

Short communication

## Non-isothermal studies of the decomposition course of lanthanum oxalate decahydrate

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### Abstract

The thermal decomposition of lanthanum oxalate hydrate  $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  till  $900^\circ\text{C}$ , in air, is investigated by non-isothermal gravimetry and differential thermal analyses. Intermediates and final solid products were characterized by X-ray diffraction (XRD) and IR-spectroscopy, the results show that  $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  dehydrates in stepwise at  $86\text{--}360^\circ\text{C}$  and decomposes to  $\text{La}_2\text{O}_3$  at  $710^\circ\text{C}$  through different intermediates,  $\text{La}_2(\text{C}_2\text{O}_4)_3$ ,  $\text{La}_2\text{O}(\text{CO}_3)_2$  and  $\text{La}_2\text{O}_2\text{CO}_3$ , that form at  $400$ ,  $425$  and  $470^\circ\text{C}$ , respectively. The final product  $\text{La}_2\text{O}_3$  obtained at  $800^\circ\text{C}$  has a surface area of  $13.4\text{ m}^2/\text{g}$ . The activation energy,  $\Delta E$  of the observed thermal processes is obtained by the non-isothermal method. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** La-oxalate; La-oxide; Decomposition; DTA; TG; IR; XRD;  $S_{\text{BET}}$

### 1. Introduction

The hexagonal [1] structure, lanthanum sesquioxide,  $\text{La}_2\text{O}_3$ , the final decomposition course studied in the present investigation, is the only stable oxide of lanthanum up to  $2050^\circ\text{C}$ .  $\text{La}_2\text{O}_3$  has numerous applications in various industrial and the technological fields. It is an important component of automobile exhaust—gas conversion [2], as a catalyst support in the formation of gas conversion catalyst [3,4], and as a catalyst of oxidative coupling of methane [5–7]. It is also used as a refractory oxide for calcium lights, optical glass [8], and in the formation of ceramics as a core for carbon arc electrodes [8].

The aim of the present study is to characterize the thermal decomposition of  $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  to the onset of  $\text{La}_2\text{O}_3$  by means of thermogravimetry (TG) and differential thermal analysis (DTA). The solid products of the reaction were analyzed by IR-spectroscopy and X-ray diffractometry. The surface area ( $S_{\text{BET}}$ ) was measured by  $\text{N}_2$ -adsorption isotherm. The activation energy,  $\Delta E$  of the observed thermal processes is obtained by the non-isothermal method of thermoanalytical data analysis.

### 2. Experimental

#### 2.1. Materials

Lanthanum acetate tetrahydrate ( $\text{LaAc}$ ,  $\text{La}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$ ) (99.9% pure from Aldrich, USA),

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ammonium oxalate ((NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), ammonium hydroxide (NH<sub>4</sub>OH) and glacial acetic acid were used for the preparation of oxalate.

## 2.2. Preparation of oxalate

Oxalates of La(III) from LaAc was prepared by dropwise addition of a hot 4% ammonium oxalate solution to a stirred hot solution of acetates after their dissolution in glacial acetic acid then neutralized to pH = 7 with (1:1) NH<sub>4</sub>OH. The precipitates formed were left to stand at room temperature for 1 h, filtered off, washed with a diluted ammonium oxalate solution and finally dried at 80 °C to a constant weight.

The calcination products were obtained by heating at various temperatures 200–800 °C, in a static atmosphere of air for 1 h. The calcination temperatures were chosen on basis of the thermal analysis results. The calcination products indicate throughout the text by the oxalate designation and the temperature applied, thus LaOx-800 indicates the calcination product at 800 °C. The abbreviation WL stands for weight loss.

## 2.3. Thermal analysis

TG and DTA of lanthanum oxalate were carried out on heating at various rates ( $\theta = 5, 10, 20, 30$  °C/min) up to 900 °C in a dynamic atmosphere of air (20 ml/min), using a 7-series thermal analysis model Perkin-Elmer Analyzer. Ten to fifteen milligrams portions of the test sample were used for the TG measurements, and highly sintered  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was the thermally inert reference for the DTA. Shifts experienced by the DTA peak temperature ( $T_{\max}$ ) as a function of the heating rate ( $\theta$ ) were implemented to calculate the activation energy,  $\Delta E$  (kJ/mol) corresponding to each of the thermal events monitored, according to the following equation [9]:

$$\Delta E = -\frac{R}{bd \log \theta d} \left( \frac{1}{T_{\max}} \right)$$

where  $R$  is the gas constant (=8.314 kJ/mol) and  $b$  is a unitless constant (=0.457).

