Thermochimica Acta, 137 (1989) 319–330
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF THE HYDRATED BASIC CARBONATES OF LANTHANIDES AND YTTRIUM

L. MOSCARDINI D'ASSUNÇÃO

Faculdade de Ciências Agrárias, Fundação de Ensino e Tecnologia, Alfenas, MG (Brazil)

I. GIOLITO *

Instituto de Química, Universidade de São Paulo, São Paulo, SP, CP 20.780,
CEP 01498 (Brazil)

M. IONASHIRO

Instituto de Química, Universidade Estadual Paulista, Araraquara, SP (Brazil)

(Received 18 February 1988)

ABSTRACT

Thermogravimetry, differential thermal analysis, differential scanning calorimetry, IR absorption spectroscopy, X-ray diffraction, and other methods of analysis have been used in the characterization and study of the thermal decomposition of the basic carbonate hydrates of lanthanides and yttrium. These compounds were obtained by precipitation from homogeneous solutions via the hydrolysis of urea, without the addition of an auxiliary anion. The results show that the TG and DTA curves are characteristic for each compound. The results also permit suggestions concerning the compositions and mechanisms of thermal decomposition of these compounds.

INTRODUCTION

Several methods for the preparation of lanthanide and yttrium carbonates, as well as studies on the thermal behaviour of these compounds, have been carried out [1–9]. The results of these studies show some disagreement, especially regarding mechanisms of thermal decomposition.

Only one reference was found to the preparation and characterization of lanthanum and neodymium carbonates obtained from homogenous solution using urea [3]. No references were found concerning the preparation, characterization and application of TG, DTA and DSC methods in the study of the remaining lanthanides and yttrium carbonates obtained in this way.

---

* Author to whom correspondence should be addressed.

0040-6031/89/$03.50

EXPERIMENTAL

Cesium(III) basic carbonate was prepared from cesium(III) chloride (99.5% pure). The other compounds were prepared from the corresponding lanthanide and yttrium oxides (99.9% pure).

The basic carbonates were prepared by dissolving 3.0 g of lanthanide ion, as the oxide, in hot concentrated hydrochloric acid. In the case of praseodymium and terbium oxides total dissolution was obtained after the addition of a few drops of 30% hydrogen peroxide. The solutions were evaporated nearly to dryness. The crystals formed were redissolved in distilled water and again evaporated to near dryness until the elimination of the excess acid had occurred. The chloride solutions were transferred to Erlenmeyer flasks equipped with condensers and the volume was made up to 1.2 l with distilled water. After the addition of 60 g of urea the solutions were heated slowly up to ebullition. For quantitative precipitation the solutions were boiled for 2 h and then left standing for 24 h.

The very dense precipitates were washed by decantation with 0.5 l portions of distilled water until complete elimination of the chloride ion in the decanted liquid (negative test with silver nitrate solution) had taken place. The compounds were filtered through sintered glass crucibles and kept in a desiccator over anhydrous calcium chloride until a constant weight was attained.

Lanthanide and yttrium ions were determined by the usual oxalate–oxide method, carbon and hydrogen by microanalytical procedures using a Perkin-Elmer 240 Elemental Analyser. The total amounts of carbonate and hydroxyl ions were determined by back-titration alkalimetry. The total number of equivalents obtained in the titrations was subtracted from the number of equivalents of carbonate obtained by elemental analysis, thus giving the number of equivalents of the hydroxyl ions present in each compound. Water of crystallization contents were determined through TG curves by considering the loss of mass up to 200 ° C. Use of the Karl Fischer method did not give satisfactory results.

The solid state IR absorption spectra were obtained in a Perkin-Elmer 180 IR Spectrophotometer using Fluorolube (4.000–1.400 cm^{-1}) and Nujol (1.400–400 cm^{-1}) mulls between CsI plates.

The X-ray powder diffraction patterns were obtained in a Philips Norelco Diffractometer using Cu $K\alpha$ radiation.

