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The thermal transformation from lanthanum hydroxide to lanthanum hydroxide oxide

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Abstract

The thermal transformation from lanthanum hydroxide ($La(OH)_3$) to lanthanum oxide (La_2O_3) results in two successive endothermic effects, caused by a loss of water. Thermal analysis (DTA/TG, DSC), and high-temperature powder X-ray diffraction (HT-XRD) were used to characterize this process. Lanthanum hydroxide oxide (LaOOH) was obtained as temporary product at ∼330 °C. The structure of lanthanum hydroxide oxide was characterized by X-ray powder diffraction methods and subsequent Rietveld refinement. LaOOH crystallizes in the monoclinic space group $P2_1/m$ (no. 11) with the lattice parameters $a = 444.76(9)$ pm, $b = 397.10(7)$ pm, $c = 661.9(1)$ pm, and $\beta = 111.93(1)°$.

The reaction enthalpies of the dehydration process were calculated by DSC to ∼87 kJ mol^{-1} (transformation: $La(OH)_3$ to LaOOH), and to ∼54 kJ mol^{-1} (transformation: LaOOH to La_2O_3). Further, the activation energy $E_A = 76$ kJ mol^{-1} of the transformation lanthanum hydroxide to lanthanum hydroxide oxide was estimated by isothermal TG studies.

Keywords: Lanthanum hydroxide oxide; Structure parameters; Thermal analysis; HT-XRD; Activation energy

1. Introduction

Lanthanum hydroxide and lanthanum oxide are of great research interest because of their prospect as catalytic material [1–4] and application in high-potential oxide ceramics [5]. Lanthanum oxide is an important oxide, because of its magnetic properties. It is used to produce a ceramic superconductor (lanthanum barium copper oxide), which could modify its magnetic properties by inducing of light [6]. Lanthanum copper oxides are important antiferromagnetic materials [7,8]. Furthermore, the subsequent dehydration process of rare earth hydroxides to rare earth oxides results in nanostructures, which are of special interest for catalysis and optoelectronic devices [9].

Only a few experimental thermodynamic and kinetic data of the dehydration of lanthanide hydroxides are described elsewhere [10]. So the aim of the presented research is to study the thermal properties of the transformation from hexagonal lanthanum hydroxide ($La(OH)_3$) to hexagonal lanthanum oxide (La_2O_3) by thermal analysis (DTA/TG, DSC) and high-temperature powder X-ray diffraction (HT-XRD).

The experimental results should be useful to understand the mechanism of the dehydration process, which can generally be described for rare earth hydroxides by the two equations [11–13]:

$$Ln(OH)_3 \rightarrow LnOOH + H_2O$$

$$2LnOOH \rightarrow Ln_2O_3 + H_2O$$

The expected temporary formed lanthanum hydroxide oxide should be prepared and characterized, because of its research interest in material science.

Kinetic data (isothermal TG studies) as well as reaction enthalpies (DSC) of the dehydration process should be determined.

2. Experimental

Lanthanum hydroxide (99.95 wt.%, Alfa Aesar) was used for the study of dehydration. DTA/TG analysis were carried

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out in corundum crucibles (heating rate, 5 K min^{-1}) by using a thermobalance L 81 II (Linseis, Germany). DSC experiments (aluminum pans; heating rate, 5 K min^{-1}) were done in a differential scanning calorimeter DSC 204 F1 Phoenix® (Netzsch Gerätebau, Germany).

The powder X-ray diffraction was conducted on a Siemens D5000 diffractometer using Cu Kα_1 radiation in a 2θ range of 10–85°. Rietveld structure refinement was done by using the program GSAS [14].

High-temperature powder X-ray diffraction results were obtained by using a Stoe Stadi P diffractometer (Mo Kα_1 radiation) with image plate detector. The samples were filled in 0.3 mm fused silica capillaries and heated up from 25 to 800 °C in temperature steps of 50 °C.