## 2.4. Infrared spectroscopy

IR-spectra were obtained at a resolution of 4 cm<sup>-1</sup>, over the range 4000–400 cm<sup>-1</sup>, using a model FT-IR-

410 JASCO (Japan). IR-spectra of LaOx and its solid calcination products were obtained from thin (>20 mg/m<sup>2</sup>), lightly loaded (<1%) KBr-supported discs.

## 2.5. X-ray diffraction

X-ray diffraction (XRD) powder patterns were obtained with JSX-60P JEOL diffractometer (Japan). The X-ray generator is equipped with Ni-filter and generates a beam of Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). The operational settings for all the XRD scans are voltage: 40 kV, current: 30 mA, range: 4–60° ( $2\theta$ ), scanning speed: 8°/min, slit width: 0.02°. For identification purpose, the relative intensities ( $I/I^0$ ) and the  $d$ -spacing (Å) are compared to standard diffraction patterns in the ASTM powder diffraction file [10].

## 2.6. N<sub>2</sub>-adsorption measurements

N<sub>2</sub> sorption isotherms were determined volumetrically at –195 °C using a micro apparatus based on the design, which was described by Lippens et al. [11]. Test samples were outgassed at 220 °C for 6 h while evacuation at 10<sup>-5</sup> Torr was performed. The reproducibility of the isotherm measurements was better than 97%.

# 3. Results and discussion

## 3.1. Characterization of the decomposition course

TG and DTA curves (Fig. 1) monitor 12 WL events (designated I–XIII) in the decomposition course of LaOx·10H<sub>2</sub>O, only three of these events are exothermic (event IX, X and XI), whereas the others are endothermic. The WL effected via the first eight events (I–VIII) accounts for a stepwise dehydration of LaOx·10H<sub>2</sub>O, in which event I and II (WL = 2.7%,  $T_{\max} = 86$  °C) and (WL = 5.2%,  $T_{\max} = 110$  °C), respectively, each involves the elimination of 1 mol of water, and thermal event III (WL = 9.9%,  $T_{\max} = 130$  °C) leads to the removal of another 2 mol of H<sub>2</sub>O. Events (IV–VII) (WL = 12.5, 15, 17.5, 20% ) and ( $T_{\max} = 155, 174, 195, 225$  °C), respectively leads to the removal of another 4 mol of water. The corresponding activation energy values

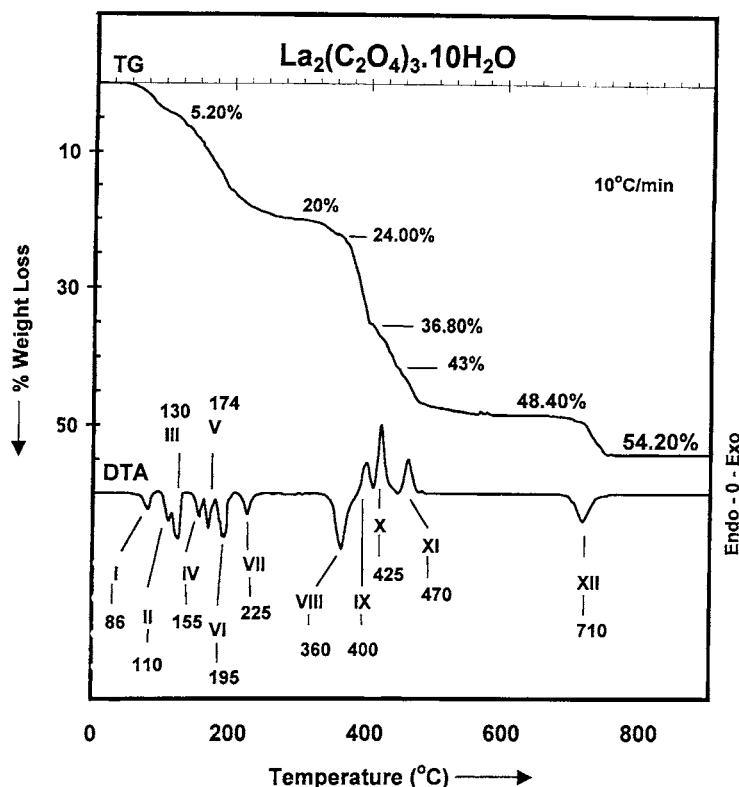


Fig. 1. TG and DTA curves recorded for LaOx at the heating rates indicated, in a dynamic (20 ml/min) atmosphere of air.