The DSC curves were obtained using a Perkin-Elmer DSC-1B, with a nitrogen flux of 60 cm^3 min^{-1}, heating rate 10 ° C min^{-1} and sensitivity 16 m cal. For standardization 7.80 mg of indium was used. The average mass of the samples was about 17 mg.

The TG curves were obtained using a Deltatherm thermobalance model D-4000-16 equipped with a RH Cahn Electrobalance. A Pt/Pt–Rh 13% thermocouple was used to measure the furnace temperature. Samples of about 24 mg were placed in a 0.4 ml platinum crucible and heated at a rate of 5.2 °C min^{-1} inside a ceramic hang-down tube in a static air atmosphere at ambient pressure.

The DTA curves were obtained using a four-channel Deltatherm D-2000-16 DTA module. Pt/Pt–Rh 13% differential thermocouples and a block temperature thermocouple were used to measure the temperature. α-alumina, heated at 1200 °C prior to the experiment, was used as the reference material. The samples were diluted to 20% w/w with α-alumina and diluted samples of about 500 mg together with the reference material were tightly and homogeneously packed into the cylindrical holes of the Inconel block of the specimen-holder assembly. The heating rate was 10.0 °C min^{-1} under a static air atmosphere at ambient pressure. Since the DTA curve obtained with the basic carbonate of lutetium (diluted to 20%) was a straight line, apparently indicating the non-occurrence of thermal events, this run was repeated at 50% dilution (see Fig. 4, next section).

RESULTS AND DISCUSSION

The preparation of these compounds, involving the following conditions: ebullition, pH > 6, a low concentration of CO_2 owing to the slow hydrolysis of urea, and prolonged contact of the compounds with their mother liquors, seems to favour the formation of basic carbonates [1,3–5].

Table 1 presents the analytical and thermoanalytical (TG) data of the compounds prepared having composition very nearly represented by the formula $Ln_2(OH)_2(CO_3)_2 \cdot nH_2O$. The results show no evidence of increasing of the molar ratio compound : hydroxyl ion with increasing atomic number of the lanthanide, as already reported [1,6].

The IR spectra of the compounds prepared could be easily divided in two groups, the first formed by the basic carbonates of La, Ce, Pr, Nd, Sm and Gd and the second formed by those of the rest of the lanthanides and yttrium.

Fig. 1 shows the solid state IR absorption spectra between 4000–1400 cm^{-1} of the Gd and Tm basic carbonates in a Fluorolube mull, and Fig. 2 the spectra of the same compounds between 1400–400 cm^{-1} in a Nujol mull. The splitting of the absorption band at 1400 cm^{-1} and the number of bands appearing between 1100 and 690 cm^{-1} are a strong indication of the formation of basic carbonates [10–13]. The bands at 3400 and 1075 cm^{-1} are usually attributed to the stretching and bending modes, respectively, of the hydroxyl group, but the presence of these two bands is not sufficient to prove the presence of OH^- ions because these features also appear with water. The difficulty in attributing these two bands to the OH^- ion is due to the presence of the shoulder at 1600 cm^{-1}, which indicates the presence of water in the compounds. Furthermore, the sharper band at a higher frequency