Isothermal TG investigations (corundum crucible; mass content, ~40 mg) were performed to obtain information on the kinetics of the dehydration process. The samples were heated with 5 K min^{-1} to a temperature of 20 °C below the temperature, were the isothermal dehydration starts. Then the heating rate was lowered to 1 K min^{-1} until the desired temperature was reached. All samples are measured for 600 min. Scanning electron microscopy (Hitachi S-2700, Japan) was used to identify particle geometry as well as microstructures of the samples.

3. Results and discussion

3.1. Thermogravimetry (TG) and differential thermal analysis (DTA)

TG studies of the thermal transformation of lanthanum hydroxide indicate two steps of mass loss. The experimental mass losses of ~9.3 mass% ($La(OH)_3$ to LaOOH) and ~4.1 mass% (LaOOH to La_2O_3) correspond to the theoretical values (9.5 and 4.5 mass%, respectively). DTA measurements resulted in two endothermic effects (Fig. 1).

The expected lanthanum hydroxide oxide (LaOOH) is formed at ~330 °C. A total dehydration is observed at an increase of temperature to ~490 °C, and lanthanum oxide (La_2O_3) is produced, respectively [15].

3.2. High-temperature X-ray diffraction (HT-XRD)

The result of the high-temperature X-ray diffraction measurement ($\Delta T = 50$ K) is shown in Fig. 2. The reflections of lanthanum hydroxide disappeared at ~350 °C and instead the yet non-characterized reflections were observed. Further, the reflections of well-characterized lanthanum oxide proceeded

Table 1
Structure parameters and selected details of the refinement of lanthanum hydroxide oxide (LaOOH)

Formula	LaOOH
Formula weight	172.925
Crystal system	Monoclinic
Space group	$P2_1/m$ (no. 11)
Radiation, λ (pm)	Cu Kα_1 (154.06)
Lattice parameter	
a (pm)	444.76(9)
b (pm)	397.10(7)
c (pm)	661.9(1)
β (°)	111.93(1)
Volume (10^6 pm^3)	108.44(4)
Z	2
ρ_c (g cm^{-3})	5.295
Profile range	$5° \leq 2\theta \leq 80°$
Number of data points	4021
Number of reflections	82
Atomic parameters	8
Profile parameters	20
wR_p	0.046
R_p	0.028
R_F	0.064

R_p, wR_p, and R_F refer to the Rietveld criteria of fit for profile, weighted profile, and structure factor, respectively, defined in GSAS [14].

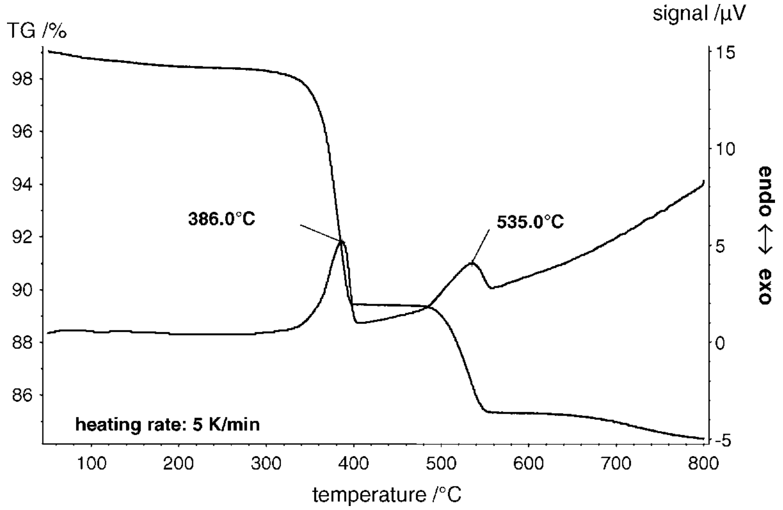

Fig. 1. DTA/TG curves of $La(OH)_3$.

