Thermochimica Acta, 219 (1993) 225–233
Elsevier Science Publishers B.V., Amsterdam

Thermal decomposition of the hydrated basic carbonates of lanthanides and yttrium in CO_2 atmosphere

L. Moscardini D'Assunção [a], M. Ionashiro [b,*], D.E. Rasera [b] and I. Giolito [c]

[a] *Instituto de Ciências Químicas e Farmacêuticas, UNIFENAS, Alfenas, MG., C.P. 23, CEP. 37130-000 (Brazil)*
[b] *Instituto de Química, UNESP, Araraquara, São Paulo, C.P. 355, CEP. 14800 (Brazil)*
[c] *Instituto de Química, USP, São Paulo SP., C.P. 20780, CEP. 01498 (Brazil)*

(Received 17 July 1992)

Abstract

The hydrated basis carbonates of lanthanides and yttrium were prepared by precipitation from homogeneous solution via the hydrolysis of urea, without the addition of an auxiliary anion. Thermogravimetry, derivative thermogravimetry (TG–DTG), and differential thermal analysis (DTA) have been used in the study of these compounds in CO_2 atmosphere. The results lead to the composition and thermal stability of the studied compounds, and also to a comparative study with reported results in air atmosphere.

INTRODUCTION

Several methods of preparing lanthanide and yttrium carbonates and several studies of the thermal behaviour of these compounds have been carried out [1–9]. The preparation of hydrated basic carbonates of lanthanides and yttrium by precipitation from homogeneous solutions via the hydrolysis of urea without the addition of an auxiliary anion, and the application of TG, DTA and DSC in a static air atmosphere at ambient pressure, have also been described [10]. This paper is an extension of the work already reported [10] by employing TG–DTG and DTA methods in CO_2 atmosphere, not found in the literature.

EXPERIMENTAL

Hydrated basic lanthanide(III) carbonates (except promethium(III) and yttrium(III) carbonates) were prepared in accordance with already described procedures [10].

The lanthanide or yttrium contents, the total carbonate and hydroxyl contents, and the water contents, were determined from TG–DTG curves.

---

[*] Corresponding author.

The TG–DTG curves were obtained by using a Mettler TA-4000 thermoanalyzer system, using a CO_2 flux of about 40 ml min^{-1}, a heating rate of 10°C min^{-1} and samples of about 9 mg in alumina crucible.

DTA curves were recorded with a Perkin-Elmer DTA-1700, using α-Al_2O_3 as reference material. Samples of about 9 mg were used in alumina crucible and heated at a rate of 20°C min^{-1} with a CO_2 flux of about 200 ml min^{-1}.

RESULTS AND DISCUSSION

Table 1 presents the TG data of the compounds having the general formula, $Ln_2(OH)_2(CO_3)_2 \cdot nH_2O$ (Ln = lanthanide or yttrium; $n = 1$, La–Sm, Gd; $n = 2$, Tb–Lu; $n = 2.5$, Eu, Y).

The TG–DTG curves for the compounds prepared are shown in Fig. 1. These curves show mass losses between 305 and 960°C for the lighter lanthanide and gadolinium compounds, and between 60 and 750°C for the heavier lanthanide and yttrium compounds.

For the lanthanium compounds (Fig. 1(a)) the mass loss occurs in two steps. The first mass loss between 305 and 580°C is ascribed to dehydration and partial CO_2 loss with formation of lanthanum (di)oxycarbonate $La_2O_2CO_3$ as intermediate. The second mass loss between 900 and 980°C is due to the thermal decomposition of the intermediate to lanthanum oxide La_2O_3, with loss of $1CO_2$.