(Table 1) are well within the range (<60 kJ/mol) encountered for removal of weakly bound water of crystallization from analogous compounds [12]. The dihydrate thus formed, LaOx·2H<sub>2</sub>O, persists upon

Table 1  
Thermal processes; temperature (°C), composition and activation energy ( $\Delta E$ , kJ/mol) proposed in each process for LaOx·10H<sub>2</sub>O

Process	Temperature (°C)	Composition	$\Delta E$ (kJ/mol)
I	86	La <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	41
II	110	La <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·8H <sub>2</sub> O	43
III	130	La <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	94
IV	155	La <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	43
V	174	La <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	51
VI	195	La <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	54
VII	225	La <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	60
VIII	360	La <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>	108
IX	400	La <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	127
X	425	La <sub>2</sub> O(CO <sub>3</sub> ) <sub>2</sub>	123
XI	470	La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	145
XII	710	La <sub>2</sub> O <sub>3</sub>	254

further heating to 300 °C at which event VIII ( $T_{\max} = 360$  °C) commences to operate. The total WL effected at 380 °C, (ca. 24%) accounts for the elimination of the remaining 2H<sub>2</sub>O and, consequently, for the formation of the unhydrous lanthanum oxalate. The IR-spectrum of the solid phase LaOx-200 (Fig. 2) bears a great deal of similarity to that of unheated La<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O because both show absorption bands arising from oxalate anions (at 1750–640 cm<sup>-1</sup>) and water of hydration (at 3440 and 1640 cm<sup>-1</sup>) [12,13]. However, the corresponding XRD pattern (Fig. 3) indicates that the products are amorphous and so water of hydration is very important for the coherency of LaOx crystal [14].

The LaOx-300 solid phase IR-spectrum (Fig. 2) shows that the C<sub>2</sub>O<sub>4</sub><sup>2-</sup> species are weakened and different band structure including absorptions at 2350 cm<sup>-1</sup> and between 1800 and 400 cm<sup>-1</sup> which is similar in shape and position to characteristic absorptions CO<sub>3</sub><sup>2-</sup> [12].

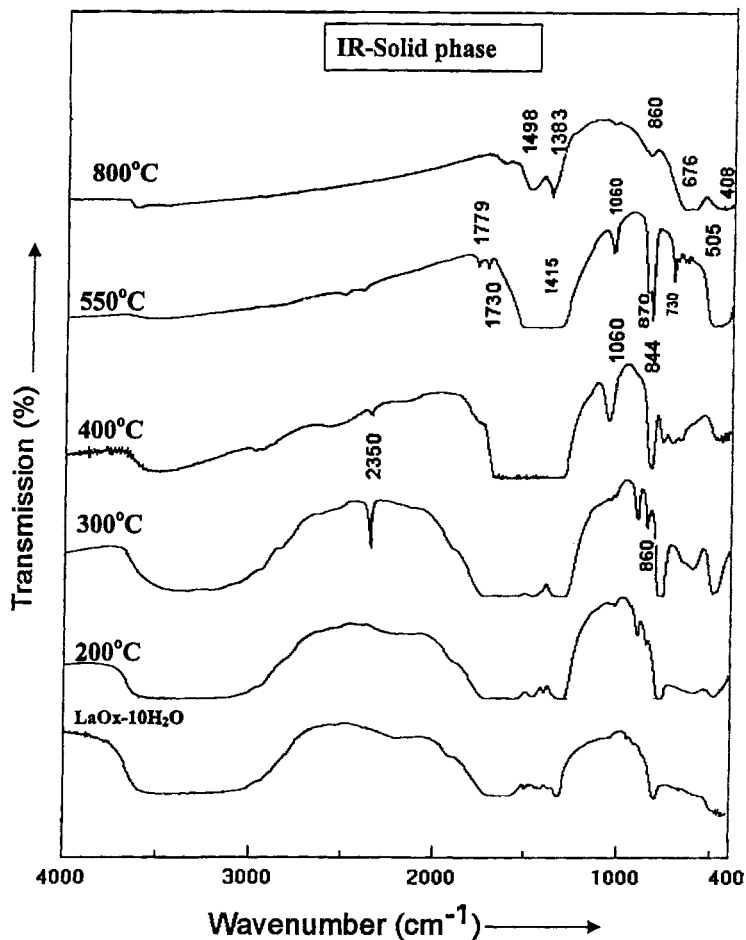
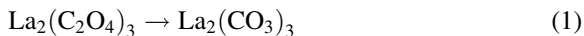


Fig. 2. IR-solid phase spectra for LaOx and its 1 h calcination products at the temperatures indicated.