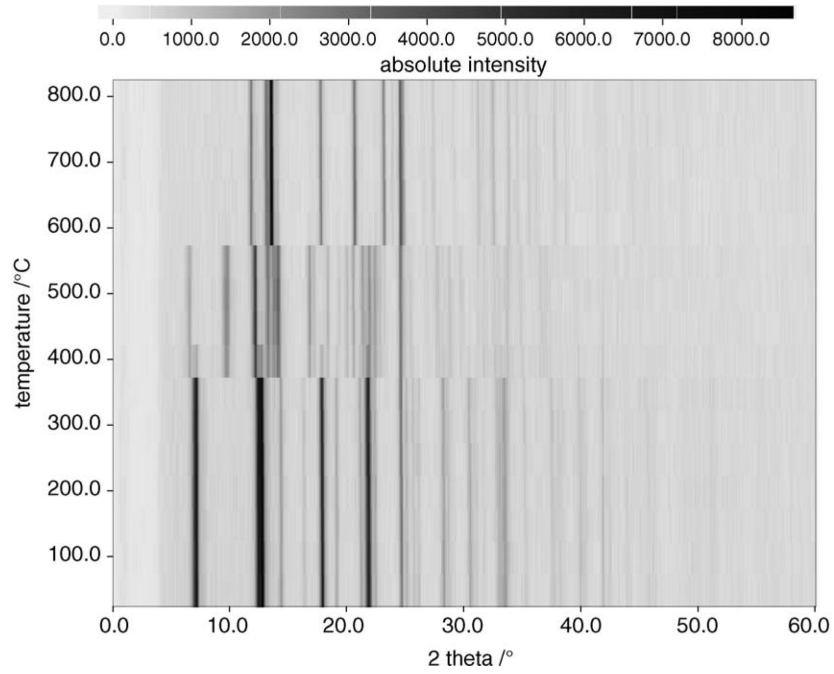

Fig. 2. HT-XRD measurement of $La(OH)_3$.

at ~550 °C. The HT-XRD results are consistent to the results observed by thermal analysis.

3.3. *X-ray diffraction (XRD)*

The non-characterized temporary product of the lanthanum hydroxide dehydration process was specially prepared in the thermobalance at 400 °C.

The product was identified as lanthanum hydroxide oxide by powder X-ray diffraction and subsequent Rietveld refinement [16]. Crystal structure data were determined. They are presented in Table 1. The structure parameters correspond to reported data obtained by Debye–Scherrer diagrams [17].

Lanthanum hydroxide oxide crystallizes in a monoclinic crystal structure with space group $P2_1/m$ (no. 11). In comparison with lanthanum hydroxide (space group $P6_3/m$), an increase of coordination number (CN) of the La^{3+} ion from CN = 6 (first sphere) to CN = 7 is observed.

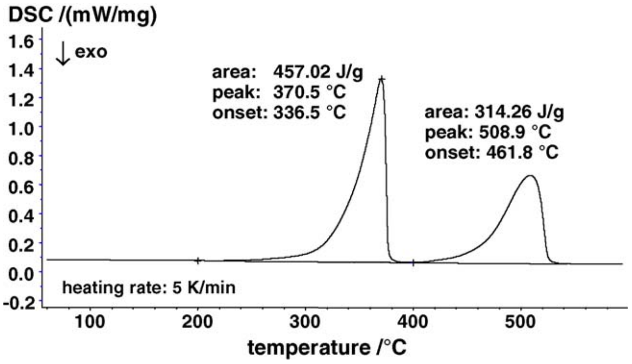

Fig. 3. DSC plot of $La(OH)_3$; heating rate, 5 K/min.

3.4. *Differential scanning calorimetry (DSC)*

The reaction enthalpy $\Delta_R H$ of the transformation of lanthanum hydroxide to lanthanum oxide could be determined by DSC measurements. The DSC curve is presented in Fig. 3.

The reaction enthalpies of the dehydration process amount to ~87 kJ mol^{-1} (transformation: $La(OH)_3$ to LaOOH), and to ~54 kJ mol^{-1} (transformation: LaOOH to La_2O_3).

3.5. *Thermogravimetry with isothermal conditions*

Isothermal TG investigations were performed to obtain information on the kinetics of the dehydration process of lanthanum hydroxide to lanthanum hydroxide oxide. Results are presented in Fig. 4.

