of the precipitate. The subsequent washing of the solid phase with a small amount of cold water contributes to the complete separation of calcium and lanthanides.

To separate a mixture of CaO and the REE oxide solid solution of based on the CeO_2 structure one can treat it with dilute HNO_3 . It was known [16] that cerium(IV) oxide annealed at high temperatures has

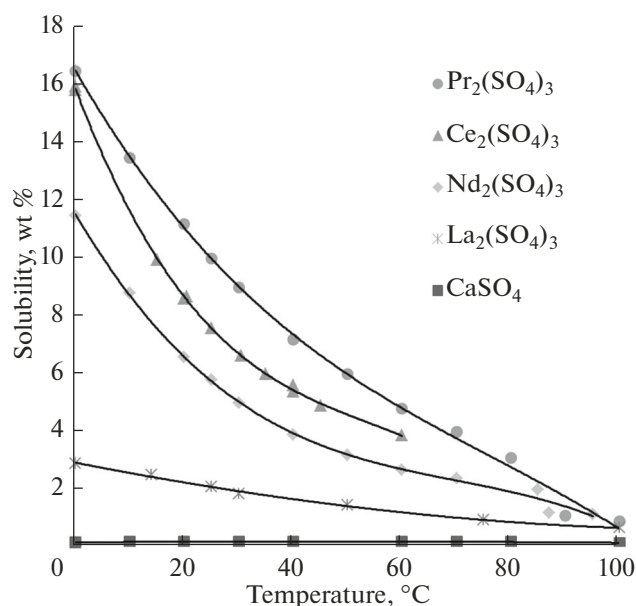


Fig. 2. Solubilities of calcium and REE sulfates in water as a function of temperature.

a low solubility in dilute mineral acids. Due to a decreased solubility of annealed REE oxides in the form of the solid solution based on the CeO_2 structure, almost all of the CaO phase passes into solution due to the formation of readily soluble salt $\text{Ca}(\text{NO}_3)_2$, which provides the oxide concentrate of the cerium-group rare-earth elements.

The separation of a mixture of CaCO_3 and CaO from REE oxides can be performed due to the difference between the specific densities of these compounds. As can be seen from Table 2, the most significant difference between specific densities is observed for CaCO_3 (2.71 g/cm^3) and CaO (3.35 g/cm^3), on the one hand, and La–Nd oxides ($5.96\text{--}7.22 \text{ g/cm}^3$), on the other. For example, in [17] the phases of calcite CaCO_3 and bastnesite LnFCO_3 ($\text{Ln} = \text{Ce, La, Y}$) were successfully separated by centrifugation in a solution of sodium polytungstate with a specific density of $2.70\text{--}2.95 \text{ g/cm}^3$. Heavy liquids, inert to calcium oxides and lanthanides, can be used to separate these compounds [18].

In some cases, the isolation of pure individual REE compounds is not required. The resulting REE oxide concentrate can be directly used to create cerium-containing catalysts [19].

Thus, the performed studies have allowed us to determine the features of the combined thermal decomposition of calcium and rare-earth oxalates not elucidated previously. The presence of Ln_2O_3 contributes to the thermal decomposition of calcium carbonate to form calcium oxide with a decrease in temperature from 883 to 736°C as a result of the expected formation and decomposition of the intermediate phases

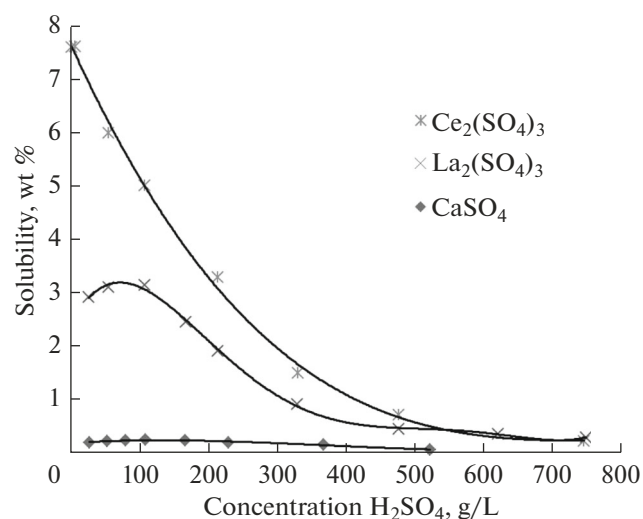


Fig. 3. Solubilities of cerium, lanthanum, and calcium sulfates in solutions of sulfuric acid H_2SO_4 at 25°C .

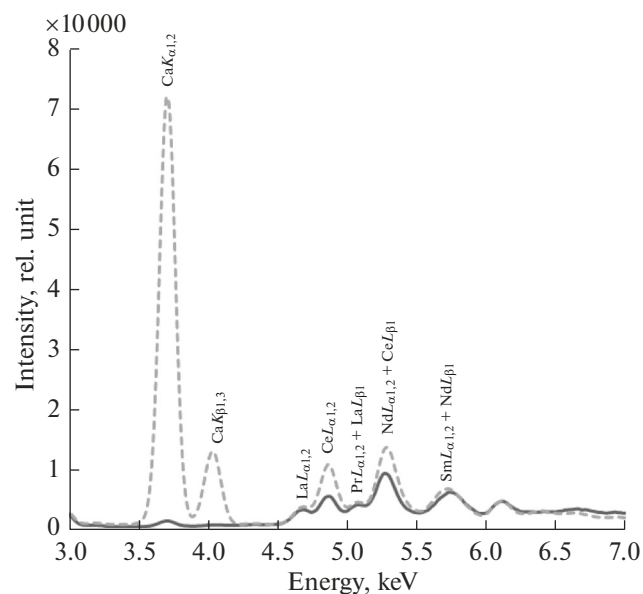


Fig. 4. XRF spectra of the liquid phase (solid line) and solid phase (dashed line) obtained by separating the mixture of CaCO_3 and REE oxides at 20°C .

of rare-earth oxocarbonates (La and Nd). In the temperature range $442\text{--}600^\circ\text{C}$, La_2O_3 , CeO_2 , Pr_6O_{11} , and Nd_2O_3 are formed, which remain individual in the presence of CaCO_3 and form no solid solution of REE oxides.

Possible methods for obtaining REE concentrates have been determined by treating the products formed during the thermal decomposition of calcium and lanthanide oxalates mixture. In the temperature range $450\text{--}600^\circ\text{C}$, CaCO_3 and REE oxide phases are

Table 2. Specific densities of calcium and REE compounds

Compound	Density, g/cm ³	ICDD no.	Compound	Density, g/cm ³	ICDD no.
CaCO ₃ (hexagonal)	2.711	05-0586	CaO (cubic)	3.345	04-0777
La ₂ O ₃ (cubic)	5.956	22-0369	Nd ₂ O ₃ (cubic)	6.590	21-0579
Pr ₆ O ₁₁ (cubic)	6.911	06-0329	CeO ₂ (cubic)	7.216	34-0394

formed with high reactivity. To separate the test compounds, it is expedient to use a significant difference in solubility between calcium and lanthanides sulfates in aqueous solution of H₂SO₄ at 20°C.

It has been found that the separation of CaO and a solid solution of REE oxides based on the CeO₂ structure can be carried out by treating them with dilute HNO₃. At temperatures higher than the total CaCO₃ decomposition temperature (736°C), the solubility of the resulting REE oxide solid solution is significantly reduced; therefore, it seems possible to separate CaO from the insoluble precipitate of the REE oxide solid solution in the form of the readily soluble salt Ca(NO₃)₂.

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