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Note

Thermal analysis of lanthanide perchlorates

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The study of the lanthanide ions in non-aqueous solvents gives a remarkable contribution to the understanding of their coordinative behaviour, since the presence of water tends to make the characteristics of the different ions similar. However, the preparation of soluble dehydrated salts presents some difficulty, owing to the strong affinity of these salts towards water. In particular, the perchlorates are salts of remarkable interest since the anion, among the most common ones, is that which has the slightest tendency to coordinate. The fact that the 'thermal stability' of these hydrated species is comparable to that of the perchloric anion has led to the research and to the use of non-thermal methods of dehydration in addition to thermal methods[1–3], but the reported experimental conditions are rather generical and control systems on the validity of these methods have not been indicated. We have investigated the influence of physical parameters on the thermal behaviour of the hydrated lanthanide perchlorates with the aim to identify the best conditions for the preparation of the anhydrous species.

The investigated hydrated lanthanide perchlorates (all except Pm, Tb, and Lu) were prepared by treating the corresponding oxides with a 30% solution of perchloric acid and then evaporating to dryness[1]. TG, DTG and DTA analyses were carried out with a Mettler thermoanalyzer at heating rates of 0.5, 2 and 4°C min^{-1} in nitrogen atmosphere at pressures of 0.01 and 1 mm Hg. Other experiments were carried out at a pressure of 0.01 mm Hg, heating at 0.5°C min^{-1} and successively holding the system under isothermal conditions at chosen temperatures between 150 and 250°C; heating was started when the sample had reached weight constancy.

The thermogravimetric curves obtained in the experiments carried out at a heating rate of 0.5°C min^{-1} and a pressure of 0.01 mm Hg are reported in Fig. 1. The separation of the dehydration process from the decomposition of the perchloric group appears satisfactory, in regard to preparative purpose, for the lighter lanthanides. In every case, in the temperature range of existence of the anhydrous species, the TG curve shows a weight loss, though very slow for the lighter lanthanides. It seems reasonable that the slope of the corresponding line is associated to the dehydration degree of the investigated sample. In Table 1 we report the slope values for TG curves at a heating rate of 0.5°C min^{-1} together with the temperature ranges of the