TABLE 1

Analytical and thermoanalytical (TG) results

Compound	Analytical results								
	Lanthanide (%)		Carbonate (%)		Hydroxyl (%)		Water (%)		Experimental ratio
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Ln : OH : CO_3 : H_2O
$La_2(OH)_2(CO_3)_2 \cdot H_2O$	61.75	61.75	26.68	26.31	7.56	7.74	4.05	4.10	2 : 2.05 : 1.97 : 1.02
$Ce_2(OH)_2(CO_3)_2 \cdot H_2O$	61.96	62.40	26.54	26.46	7.52	7.49	3.98	3.96	2 : 1.98 : 1.98 : 0.99
$Pr_2(OH)_2(CO_3)_2 \cdot H_2O$	62.09	62.55	26.44	26.72	7.50	7.48	3.97	3.96	2 : 1.98 : 2.01 : 0.99
$Nd_2(OH)_2(CO_3)_2 \cdot 2H_2O$	60.28	60.77	25.08	24.96	7.11	7.06	7.53	7.49	2 : 1.97 : 1.97 : 1.97
$Sm_2(OH)_2(CO_3)_2 \cdot H_2O$	63.61	64.11	25.39	24.51	7.20	6.67	3.81	3.53	2 : 1.84 : 1.92 : 0.92
$Eu_2(OH)_2(CO_3)_2 \cdot 2H_2O$	59.36	59.53	23.44	23.12	6.64	6.40	10.55	10.17	2 : 1.90 : 1.97 : 2.88
$Gd_2(OH)_2(CO_3)_2 \cdot H_2O$	64.64	64.73	24.67	24.62	6.99	6.48	3.70	3.43	2 : 1.85 : 1.99 : 0.92
$Tb_2(OH)_2(CO_3)_2 \cdot 2H_2O$	62.58	62.02	23.62	23.84	6.70	6.75	7.10	7.15	2 : 2.02 : 2.04 : 2.03
$Dy_2(OH)_2(CO_3)_2 \cdot 2H_2O$	63.10	63.15	23.30	23.90	6.60	6.30	7.00	6.68	2 : 1.91 : 2.05 : 1.91
$Ho_2(OH)_2(CO_3)_2 \cdot 2H_2O$	63.44	63.70	23.08	22.29	6.54	6.73	6.93	7.12	2 : 2.05 : 1.92 : 2.05
$Er_2(OH)_2(CO_3)_2 \cdot 2H_2O$	63.77	62.23	22.88	21.28	6.48	6.45	6.87	6.83	2 : 2.01 : 1.88 : 2.01
$Tm_2(OH)_2(CO_3)_2 \cdot 2H_2O$	64.00	64.39	22.73	22.32	6.44	6.49	6.83	6.88	2 : 2.00 : 1.95 : 2.00
$Yb_2(OH)_2(CO_3)_2 \cdot 2H_2O$	64.55	65.50	22.38	21.45	6.35	6.10	6.72	6.46	2 : 1.89 : 1.89 : 1.89
$Lu_2(OH)_2(CO_3)_2 \cdot 2H_2O$	64.80	62.21	22.22	21.27	6.30	6.43	6.67	6.81	2 : 2.03 : 1.90 : 2.03
$Y_2(OH)_2(CO_3)_2 \cdot 2H_2O$	48.33	47.95	32.62	33.21	9.25	9.27	9.80	9.82	2 : 2.02 : 2.05 : 2.02

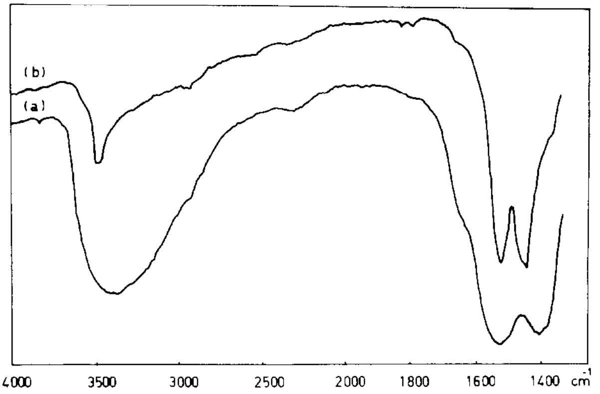

Fig. 1. Infrared absorption spectra between 4000 and 1400 cm^{-1} of the basic carbonates of (a) Gd and (b) Tm in a Fluorolube mull between CsI plates.

(3400 cm^{-1}) is a strong indication that the water is more strongly bonded in the compounds of the first group (basic carbonates of La, Ce, Pr, Nd, Sm and Gd).