For the cerium compound (Fig. 1(b)) the mass loss also occurs in two steps. The first step between 320 and 380°C is due to losses of $2H_2O$ and $1.75CO_2$, with formation of the intermediate $CeO_{1.75}(CO_3)_{0.25}$. The second

TABLE 1

TG results

Compound	m_i (mg)	Δm (mg)	Δm (%)		Mass of residue (mg)	Ln (%)	
			TG	Calc.		TG	Calc.
$La_2(OH)_2(CO_3)_2 \cdot H_2O$	9.673	2.705	27.96	27.57	6.968	61.42	61.75
$Ce_2(OH)_2(CO_3)_2 \cdot H_2O$	9.425	2.249	23.87	23.89	7.176	61.98	61.96
$Pr_2(OH)_2(CO_3)_2 \cdot H_2O$	9.819	2.647	26.96	27.34	7.172	60.47	62.09
$Nd_2(OH)_2(CO_3)_2 \cdot H_2O$	9.526	2.620	27.50	26.94	6.906	62.15	62.64
$Sm_2(OH)_2(CO_3)_2 \cdot H_2O$	9.570	2.528	26.41	26.24	7.042	63.46	63.61
$Eu_2(OH)_2(CO_3)_2 \cdot 2.5H_2O$	9.500	2.891	30.43	30.03	6.609	60.08	60.42
$Gd_2(OH)_2(CO_3)_2 \cdot H_2O$	9.735	2.520	25.89	25.49	7.215	64.30	64.64
$Tb_2(OH)_2(CO_3)_2 \cdot 2H_2O$	9.352	2.624	28.05	27.78	6.728	61.16	62.58
$Dy_2(OH)_2(CO_3)_2 \cdot 2H_2O$	9.626	2.719	28.25	27.59	6.907	62.52	63.10
$Ho_2(OH)_2(CO_3)_2 \cdot 2H_2O$	9.282	2.558	27.55	27.32	6.724	63.24	63.44
$Er_2(OH)_2(CO_3)_2 \cdot 2H_2O$	9.399	2.572	27.36	27.08	6.827	63.52	63.77
$Tm_2(OH)_2(CO_3)_2 \cdot 2H_2O$	9.654	2.635	27.30	26.92	7.019	63.66	64.00
$Yb_2(OH)_2(CO_3)_2 \cdot 2H_2O$	9.516	2.560	26.90	26.50	6.956	64.19	64.55
$Lu_2(OH)_2(CO_3)_2 \cdot 2H_2O$	9.454	2.523	26.69	26.31	6.931	64.47	64.80
$Y_2(OH)_2(CO_3)_2 \cdot 2.5H_2O$	9.498	3.843	40.46	40.08	5.655	46.88	47.18

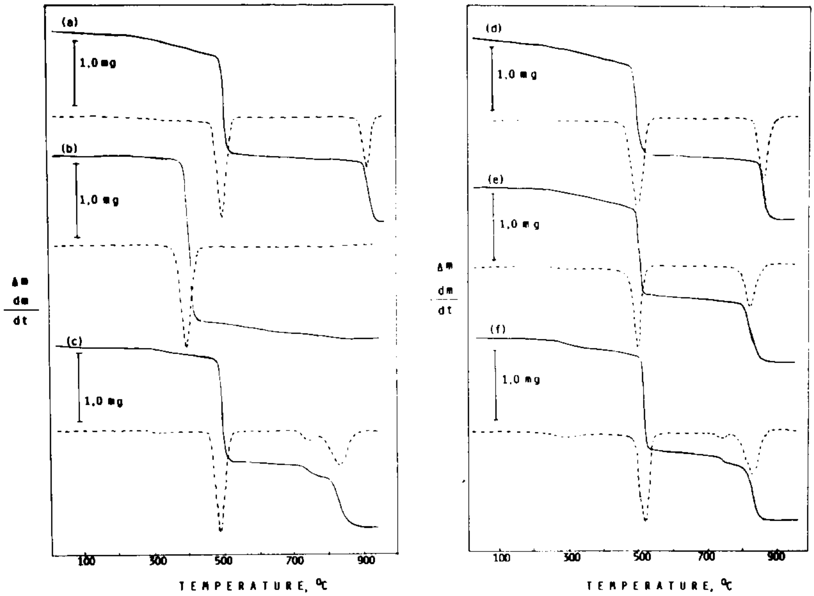

Fig. 1. TG–DTG curves of the hydrated basic carbonates of lanthanides and yttrium. Heating rate 10°C min^{-1}; CO_2 flux ≈40 ml min^{-1}; (a) La (9.673 mg); (b) Ce (9.245 mg); (c) Pr (9.819 mg); (d) Nd (9.526 mg); (e) Sm (9.570 mg); (f) Gd (9.735 mg); (g) Eu (9.500 mg); (h) Dy (9.626 mg); (i) Y (9.498 mg); (j) Tb (9.352 mg); (k) Ho (9.282 mg); (l) Er (9.399 mg); (m) Tm (9.654 mg); (n) Yb (9.516 mg); (o) Lu (9.454 mg).

step between 380 and 500°C is ascribed to the thermal decomposition of the intermediate to the cerium(IV) oxide CeO_2, with elimination of $0.25CO_2$.