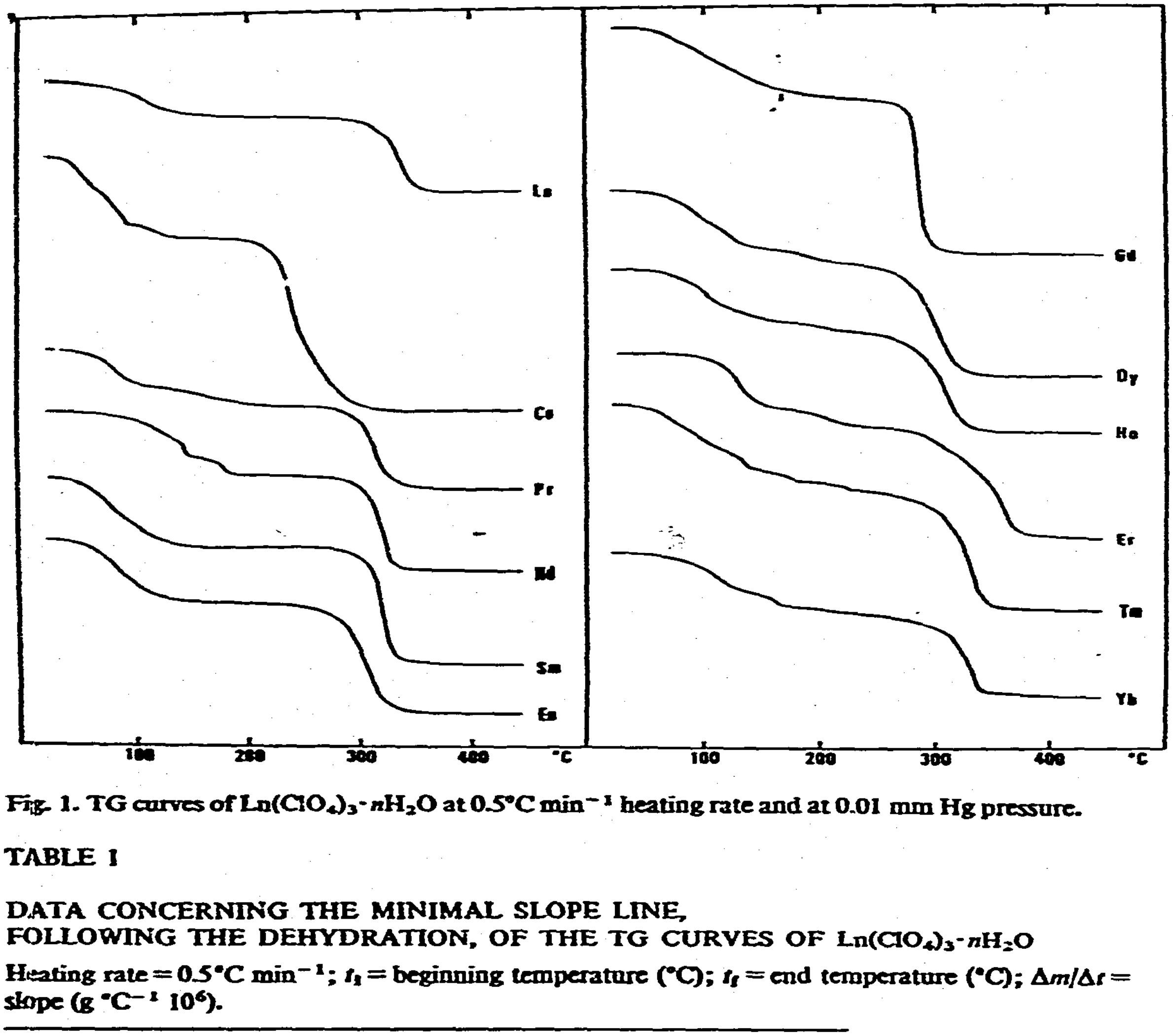

Fig. 1. TG curves of $Ln(ClO_4)_3 \cdot nH_2O$ at 0.5°C min^{-1} heating rate and at 0.01 mm Hg pressure.

TABLE I

DATA CONCERNING THE MINIMAL SLOPE LINE, FOLLOWING THE DEHYDRATION, OF THE TG CURVES OF $Ln(ClO_4)_3 \cdot nH_2O$

Heating rate = 0.5°C min^{-1}; t_i = beginning temperature (°C); t_f = end temperature (°C); $\Delta m/\Delta t$ = slope (g °C^{-1} 10^6).

Lanthanide	*p = 1 mm Hg*			*p = 0.01 mm Hg*		
	t_i	t_f	$\Delta m/\Delta t$	t_i	t_f	$\Delta m/\Delta t$
La	206	274	16	186	312	4
Ce	204	222	28	130	198	4
Pr	226	290	8	170	289	5
Nd	206	282	9	208	298	3
Sm	206	250	16	148	280	2
Eu	202	252	14	152	260	5
Gd	202	254	13	186	256	7
Dy	[a]	[a]	[a]	190	246	13
Ho	[a]	[a]	[a]	218	248	33
Er	[b]	[b]	[b]	204	266	13
Tm	[a]	[a]	[a]	188	252	16
Yb	[b]	[b]	[b]	174	250	46

[a] Experiment not performed. [b] The TG curve has an almost constant slope until nearly complete decomposition.

minimal slope line for different pressures. The pressure influences the dehydration process more than the decomposition of the perchloric group. Thus by decreasing the pressure, the formation of anhydrous perchlorates is favoured. It can be expected that also the anhydrous perchlorates of the heavier lanthanides can be obtained by thermal methods under higher vacuum.

The data of the TG curves at heating rates of 2 and 4°C min^{-1} were not reported because it was impossible to identify lines with minimal slope owing to the sharp overlapping of the decomposition to the dehydration. Although these results show that it is convenient to operate at lower heating rates, it has been impossible to obtain the anhydrous perchlorates of the heavier lanthanides, in the experiments carried out under isothermal conditions, in which we have observed two different behaviours depending on the temperature. At temperatures near the beginning of the minimal slope line, once obtained the weight constancy, raising the temperature at 0.5°C min^{-1}, another step due to water release is observed before the decomposition of the perchloric group. At higher temperatures, after a few days the TG curves showed a total weight loss too great to be due only to the water loss and the velocity of the process was still significant, indicating the overlapping of other processes to the water release.

The decomposition of the perchloric group, in the experiments carried out under non-isothermal conditions, gives rise to a definite reaction product that, when it has been possible to identify sharp steps of dehydration, corresponds stoichiometrically to the lanthanide chloride. The weight loss is comparatively fast and the start temperatures are remarkably higher than those used for the experiments carried out under isothermal conditions. The different behaviour observed at constant temperature can be explained by the occurrence of the perchlorates hydrolysis, due to the presence of unreleased water at higher temperature. The hydrolysis occurs also under non-isothermal conditions, but the process is slow and the amount of oxychloride formed, at 0.5°C min^{-1} heating rate, in the time necessary to reduce the perchlorate to chloride, is small.

In order to obtain the anhydrous perchlorates, it seems convenient to operate at a very low pressure and at a heating rate that satisfies both the needs to finish the dehydration and to keep the formation of oxychlorides within an acceptable level.

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