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A study of the thermal decomposition of some lanthanon hydroxy chromates $Ln(OH)CrO_4$ (where Ln is La, Pr, Nd)

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Abstract

The chemical decomposition of $Ln(OH)CrO_4$ (where Ln is La, Pr and Nd) has been studied by TG, DTG and DTA. $La(OH)CrO_4$ and $Pr(OH)CrO_4$ decompose in three steps giving $Ln_2Cr_2O_9$, $LnCrO_4$ and $LnCrO_3$.

INTRODUCTION

In previous work, we have determined the structure of this family of compounds, $Ln(OH)CrO_4$ (Ln is La-Nd), using single-crystal X-ray diffractometry [1]. We have also studied their magnetic properties and their vibrational behaviour using IR and Raman spectroscopies [2].

In this paper we report the thermal decomposition of these compounds because they can be excellent precursors for mixed oxides of chromium and lanthanide.

EXPERIMENTAL

The compounds $Ln(OH)CrO_4$ (where Ln is La, Pr, Nd) can only be obtained as single crystals. They were prepared by a hydrothermal procedure starting from Ln_2O_3 (where Ln is La, Nd), CrO_3 and LiOH in a molar ratio of 1:4:3, and from Pr_6O_{11}, CrO_3 and LiOH in a molar ratio of 1:12:9, using sealed glass tubes heated isothermally at 125°C for 40 h.

The thermal decomposition in flowing N_2 was recorded on a Stanton 781 thermoanalyzer at 5°C min^{-1}, using Pt-Rh crucibles and Al_2O_3 as reference.

The X-ray powder patterns were recorded using a Siemens Kristallofex 810 diffractometer and a D-500 goniometer with nickel-filtered copper radiation ($\lambda = 1.54088145$ Å). Silicon ($a = 5.430881$ Å) was employed as an internal standard.

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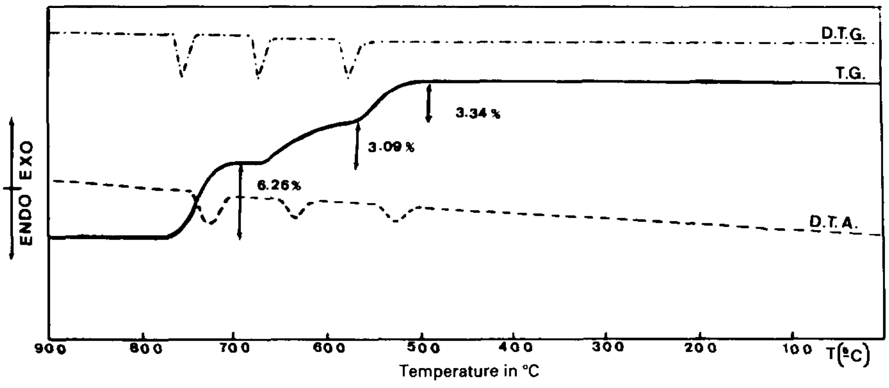

Fig. 1. TG, DTG and TGA curves for the decomposition of $La(OH)CrO_4$.

RESULTS AND DISCUSSION

Decomposition of La(OH)CrO₄

The TG, DTG and DTA curves corresponding to the decomposition of $La(OH)CrO_4$ are shown in Fig. 1. The decomposition process can be explained by the equations

$$La(OH)CrO_4 \rightarrow 0.5La_2Cr_2O_9 + 0.5H_2O \quad (1)$$

$$0.5La_2Cr_2O_9 \rightarrow LaCrO_4 + 0.25O_2 \quad (2)$$

$$LaCrO_4 \rightarrow LaCrO_3 + 0.5O_2 \quad (3)$$

The decomposition temperature ranges and weight losses are recorded in Table 1.

We can isolate $La_2Cr_2O_9$ after 1 h of isothermal treatment at 570°C and $LaCrO_4$ after 1 h of isothermal treatment at 670°C, both as very pure phases from the data on the TG curve.

$La_2Cr_2O_9$ has not previously been synthesized, although oxides of the same formula, $La_2M_2^{VI}O_9$, have been described for Mo^{VI} [3, 4] and W^{VI} [5].

TABLE 1

The temperature range of decomposition and the observed and calculated weight losses for $La(OH)CrO_4$

Stage	(T_1-T_2)/°C	Δm_{obs}/%	Δm_{cal}/%
1	500–570	3.34	3.31
2	570–670	3.09	3.04
3	700–775	6.26	6.28