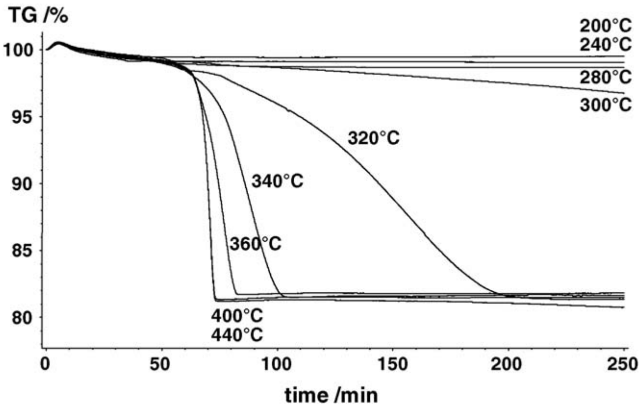

Fig. 4. Time dependent isothermal mass loss of lanthanum hydroxide.

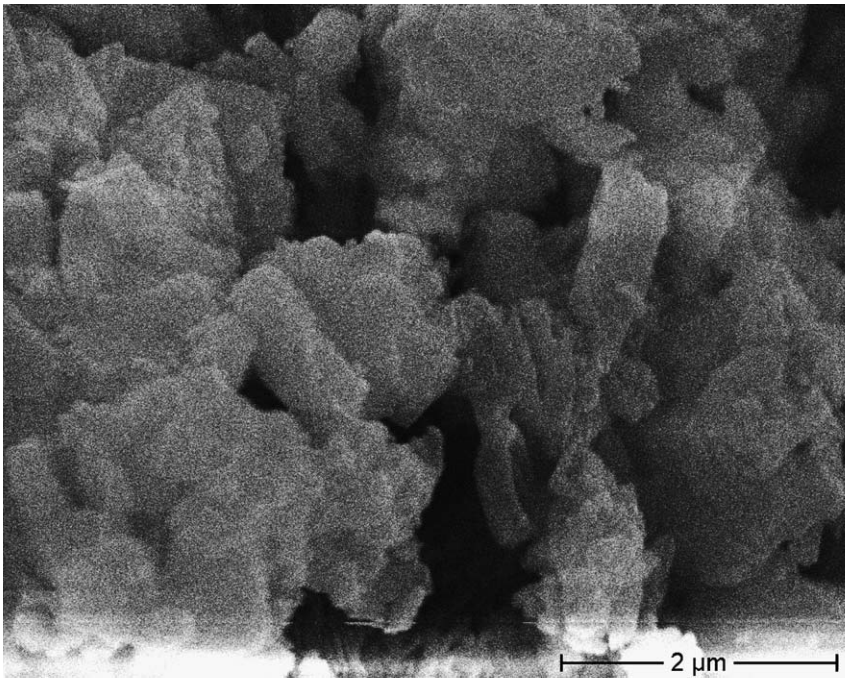

Fig. 5. REM image of $La(OH)_3$ (magnification, 20,000×).

The mass decrease during the induction period (∼70 min) results from loss of surface water. As long as the temperatures are below the dehydration temperature of lanthanum hydroxide at ∼330 °C, no further mass change was observed. The dehydration proceeds continuously over a period of several hours at 300 °C. Above 320 °C, shorter times are sufficient for completion of the dehydration process.

The degree of transformation α can be determined by mass loss of lanthanum hydroxide. The reaction rate k of the dehydration process was calculated according to the so-called shrinking-core model. For reactions of approximately