For the praseodymium compound (Fig. 1(c)) the mass loss occurs in three steps. The first step between 370 and 550°C is due to losses of $2H_2O$ and $1CO_2$, with formation of the intermediate $Pr_2O_2CO_3$. The second small mass loss between 720 and 780°C is ascribed to partial thermal decomposition of the $Pr_2O_2CO_3$ to $Pr_2O_{2.1}(CO_3)_{0.9}$, with loss of $0.1CO_2$. The third step between 800 and 900°C is due to final thermal decomposition of the last intermediate to praseodymium oxide Pr_6O_{11}, with loss of $0.9CO_2$.

For the neodymium and samarium compounds (Fig. 1(d) and (e)) the mass losses occur in two steps. The first step between 320 and 550°C for Nd and between 270 and 520°C for Sm is due to losses of $2H_2O$ and $1CO_2$, with formation of the intermediates $Ln_2O_2CO_3$. The second step between 870 and 900°C for Nd and between 770 and 870°C for Sm is due to the thermal decomposition of the intermediates to neodymium and samarium oxides, respectively, with elimination of $1CO_2$.

For the gadolinium compound (Fig. 1(f)) the mass loss occurs in four steps. The first step between 310 and 400°C is due to partial dehydration, with loss of $0.5H_2O$. The second step between 400 and 500°C is ascribed to losses of $1.5H_2O$ and $1CO_2$, with formation of (di)oxycarbonate of gadolinium $Gd_2O_2CO_3$ as intermediate. The third step between 700 and