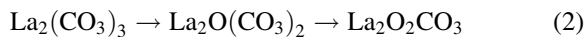
Upon further heating event VIII is overlapped by two rapid exothermic WL processes (event IX,  $T_{\max} = 400\text{ }^{\circ}\text{C}$  and event X,  $T_{\max} = 425\text{ }^{\circ}\text{C}$ ). The WL for IX is 36.9% which is close to that theoretically calculated (36.6%) for the formation of  $\text{La}_2(\text{CO}_3)_2$ , as follows:



The IR-spectrum of LaOx-400 shows relieved of the  $\delta\text{HOH}$  absorption of hydration of water [13], which is strong, broad absorption observed in the spectrum of both the parent, LaOx-200 and LaOx-300 between 1600 and 1750  $\text{cm}^{-1}$ . The fundamental modes of vibration of the  $\text{CO}_3^{2-}$  species between 1800 and 400  $\text{cm}^{-1}$  are weakened and different band structure begin to appear between 1600 and 1300  $\text{cm}^{-1}$  which is

similar in shape and position to characteristic absorptions of oxycarbonates [13]. XRD pattern for LaOx-400 (Fig. 3), reveals that the  $\text{La}_2(\text{CO}_3)_3$  product inferred from the TG and IR-data is amorphous.

The WL for event X is 42.5% (expected WL is 42.7%) accounts for the conversion of  $\text{La}_2(\text{CO}_3)_3$  to  $\text{La}_2\text{O}(\text{CO}_3)_2$  which converts immediately to  $\text{La}_2\text{O}_2\text{CO}_3$  (thermal event XI, WL = 48.4%,  $T_{\max} = 470\text{ }^{\circ}\text{C}$ ) (Fig. 1), as follows:



Events IX, X and XI must have overlapped between 420 and 550  $^{\circ}\text{C}$ . The similarity of the activation energy values (Table 1) for process IX, X and XI justifies their overlapping.

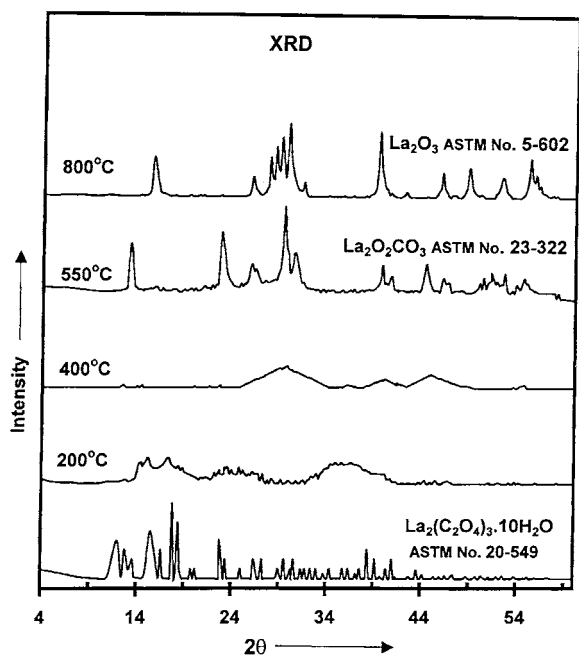


Fig. 3. X-ray powder diffractograms for LaOx and its 1 h calcination products at the temperatures indicated.

The IR-spectrum (Fig. 2) and XRD patterns (Fig. 3) support reaction (2). The IR-spectrum LaOx-550 displays strong absorptions between  $1600$  and  $1300\text{ cm}^{-1}$  and also at  $1060$  and  $870\text{ cm}^{-1}$  assignable to oxycarbonate species [13]. The absorption appearing at  $730\text{--}500\text{ cm}^{-1}$  are related to La–O vibrational lattice mode [15].

The corresponding XRD pattern for LaOx-550 shows the pattern for crystalline  $\text{La}_2\text{O}_2\text{CO}_3$  (ASTM no. 23-320).