TABLE 2

Interplanar spacings of $La_2Cr_2O_9$ [a]

hkl	d_o	d_c	I/I_o	hkl	d_o	d_c	I/I_o
200	6.657	6.689	42	$\bar{4}05$	2.306	2.310	27
002	5.527	5.527	21	$\bar{1}15$	2.264	2.264	9
$\bar{3}01$	4.848	4.851	18	600	2.230	2.230	14
020	4.647	4.643	25	214	2.199	2.195	16
112	4.058	4.063	47	$\bar{1}42$	2.163	2.166	11
301	3.666	3.665	31	$\bar{5}15$	2.120	2.119	36
202	3.616	3.618	40	$\bar{3}41$	2.093	2.094	12
311	3.404	3.409	35	$\bar{7}01$	2.022	2.022	19
$\bar{3}21$	3.361	3.354	23	$\bar{4}42$	1.942	1.942	10
$\bar{4}12$	3.309	3.313	23	143	1.887	1.887	10
$\bar{4}03$	3.182	3.176	58	$\bar{4}43$	1.876	1.874	8
030	3.107	3.096	100	602	1.834	1.832	21
113	3.061	3.060	63	$\bar{6}34$	1.800	1.800	21
$\bar{3}04$	2.918	2.920	24	$\bar{2}51$	1.795	1.797	17
321	2.881	2.877	15	052	1.761	1.760	27
$\bar{4}22$	2.815	2.818	14	251	1.738	1.738	21
$\bar{4}04$	2.718	2.721	14	$\bar{8}15$	1.664	1.665	6
500	2.672	2.675	8	$\bar{6}45$	1.520	1.522	12
014	2.649	2.649	8	$\bar{3}46$	1.518	1.517	8
$\bar{5}10$	2.575	2.571	8	064	1.349	1.350	26
$\bar{3}32$	2.532	2.536	18				

[a] d_o, observed spacing; d_c, calculated spacing; I_o, observed intensity.

The X-ray diffraction data of this new compound $La_2Cr_2O_9$ are given in Table 2. It crystallizes in the monoclinic system, space group $P2_1/m$ and $Z = 6$. Table 3 shows the calculated parameters [6, 7].

$LaCrO_4$, which crystallizes in the monoclinic system, space group $P2_1/n$ and $Z = 4$, is isomorphous with monazite [8], and has been obtained previously by other techniques [9–15].

In the final decomposition step, after 775°C, perovskite structure [16] appears as the unique phase.

TABLE 3

Crystal data for $La_2Cr_2O_9$

a/Å	b/Å	c/Å	°C	V/Å^3	D_x/g cm^{-3}
9.734(4)	13.462(7)	8.487(4)	94.5(2)	1108.41(3)	4.73

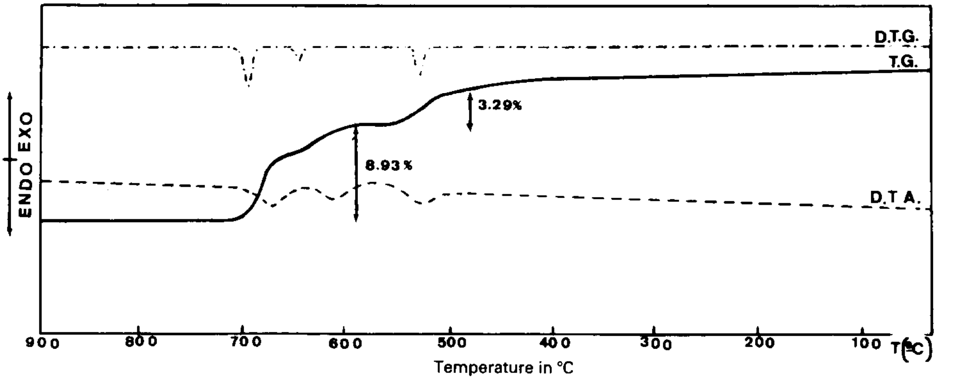

Fig. 2. TG, DTG and TGA curves for the decomposition of $Pr(OH)CrO_4$.

Decomposition of $Pr(OH)CrO_4$

The TG, DTG and DTA curves corresponding to the decomposition of $Pr(OH)CrO_4$ are shown in Fig. 2. The decomposition of this compound takes place in a similar way to that of $La(OH)CrO_4$ and can be explained by the following partial processes

$$Pr(OH)CrO_4 \rightarrow 0.5Pr_2Cr_2O_9 + 0.5H_2O \quad (4)$$

$$0.5Pr_2Cr_2O_9 \rightarrow PrCrO_4 + 0.25O_2 \quad (5)$$

$$PrCrO_4 \rightarrow PrCrO_3 + 0.5O_2 \quad (6)$$

The decomposition temperature ranges and the losses are recorded in Table 4.

We have isolated $Pr_2Cr_2O_9$ by isothermal treatment at 550°C, as indicated on the TG curve. This new compound is isomorphous with $La_2Cr_2O_9$ but is less stable.

$PrCrO_4$ was obtained by the isothermal procedure when the TG temperature reached 650°C. This compound can be dimorphic [11, 13, 17, 18] with either monoclinic monazite or tetragonal zircon structures. In the present case, all the experiments produced only the monazite structure, analogous to $LaCrO_4$.