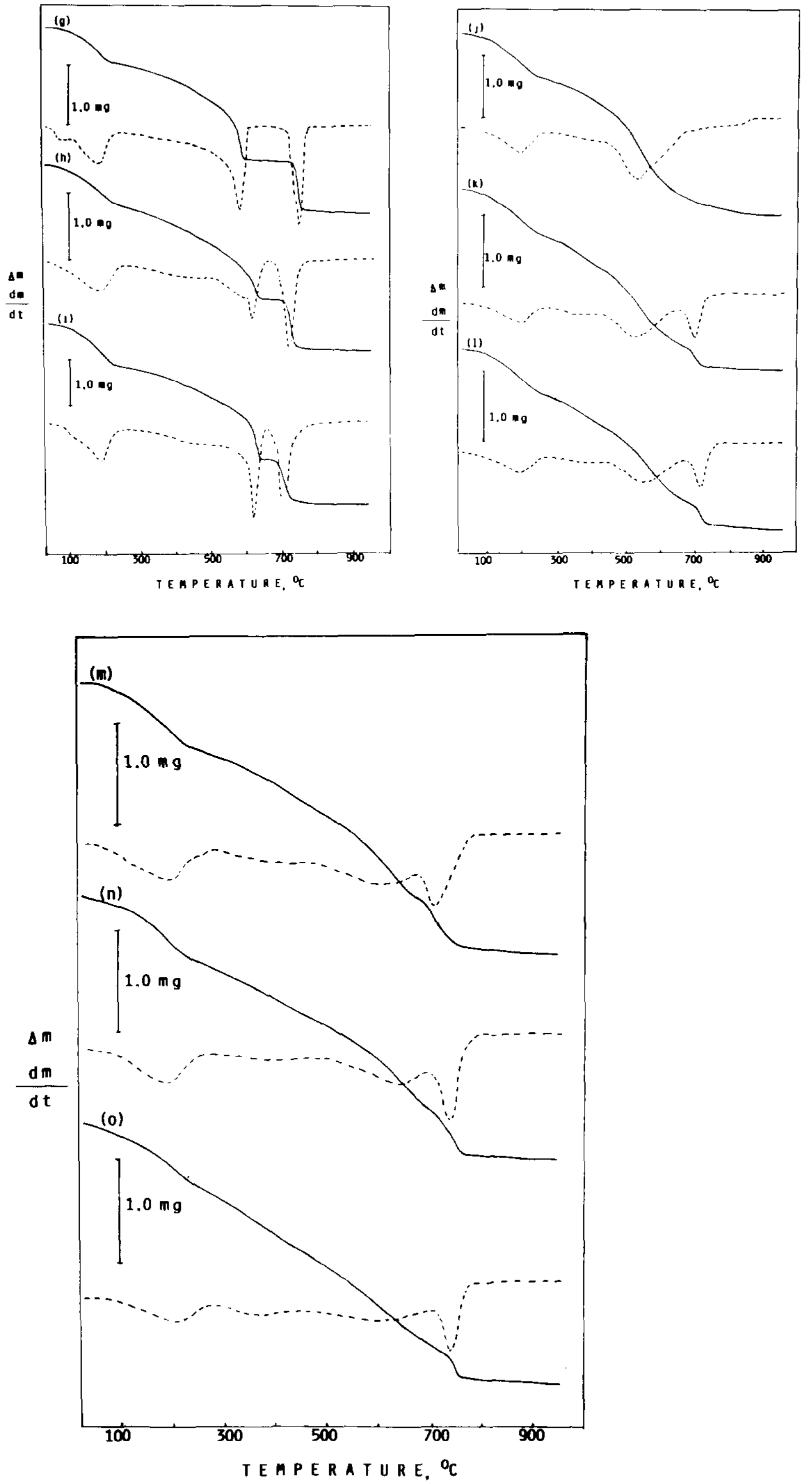

Fig. 1. (continued)

750°C, for which a small mass loss occurs, is ascribed to the partial thermal decomposition of the intermediate to $Gd_2O_{2.1}(CO_3)_{0.9}$ with loss of $0.1CO_2$. The fourth step between 770 and 850°C is due to final thermal decomposition of the last intermediate to gadolinium oxide Gd_2O_3, with loss of $0.9CO_2$.

For the europium, dysprosium and yttrium compounds (Fig. 1(g)–(i)) the mass losses occur in three steps between 70 and 200°C, 200 and 580°C, 710 and 750°C for Eu, between 60 and 215°C, 215 and 620°C, 680 and 730°C for Dy, and between 60 and 220°C, 220 and 620°C, 660 and 750°C for Y. The first step is due to partial dehydration, with losses of $1.5H_2O$ (Eu, Dy) and $2H_2O$ (Y). The second step is ascribed to losses of $2H_2O$ and $1CO_2$ (Eu), $1.5H_2O$ and $1.1CO_2$ (Dy), $1.5H_2O$ and $1.2CO_2$ (Y), with formation of the intermediates $Eu_2O_2CO_3$, $Dy_2O_{2.1}(CO_3)_{0.9}$ and $Y_2O_{2.2}(CO_3)_{0.8}$. The last step is ascribed to the thermal decomposition of the intermediates to the respective oxides Ln_2O_3, with the loss of $1CO_2$, $0.9CO_2$ and $0.8CO_2$, respectively.

For the terbium and holmium to lutetium compounds (Fig. 1(j)–(o)) the mass losses occur in two consecutive steps from 60 up to 850°C, without formation of stable intermediates. The first step between 60 and 240°C is due to losses of $2H_2O$. The second step is due to losses of $1H_2O$ and $2CO_2$, with formation of the respective oxides Tb_4O_7 and Ln_2O_3.

The temperature range and mass losses for all hydrated basic carbonates in CO_2 atmosphere are shown in Table 2.

The DTA curves of the prepared compounds are shown in Fig. 2. For the hydrated basic carbonates of lanthanum to samarium, (Fig. 2(a)–(e)) gadolinium (Fig. 2(f)) europium and yttrium (Fig. 2(g) and (h)) the DTA curves show endothermic peaks, all in correspondence with the mass losses observed in the TG curves. Only for the dysprosium compound is an exothermic peak (at 620°C) observed. This is probably due to structural rearrangement.