The X-ray powder diffraction data (Table 2) show that only the La, Ce, Pr, Nd, Sm and Gd compounds tend towards a crystalline structure with evidence of the formation of isomorphous series. The diffraction patterns of the rest of the lanthanide and yttrium compounds indicated amorphous structures.

The TG curves of the prepared compounds are shown in Fig. 3. Calculations based on the mass losses observed in these curves are in good agreement with the information obtained through the IR spectra, thus supporting the supposition of the formation of basic carbonate hydrates.

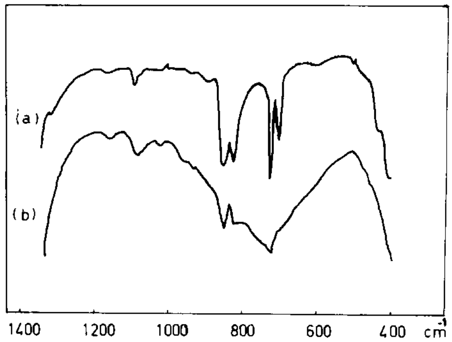

Fig. 2. Infrared absorption spectra between 1400 and 400 cm^{-1} of the basic carbonates of (a) Gd and (b) Tm in a Nujol mull between CsI plates.

TABLE 2

X-Ray powder diffraction data of the basic carbonates $Ln_2(OH)_2(CO_3)_2 \cdot nH_2O$ of the first group

La		Ce		Pr		Nd		Sm		Gd	
I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)
5.1	5.53	5.8	5.47	6.2	5.43	3.9	5.40	2.1	5.37	5.1	5.37
9.1	4.30	3.4	4.27	3.9	4.29	10	4.23	10	4.19	10	4.17
9.3	3.68	6.1	3.62	5.1	3.67	7.1	3.63	5.2	3.60	8.9	3.60
10	2.96	10	3.34	10	3.32	3.0	3.29	1.8	3.24	5.0	3.23
–	–	8.6	2.92	5.1	2.92	5.1	2.90	–	–	1.3	2.90
4.6	2.65	2.5	2.64	1.6	2.64	3.9	2.61	1.8	2.60	2.7	2.60
2.2	2.44	1.4	2.42	1.6	2.41	1.1	2.42	2.4	2.45	1.7	2.43
6.2	2.35	9.5	2.33	8.2	2.32	6.5	2.31	3.2	2.31	1.5	2.35
1.8	2.14	1.1	2.11	1.3	2.10	1.4	2.11	1.3	2.11	1.6	2.10
1.7	2.06	1.2	2.04	0.8	2.03	4.3	2.03	3.1	2.03	1.4	2.04
3.2	2.02	2.1	2.00	1.4	1.99	3.0	1.98	–	–	–	–
2.7	1.96	3.1	1.94	2.7	1.93	1.4	1.92	2.1	1.96	2.8	1.94
3.3	1.86	3.6	1.85	3.6	1.84	1.8	1.83	–	–	2.4	1.87

The reactions occurring during the thermal decomposition of the basic carbonates of lanthanides and yttrium can be summarized by the following equations:

$$Ln_2(OH)_2(CO_3)_2 \cdot nH_2O \rightarrow Ln_2(OH)_2(CO_3)_2 \cdot H_2O + (n-1)H_2O \tag{1}$$

$$Ln_2(OH)_2(CO_3)_2 \cdot H_2O \rightarrow Ln_2O_2CO_3 + CO_2 + 2H_2O \tag{2}$$

$$Ln_2O_2CO_3 \rightarrow Ln_2O_3 + O_2 \tag{3}$$

$$Ln_2O_2CO_3 \rightarrow Ln_2O_{(2-x)}(CO_3)_{(1-x)} + xCO_2 \tag{4}$$

$$Ln_2O_{(2+x)}(CO_3)_{(1-x)} \rightarrow Ln_2O_3 + (1-x)CO_2 \tag{5}$$

$$Ln_2(OH)_2(CO_3)_2 \cdot nH_2O \rightarrow Ln_2(OH)_2(CO_3)_2 + nH_2O \tag{6}$$