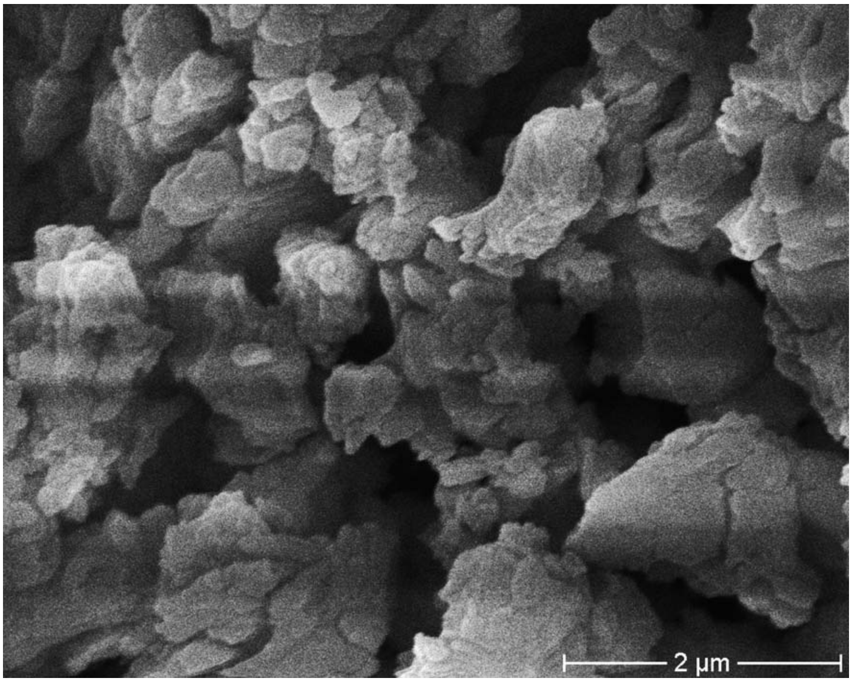

Fig. 6. REM image of prepared LaOOH (magnification, 20,000×).

spherical particles (real geometry is given in Fig. 5), the Jander relationship is used [18]:

$$[1-(1-\alpha)^{1/3}]^2 = \frac{2k}{r^2}t$$

where α is the degree of transformation, k the reaction rate constant, r the particle radius calculated by SEM experiments, and t is the time.

The activation energy is calculated from the corresponding Arrhenius equation:

$$\ln k = \ln A - E_A/RT$$

where A is the Arrhenius constant, E the activation energy, R the universal gas constant, and T is the temperature.

For the thermal transformation of lanthanum hydroxide to lanthanum hydroxide oxide, an activation energy of $E_A = 76\,\text{kJ mol}^{-1}$, was calculated.

3.6. Scanning electron microscopy (SEM)

The variation of surface during the reaction process is shown by SEM experiments. Figs. 5 and 6 show the morphology of lanthanum hydroxide and lanthanum hydroxide oxide, respectively. Crystalline particles of lanthanum hydroxide (diameter, ~1 μm) are observed (Fig. 5). A small decrease of particle size combined with a non-compact surface morphology is detected for the prepared lanthanum hydroxide oxide (Fig. 6).

4. Conclusion

The thermal dehydration of lanthanum hydroxide investigated by DTA/TG studies as well as high-temperature X-ray diffraction confirm the postulated double-step mechanism. Two endothermic effects, caused by a loss of water, are observed. The mechanism corresponds to the mechanism of the dehydrations of $Fe(OH)_3$ and $Al(OH)_3$ [19,20]. The temporary formed lanthanum hydroxide oxide can be prepared by dehydration of lanthanum hydroxide and well-defined by X-ray diffraction. LaOOH crystallizes in a monoclinic crystal structure with the space group $P2_1/m$ (no. 11).

At the same time, differences between the thermal behaviour of lanthanum hydroxide and lanthanide hydroxides $Ln(OH)_3$ (Ln = Nd, Pr, Sm) are observed, respectively. Lanthanide hydroxides suggest indeed a double-step mechanism observed by thermal analysis, however, it is not possible to prepare crystalline lanthanide hydroxide oxides to obtain structure data by XRD [13,15,16].

The activation energy of the dehydration of lanthanum hydroxide is calculated to $76\,\text{kJ mol}^{-1}$. The reaction enthalpies of $87\,\text{kJ mol}^{-1}$ ($La(OH)_3$ to LaOOH) and $54\,\text{kJ mol}^{-1}$ (LaOOH to La_2O_3) correspond to the values of $Al(OH)_3$ ($Al(OH)_3$ to AlOOH, $\sim 55\,\text{kJ mol}^{-1}$; AlOOH to Al_2O_3, $\sim 47\,\text{kJ mol}^{-1}$) [21].

The results suggest the use of lanthanum hydroxide oxide for further research in material science concerning new applications.

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