For the terbium to lutetium compounds (Fig. 2(j)–(o)) the DTA curves show an endothermic peak, ascribed to partial dehydration, in correspondence with TG data. No evidence of an endothermic peak due to thermal decomposition is found in the thulium and lutetium basic carbonates after the partial dehydration, but some evidence of a small endothermic peak is observed at about 500°C for Tb, Ho, Er, and at about 400°C for Yb. These data are in agreement with the TG curves, where after the first step the mass loss occurs through a slow process; the absorbed heat in this step is probably insufficient to produce a well defined endothermic peak. The small exothermic peak at about 730°C (except for Tb) is probably due to the structural rearrangement.

The temperature of each DTA peak and its probable interpretation is summarized in Table 3.

The TG–DTG and DTA curves in CO_2 atmosphere for lanthanum to

TABLE 2

Temperature range (°C) and mass loss observed in the TG curves

Compound	m_i (mg)	ΔT (°C)	Δm (mg)		Δm (%)	
					TG	Calc.
$La_2(OH)_2(CO_3)_2 \cdot H_2O$	9.673	305–580	1.759	$2H_2O, CO_2$	18.18	17.79
		900–960	0.946	CO_2	9.78	9.78
$Ce_2(OH)_2(CO_3)_2 \cdot H_2O$	9.425	320–380	2.026	$2H_2O, 1.75CO_2$	21.50	21.46
		380–500	0.223	$0.25CO_2$	2.37	2.43
$Pr_2(OH)_2(CO_3)_2 \cdot H_2O$	9.819	370–550	1.684	$2H_2O, CO_2$	17.15	17.64
		720–780	0.093	$0.1CO_2$	0.95	0.97
		800–900	0.870	$0.9CO_2$	8.86	8.73
$Nd_2(OH)_2(CO_3)_2 \cdot H_2O$	9.526	320–550	1.691	$2H_2O, CO_2$	17.75	17.38
		870–900	0.929	CO_2	9.75	9.56
$Sm_2(OH)_2(CO_3)_2 \cdot H_2O$	9.570	270–520	1.609	$2H_2O, CO_2$	16.81	16.93
		770–870	0.919	CO_2	9.60	9.31
$Gd_2(OH)_2(CO_3)_2 \cdot H_2O$	9.735	310–400	0.188	$0.5H_2O$	1.93	1.85
		400–500	1.421	$1.5H_2O, CO_2$	14.60	14.60
		700–750	0.097	$0.1CO_2$	1.0	0.90
		770–850	0.814	$0.9CO_2$	8.36	8.14
$Eu(OH)_2(CO_3)_2 \cdot 2.5H_2O$	9.500	70–200	0.525	$1.5H_2O$	5.53	5.37
		200–580	1.548	$2H_2O, CO_2$	16.29	15.91
		710–750	0.816	CO_2	8.61	8.75
$Dy_2(OH)_2(CO_3)_2 \cdot 2H_2O$	9.626	60–215	0.528	$1.5H_2O$	5.49	5.25
		215–620	1.441	$1.5H_2O, 1.1CO_2$	14.97	14.65
		680–730	0.750	$0.9CO_2$	7.79	7.69
$Y_2(OH)_2(CO_3)_2 \cdot 2.5H_2O$	9.498	60–220	0.871	$2H_2O$	9.17	9.56
		220–620	2.066	$1.5H_2O, 1.2CO_2$	21.75	21.18
		660–750	0.906	$0.8CO_2$	9.54	9.34
$Tb_2(OH)_2(CO_3)_2 \cdot 2H_2O$	9.352	60–230	0.624	$2H_2O$	6.86	7.10
		230–850	1.982	$H_2O, 2CO_2$	21.19	20.88
$Ho_2(OH)_2(CO_3)_2 \cdot 2H_2O$	9.282	60–240	0.614	$2H_2O$	6.61	6.93
		240–720	1.944	$H_2O, 2CO_2$	20.94	20.39
$Er_2(OH)_2(CO_3)_2 \cdot 2H_2O$	9.399	60–245	0.626	$2H_2O$	6.66	6.87
		245–730	1.946	$H_2O, 2CO_2$	20.70	20.21
$Tm_2(OH)_2(CO_3)_2 \cdot 2H_2O$	9.654	60–245	0.643	$2H_2O$	6.66	6.83
		245–750	1.992	$H_2O, 2CO_2$	20.64	20.09
$Yb_2(OH)_2(CO_3)_2 \cdot 2H_2O$	9.516	60–230	0.645	$2H_2O$	6.78	6.72
		230–750	1.915	$H_2O, 2CO_2$	20.12	19.78
$Lu_2(OH)_2(CO_3)_2 \cdot 2H_2O$	9.454	60–245	0.624	$2H_2O$	6.60	6.67
		245–700	1.899	$H_2O, 2CO_2$	20.09	19.64