$$Ln_2(OH)_2(CO_3)_2 \rightarrow Ln_2O_3 + CO_2 + H_2O \tag{7}$$

$$Ln_2(OH)_2(CO_3)_2 \cdot H_2O \rightarrow Ln_2O_{(4-x)}(CO_3)_x + (2-x)CO_3 + 2H_2O \tag{8}$$

$$Ln_2O_{(4-x)}(CO_3)_x \rightarrow 2Ln_2O_2 + xCO_2 \tag{9}$$

(In the cases of Pr and Tb, Pr_6O_{11} is the final residue in stage (5) and Tb_4O_7 is the final residue in stage (7), respectively.)

Table 3 attributes to each compound their probable reactions from those above and the temperature ranges over which they occur, according to the various mass losses observed in the TG curves.

The general aspect of the TG curves also allows the division of these compounds into the two groups already mentioned regarding IR absorption spectra.

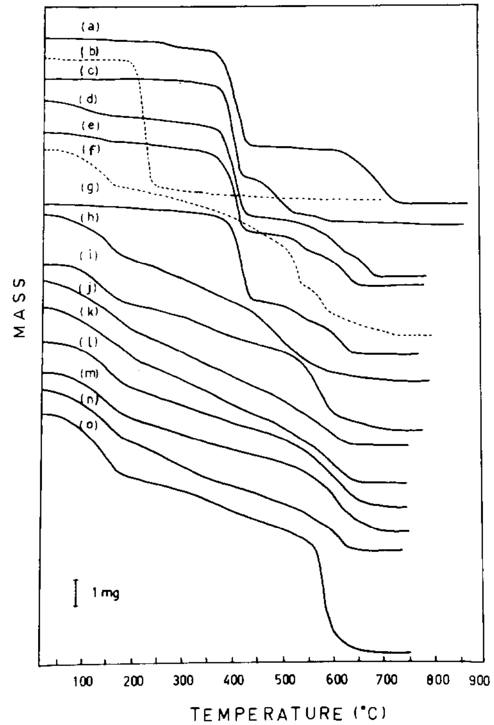

Fig. 3. TG curves of the basic carbonates of lanthanide and yttrium. Heating rate 5.2 °C min^{-1}. (a) La (23.92 mg); (b) Ce (23.96 mg); (c) Pr (23.98 mg); (d) Nd (24.04 mg); (e) Sm (23.96 mg); (f) Eu (23.82 mg); (g) Gd (23.86 mg); (h) Tb (24.20 mg); (i) Dy (23.96 mg); (j) Ho (23.86 mg); (k) Er (24.16 mg); (l) Tm (23.96 mg); (m) Yb (24.00 mg); (n) Lu (24.20 mg); (o) Y (23.92 mg).

Considering the TG curves of the compounds of the first group, the initial mass losses observed for the La, Pr and Gd compounds between 230 and 463 °C and for the Sm compounds between 40 and 463 °C, are probably due to the simultaneous loss of water of crystallization "hydroxyl" water and one molecule of CO_2. The same process of thermal degradation also occurs in the case of the Nd compound between 150 and 440 °C, but this proceeds by the loss of one molecule of water between 40 and 150 °C.

The second set of mass losses observed in the TG curves of the compounds of the first group are probably due to the decomposition of the intermediate compound $Ln_2O_2CO_3$ to the corresponding oxide. Only in the case of the lanthanum basic carbonate does that decomposition occur in one single step (at 576–746 °C). Pr, Nd, Sm and Gd compounds undergo the final decomposition in two steps, indicating the formation of the following probable intermediate compounds: $Pr_2O_{2.6}(CO_3)_{0.4}$, $Nd_2O_{2.5}(CO_3)_{0.5}$, $Sm_2O_{2.5}(CO_3)_{0.5}$ and $Gd_2O_{2.4}(CO_3)_{0.6}$, which finally decompose to the corresponding oxides.