TABLE 4

The temperature range of decomposition and the observed and calculated weight losses for $Pr(OH)CrO_4$

Stage	$(T_1 - T_2)$/°C	Δm_{obs}/%	Δm_{cal}/%
1	490–550	3.28	3.29
2, 3	550–720	9.06	8.93

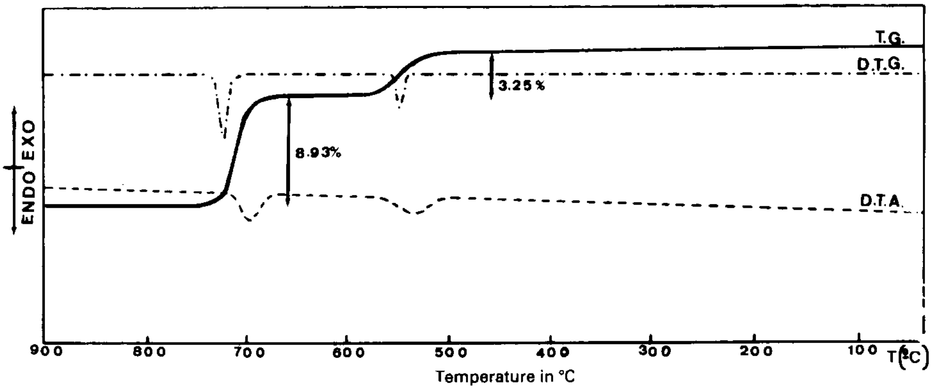

Fig. 3. TG, DTG and TGA curves for the decomposition of $Nd(OH)CrO_4$.

In the last step of the decomposition of $Pr(OH)CrO_4$, after 720°C, the final product is praseodymium chromite, $PrCrO_3$, alone, with a distorted perovskite structure [12].

Decomposition of $Nd(OH)CrO_4$

The TG, DTG and DTA curves corresponding to the decomposition of $Nd(OH)CrO_4$ are shown in Fig. 3. $Nd(OH)CrO_4$, the last member of the first isomorphous series $Ln(OH)CrO_4$, decomposes in only two steps, the partial processes of which can be expressed by the equations

$$Nd(OH)CrO_4 \rightarrow 0.5Nd_2Cr_2O_9 + 0.5H_2O \quad (7)$$

$$0.5Nd_2Cr_2O_9 \rightarrow NdCrO_3 + 0.75O_2 \quad (8)$$

Table 5 shown the decomposition temperature ranges. The observed weight losses are in very good agreement with the calculated values.

By isothermal treatment at 580°C for 2 h, $Nd_2Cr_2O_9$ could be isolated. The crystallographic study indicated that $Nd_2Cr_2O_9$ crystallizes in the tetragonal system, space group $I4_1/amd$, with zircon structure, being isostructural with $NdCrO_4$.

TABLE 5

The temperature range of decomposition and the observed and calculated weight losses for $Nd(OH)CrO_4$

Stage	$(T_1-T_2)/°C$	$\Delta m_{obs}/\%$	$\Delta m_{cal}/\%$
1	500–580	3.25	3.25
2	650–750	8.95	8.93

REFERENCES

1 I. Bueno, C. Parada, E. Gutierrez Puebla, A. Monge and C. Ruiz Valero, J. Solid State Chem., 78 (1989) 78.
2 I. Bueno, C. Parada, R. Saez Puche, L. Botto and E.J. Baran, J. Less-Common Metals, 169 (1991) 105.
3 J.P. Fournier, J. Fournier and R. Kholmuller, Bull. Soc. Chim. Fr., (1970) 4277.
4 A. Alekseev, Russ. J. Inorg. Chem., 14 (1969) 1558.
5 V.I. Maksin, Ukr. Khim. Zhur., 48 (1982) 576.
6 D.E. Appleman, U.S. Geological Survey, Washington D.C., P.B-216, 1973, 188.
7 P.E. Werner, University of Stockholm, S-106, 91 Stockholm, Sweden, 1984.
8 A. Pabst and C.O. Hutton, Am. Mineral., 36 (1951) 60.
9 Von H. Schwarz, Z. Anorg. Allg. Chem., 322 (1963) 1.
10 W.P. Doyle and I.J. Pryde, J. Inorg. Nucl. Chem., 38 (1976) 733.
11 A. Roy, M. Chandhury and K. Nag, Bull. Chem. Soc. Jpn., 51 (1978) 1243.
12 A. Roy and K. Nag, J. Inorg. Nucl. Chem., 40 (1978) 1501.
13 S.G. Manca and E.J. Baran, J. Phys. Chem. Solids, 42 (1981) 923.
14 D.F. Mullica, W.O. Milligan, D.A. Grossie, G.W. Beall and L.A. Bochter, Inorg. Chim. Acta, 95 (1984) 231.
15 S.G. Manca and E.J. Baran, J. Appl. Crystallogr., 15 (1982) 102.
16 A.S.T.M. Powder Diffraction File, 33–701.
17 B.V.R. Chowdari and Ravi Sekhar, J. Chem. Phys., 75 (1981) 2515.
18 N.S. Dallal, A.H. Reddoch and D.J. Nothcott, Chem. Phys. Lett., 58 (1978) 533.