samarium and gadolinium show an increase in the temperature of thermal decomposition compared with the TG and DTA curves in air atmosphere, mainly for the intermediate $Ln_2O_2CO_3$.

For europium, dysprosium and yttrium compounds, the TG curves in CO_2 atmosphere show the formation of a stable intermediate $Ln_2O_2CO_3$,

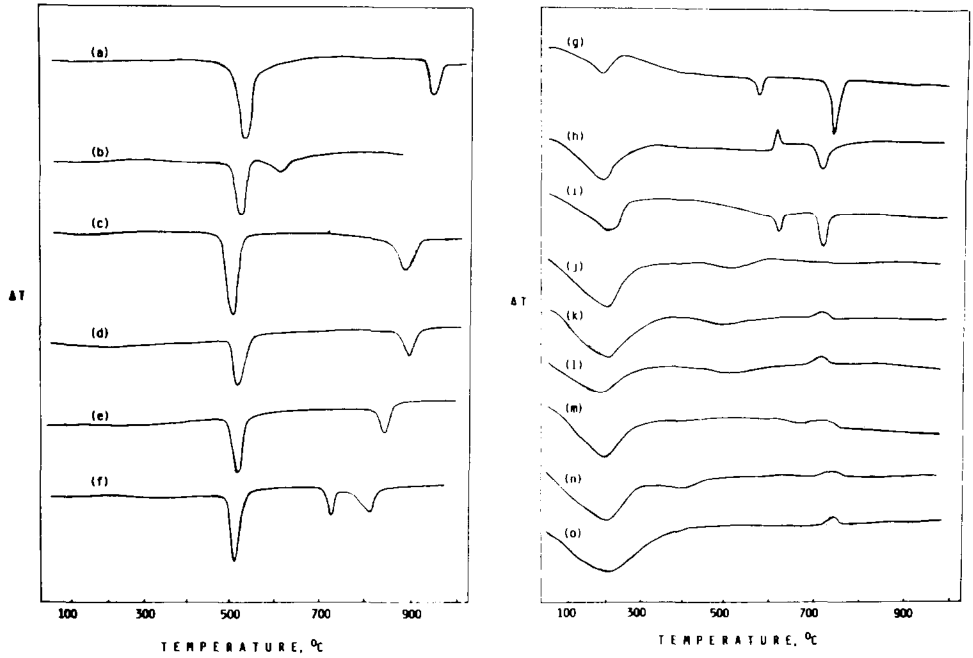

Fig. 2. DTA curves of the hydrated basic carbonates of lanthanides and yttrium: heating rate 20°C min^{-1}; CO_2 flux ≈40 ml min^{-1}; reference material α-Al_2O_3; (a) La; (b) Ce; (c) Pr; (d) Nd; (e) Sm; (f) Gd; (g) Eu; (h) Dy; (i) Y; (j) Tb; (k) Ho; (l) Er; (m) Tm; (n) Yb; (o) Lu.

whereas the TG curves in air atmosphere only show an indication of this intermediate for europium and dysprosium compounds. However, the DTA curves in CO_2 and in air atmosphere show some resemblance, except that the corresponding temperatures of the endothermic peaks due to thermal decomposition are higher in CO_2 atmosphere.