TABLE 3

Reactions (eqns (1)–(9)) and corresponding temperature ranges observed in the TG curves of the compounds $Ln_2(OH)_2(CO_3)_2 \cdot nH_2O$

Compound	Temperature range of mass loss reactions (1)–(9) in the TG curves (° C)								
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
$La_2(OH)_2(CO_3)_2 \cdot H_2O$	–	236–440	579–746	–	–	–	–	–	–
$Ce_2(OH)_2(CO_3)_2 \cdot H_2O$	–	–	–	–	–	–	–	191–250	250–488
$Pr_2(OH)_2(CO_3)_2 \cdot H_2O$	–	288–341	–	431–524	524–580	–	–	–	–
$Nd_2(OH)_2(CO_3)_2 \cdot 2H_2O$	40–150	150–440	–	469–629	629–696	–	–	–	–
$Sm_2(OH)_2(CO_3)_2 \cdot H_2O$	–	38–463	–	436–569	569–660	–	–	–	–
$Eu_2(OH)_2(CO_3)_2 \cdot 3H_2O$	38–178	178–545	–	545–600	600–732	–	–	–	–
$Gd_2(OH)_2(CO_3)_2 \cdot H_2O$	–	220–463	–	463–550	550–642	–	–	–	–
$Tb_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	–	38–200	200–688	–	–
$Dy_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	–	34–192	192–727	–	–
$Ho_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	–	29–200	200–639	–	–
$Er_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	–	33–200	200–650	–	–
$Tm_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	–	29–187	187–690	–	–
$Yb_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	–	33–188	188–690	–	–
$Lu_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	–	33–187	187–644	–	–
$Y_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	–	33–200	200–650	–	–

In the case of the TG curve of Ce(III) basic carbonate, it can be seen that thermal decomposition occurs in two consecutive steps with the final formation of CeO_2. The first mass loss, occurring through a fast process (191–250 ° C), is probably due to loss of water of crystallization, "hydroxyl" water and 1.6 molecules of CO_2, with the intermediate formation of $Ce_2O_{3.6}(CO_3)_{0.4}$. This undergoes decomposition up to 600 ° C through a very slow process.

The fact that for the basic carbonates of the first group dehydration occurs almost simultaneously with the loss of CO_2, suggests that the molecules of water of crystallization must be strongly bonded, thus confirming the IR data. This is also in accordance with the fact that these compounds show evidence of crystalline structure. The formation of intermediate compounds in the case of the basic carbonates of the first group is probably related to the type of bond between carbonate and lanthanide ions, the former acting in this case as a unidentate ligand.

The TG curves of the compounds of the second group show mass losses that are more-or-less continuous without well-defined steps.

In the case of the Eu compound the mass loss observed between 38 and 178 ° C corresponds to partial dehydration with the formation of a monohydrated compound which undergoes decomposition (178–545 ° C) to form $Eu_2O_2CO_3$. This compound undergoes loss of CO_2 (545–732 ° C), probably with the formation of $Eu_2O_{(2+x)}CO_{3(1-x)}$ as an intermediate which finally decomposes to Eu_2O_3.

The mass losses between 29 and 200 ° C observed in the TG curves of the remaining compounds of the second group are probably due to the dehydration of these basic salts with the formation of the corresponding unstable anhydrous basic carbonates $Ln_2(OH)_2(CO_3)_2$. The second mass losses, occurring immediately after dehydration, can be attributed to the decomposition of the anhydrous basic salt into the corresponding oxides; this is a slow process. The TG curves show no evidence of intermediate compound formation and this suggests that in the compounds of the second group, the carbonate ions probably act as bidentate ligands.

The DTA curves (Fig. 4) show peaks in correspondence with the mass losses observed in the TG curves and exothermic peaks probably due to structural rearrangements. The temperature of each DTA peak and its probable interpretation are summarized in Table 4.