At  $<600\text{ }^\circ\text{C}$ , process XI slows down ending up with a weight invariant behavior at  $670\text{ }^\circ\text{C}$ . Process XII takes place endothermally at  $T_{\text{max}} = 710\text{ }^\circ\text{C}$ . The maximum WL determined ( $54.2\%$ ) agrees well with that expected ( $54.8\%$ ) to accompany the overall conversion of  $\text{LaOx}\cdot 10\text{H}_2\text{O}$  to  $\text{La}_2\text{O}_3$ , i.e. process XII include the following pathway:

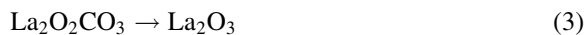


Table 1 indicates that event XII has the highest activation energy ( $\Delta E = 254\text{ kJ/mol}$ ) in the overall decomposition course of  $\text{LaOx}\cdot 10\text{H}_2\text{O}$ , a fact that justifies its lowest kinetics.

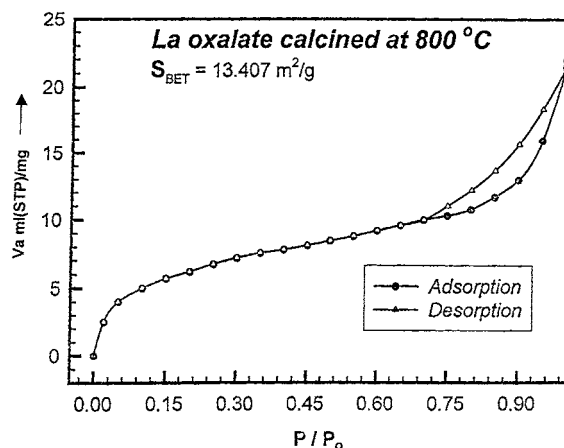


Fig. 4.  $\text{N}_2$ -adsorption isotherm obtained at  $-195\text{ }^\circ\text{C}$  (using BET Method) for LaOx-800.

The IR-spectrum of LaOx-800 (Fig. 2), shows no detectable absorptions due to oxycarbonate species. The absorptions below  $700\text{ cm}^{-1}$  are related to lattice vibration modes of  $\text{La}_2\text{O}_3$  [15]. The weak bands around  $1600$ ,  $1500$  and  $1380\text{ cm}^{-1}$  are most probably due to surface contamination by carbonate and moisture since it is known that  $\text{La}_2\text{O}_3$  is a basic oxide [16].

In support, the XRD pattern of LaOx-800 detect a crystalline phase of  $\text{La}_2\text{O}_3$  (ASTM no. 5-602).

### 3.2. Nitrogen sorption and surface area measurement of $\text{La}_2\text{O}_3$

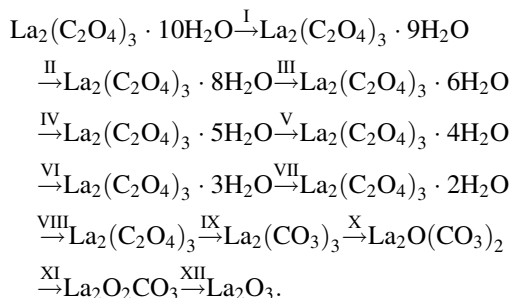
The  $\text{N}_2$ -adsorption isotherm of LaOx-800 is shown in Fig. 4. The isotherm generally belongs to type IV of BET classification [17]. The desorption isotherm closed at  $P/P^0 > 0.4$ , which give indication the hysteresis loop is nearly of type H3 [17]. The loop suggested that the surface pores are of slit-shaped or interplating [18]. The  $S_{\text{BET}}$  value determined was  $13.4\text{ m}^2/\text{g}$ .

## 4. Conclusion

The results of the present studies allow the following conclusions to be drawn:

1. The thermal decomposition course of hydrated lanthanum oxalate may include the following path

ways:



- The lower hydrate oxalate (dihydrate) is thermally stable but the anhydrous oxalate is unstable and the water of hydration is responsible of the crystal coherency of LaOx.
- Lanthanum carbonates  $\text{La}_2(\text{CO}_3)_3$  (amorphous),  $\text{La}_2\text{O}(\text{CO}_3)_2$  (amorphous),  $\text{La}_2\text{O}_2\text{CO}_3$  (crystalline), were formed as intermediates during the decomposition of lanthanum oxalate hydrate but with no region of stability.
- A crystalline phase of  $\text{La}_2\text{O}_3$  were detectable as the final decomposition product of  $\text{La}_2(\text{C}_2\text{O}_4)_3$ .
- $\text{La}_2\text{O}_3$  obtained at  $800^\circ\text{C}$  has a surface area of  $13.4\text{ m}^2/\text{g}$ .

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