For the terbium and holmium to lutetium compounds, a stable intermediate is not observed during the thermal decomposition, even in CO_2 atmosphere; thus the TG curves show mass losses that are more or less continuous without well defined steps (the same behaviour already observed in the TG curves in air atmosphere). A significant difference is observed in the DTA curves in CO_2, as compared to those in air atmosphere. The endothermic peaks at about 600°C observed in air atmosphere is not observed in CO_2 atmosphere, and the exothermic peak at about 710°C observed in CO_2 atmosphere is not observed in air atmosphere.

CONCLUDING REMARKS

In the thermal behaviour of the hydrated basic carbonates of lanthanum to gadolinium, dysprosium and yttrium, a higher stability in CO_2 than in air atmosphere was observed, mainly for the intermediate $Ln_2O_2CO_3$. For the

TABLE 3

Temperature of DTA peaks and the probable interpretations

Compound	Peak (°C) (endo)	Loss	Peak (°C) (endo)	Loss	Peak (°C) (endo)	Loss	Peak (°C) (endo)	Loss	Peak (°C) (exo)	Transition
$La_2(OH)_2(CO_3)_2 \cdot H_2O$			530	$2H_2O, CO_2$			950	CO_2		
$Ce_2(OH)_2(CO_3)_2 \cdot H_2O$			525	$2H_2O, 1.75CO_2$			610	$0.25CO_2$		
$Pr_2(OH)_2(CO_3)_2 \cdot H_2O$			505	$2H_2O, CO_2$			890	CO_2		
$Sm_2(OH)_2(CO_3)_2 \cdot H_2O$			520	$2H_2O, CO_2$			820	CO_2		
$Gd_2(OH)_2(CO_3)_2 \cdot H_2O$			510	$1.5H_2O, CO_2$	725	$0.1CO_2$	810	$0.9CO_2$		
$Eu_2(OH)_2(CO_3)_2 \cdot 2.5H_2O$	190	$1.5H_2O$	570	$2H_2O, CO_2$			745	CO_2		
$Dy_2(OH)_2(CO_3)_2 \cdot 2H_2O$	190	$1.5H_2O$	–[a]	$1.5H_2O, 1.1CO_2$			710	$0.9CO_2$	610	Structural rearrangement
$Y_2(OH)_2(CO_3)_2 \cdot 2.5H_2O$	200	$2H_2O$	615	$1.5H_2O, 1.2CO_2$			710	$0.8CO_2$		
$Tb_2(OH)_2(CO_3)_2 \cdot 2H_2O$	200	$2H_2O$	510	$H_2O, 2CO_2$						
$Ho_2(OH)_2(CO_3)_2 \cdot 2H_2O$	200	$2H_2O$	500	$H_2O, 2CO_2$					710	Structural rearrangement
$Er_2(OH)_2(CO_3)_2 \cdot 2H_2O$	190	$2H_2O$	500	$H_2O, 2CO_2$					710	Structural rearrangement
$Tm_2(OH)_2(CO_3)_2 \cdot 2H_2O$	195	$2H_2O$		$H_2O, 2CO_2$					710	Structural rearrangement
$Tb_2(OH)_2(CO_3)_2 \cdot 2H_2O$	200	$2H_2O$	400	$H_2O, 2CO_2$					720	Structural rearrangement
$Lu_2(OH)_2(CO_3)_2 \cdot 2H_2O$	200	$2H_2O$		$H_2O, 2CO_2$					720	Structural rearrangement

[a] With thermal decomposition.

other compounds, of terbium and holmium to lutetium, no stable intermediate was observed in the TG curves, even in CO_2 atmosphere.

ACKNOWLEDGMENTS

The authors acknowledge FAPESP (Proc. 90/2932-4), FINEP (Proc. 711/87), FAPEMIG (Proc. CEX 782/90) and CNPq (Proc. 150.020-90/2), for financial support.

REFERENCES

1 J. Preiss and A. Dussik, Z. Anorg. Allg. 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, 1969.
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. Allg. 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. Halley, Jr., U.S. At. Energy Comm., Pittsburgh, LADC (1962) 5579; Chem. Abstr., 61 (1964) 10304h.
9 E.L. Head and C.E. Halley, Jr., Proc. 4th Conf. on Rare Earth Research, Arizona, 1964, p. 707.
10 L. Moscardini D'Assunção, I. Giolito and M. Ionashiro, Thermochim. Acta, 137 (1989) 319.