For the compounds whose TG curves show dehydration at < 200 ° C, the corresponding DTA curves do not exhibit endothermic peaks, probably owing to structural rearrangements occurring simultaneously with the dehydration processes. The small exothermic peaks observed at 530 and 600 ° C in the Dy and Lu compounds, respectively, preceding the endothermic peaks, are probably also due to structural rearrangements.

The relatively small area of the endothermic peaks observed in the DTA curves of the basic carbonates of Eu, Tb, Ho, Er, Tm, Yb and Lu between

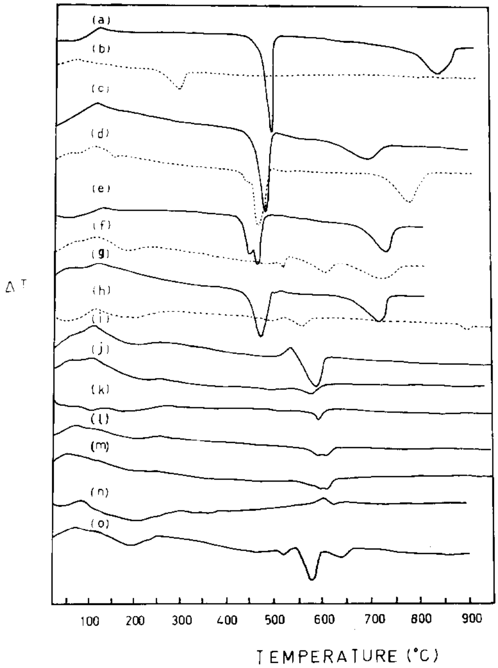

Fig. 4. DTA curves of the basic carbonates of lanthanide and yttrium diluted to 20% (Lu, 50%) with α-alumina. Heating rate 10.0 °C min^{-1}. (a) La; (b) Ce; (c) Pr; (d) Nd; (e) Sm; (f) Eu; (g) Gd; (h) Tb; (i) Dy; (j) Ho; (k) Er; (l) Tm; (m) Yb; (n) Lu; (o) Y.

TABLE 4

Temperatures (°C) of DTA peaks corresponding to reactions and transitions (eqns. (1)–(9)) of the compounds $Ln_2(OH)_2(CO_3)_2 \cdot nH_2O$

Compound	Endothermic							Exothermic
	(1)	(2)	(3)	(4)–(5)	(6)	(7)	(8)–(9)	
$La_2(OH)_2(CO_3)_2 \cdot H_2O$	–	490	845	–	–	–	–	110
$Ce_2(OH)_2(CO_3)_2 \cdot H_2O$	–	–	–	–	–	–	300	60
$Pr_2(OH)_2(CO_3)_2 \cdot H_2O$	–	480	–	690	–	–	–	110
$Nd_2(OH)_2(CO_3)_2 \cdot 2H_2O$	150	460	–	780	–	–	–	100
$Sm_2(OH)_2(CO_3)_2 \cdot H_2O$	–	450–465	–	735	–	–	–	120
$Eu_2(OH)_2(CO_3)_2 \cdot 3H_2O$	190	520	–	610–730	–	–	–	115
$Gd_2(OH)_2(CO_3)_2 \cdot H_2O$	–	470	–	720	–	–	–	115
$Tb_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	200	500–550	–	105
$Dy_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–		200	590	–	100–530
$Ho_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	220	580	–	100
$Er_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	200	590	–	–
$Tm_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	200	610	–	70
$Yb_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	200	590–610	–	50
$Lu_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	200	615	–	60–600
$Y_2(OH)_2(CO_3)_2 \cdot 2H_2O$	–	–	–	–	200	520–585–640	–	70

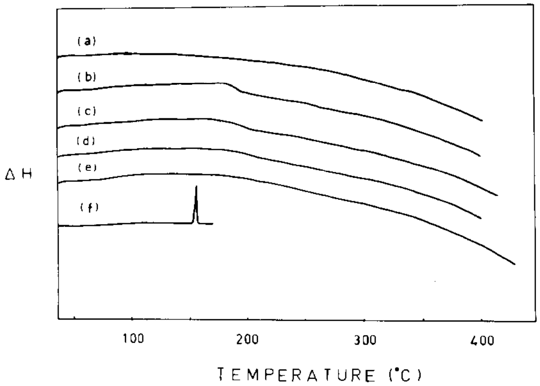

Fig. 5. DSC curves of the basic carbonates of lanthanides and yttrium. Heating rate: 10.0 °C. min^{-1}. (a) La(16.0 mg); (b) Eu(17.3 mg); (c) Y(12.2 mg); (d) Dy(16.9 mg); (e) Ho(17.2 mg); (f) In (7.80 mg).

500 and 650 °C also suggests that the final decomposition occurs with simultaneous structural rearrangements.

The single small endothermic peak (at 300 °C) in the DTA curve of Ce(III) basic carbonate corresponding to the great mass loss of the corresponding TG curve is probably due to the rapid oxidation of Ce(III) to Ce(IV), which also causes the rapid and almost total decomposition of that compound at a relatively low temperature.

Because of great similarities of the DSC curves, only the DSC curves of the La, Eu, Dy, Ho and Y basic carbonates and of metallic In are presented in Fig. 5. The DSC curves of the Ce, Pr, Nd, Sm and Gd compounds are identical to that of the La compound, and the DSC curves of the Tb, Er, Tm, Yb and Lu compounds are identical to that of the Ho compound.

The DSC curves show that the thermal decomposition of the compounds at < 400 °C occurs by a slow exothermic process without the appearance of definite peaks. This behaviour is in accordance with the observations already made from the DTA curves and are probably due to structural rearrangements caused by the continuously rising temperature. These exothermic effects are more intense in the Eu, Dy and Y compounds. The DSC curves of the compounds of the first group are relatively more straight and consequently initial decomposition processes are less exothermic; this fact seems to be related to the water of crystallization being more strongly bonded in these compounds, causing the slightly crystalline structure and the appearance of sharper bands at 3400 cm^{-1} in the IR spectra.

CONCLUDING REMARKS

The techniques used in the preparation of these compounds led to the formation of basic carbonate hydrates with compositions in very close agreement with the formula $Ln_2(OH)_2(CO_3)_2 \cdot nH_2O$. The XRD, IR, TG and DTA data allowed the separation of the compounds into two groups. Each compound can be characterized by the simultaneous examination of its TG and DTA curves.

REFERENCES

1 J. Preiss and A. Dussik, Z. Anorg. Allgem. Chem., 131 (1923) 275.
2 M.L. Salutsky and L.L. Quill, J. Am. Chem. Soc., 72 (1950) 3306.
3 J.M. Axelrod, Studies of the Rare Earth Carbonates, Ph.D. Thesis, University of Maryland, 1959.
4 R.G. Charles, J. Inorg, Nucl. Chem., 27 (1965) 1489.
5 R.L.N. Sastry, S.R. Yoganarasimhan, D.N. Mehrotra and C.N.R. Rao, J. Inorg. Nucl. Chem., 28 (1966) 1165.
6 J. Preiss and N. Rainer, Z. Anorg. Allgem. Chem., 131 (1923) 287.
7 W.W. Wendlandt and T.D. George, Texas J. Sci., 13 (1961) 316.
8 E.L. Head and C.E. Holley Jr., U.S. At. Energy Comm., LADC (1962) 5579.
9 E.L. Head and C.E. Holley Jr., Proc. 4th Conf. on Rare Earth Research, Arizona, 1964, p. 707.
10 J.R. Ferraro and W.R. Walker, Inorg. Chem., 4 (1965) 1382.
11 L.J. Bellamy, The Infrared Spectra of Complex Molecules, 3rd Edn., Wiley New York, 1975.
12 C.N.R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York, 1963.
13 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1963.