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THERMAL DECOMPOSITION OF LIGHT LANTHANIDE DIGLYCOLATES

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The conditions of thermal decomposition of La, Ce(III), Pr, Nd, Sm, Eu and Gd diglycolates have been studied. On heating, the diglycolates of Ce(III), Pr, Eu and Gd lose crystallization water and yield anhydrous salts, which are then transformed into oxides.

The diglycolates of La, Nd and Sm are decomposed in three stages. First, the diglycolates undergo dehydration to form the anhydrous salts, which are next decomposed to $Ln_2O_2CO_3$. In the last step the thermal decomposition of $Ln_2O_2CO_3$ to Ln_2O_3 takes place, accompanied by an endothermic effect.

Much work is currently being carried out on the thermal decompositions of rare earth carboxylates [1–7], to understand the mechanisms of the decompositions and the nature of the decomposition products. A search of the available literature showed that the thermal decomposition of rare earth diglycolates has not been studied so far. In a continuation of our work on the thermal decomposition of rare earth carboxylates [8–10], we now report the thermal decomposition of light lanthanide diglycolates.

Experimental

Diglycolates of La, Ce, Pr, Nd, Sm, Eu and Gd were prepared by dissolving freshly precipitated lanthanide hydroxides in the equivalent amount of hot diglycolic acid solution and crystallizing. The solids formed were filtered off, washed with hot water and dried at 303 K to constant mass. The diglycolates of the light lanthanides were obtained in crystalline form and with the colours characteristic for Ln^{3+} ions.

The contents of carbon and hydrogen were determined by elemental analysis. The contents of rare earth elements were determined by ignition of the products to oxides at 1173 K. The elemental analysis data are given in Table 1.

From the results obtained the diglycolates of La, Ce, Pr, Nd, Sm, Eu and Gd were found to be hydrated salts. Diglycolates of La and Ce were obtained as enneahydrates, and those of Pr, Nd, Sm, Eu and Gd as octahydrates.

IR spectra of diglycolic acid and the prepared complexes were also recorded over the range 4000–400 cm^{-1}.

Table 1

Analytical data

Compound	% Metal		% Carbon		% Hydrogen	
	found	calc.	found	calc.	found	calc.
$La_2(C_4H_4O_5)_3 \cdot 9H_2O$	33.21	33.23	17.21	17.22	3.86	3.61
$Ce_2(C_4H_4O_5)_3 \cdot 9H_2O$	33.38	33.43	17.18	17.17	3.54	3.57
$Pr_2(C_4H_4O_5)_3 \cdot 8H_2O$	34.26	34.28	16.47	17.52	3.41	3.41
$Nd_2(C_4H_4O_5)_3 \cdot 8H_2O$	34.85	35.92	17.31	17.38	3.38	3.37
$Sm_2(C_4H_4O_5)_3 \cdot 8H_2O$	35.92	35.76	17.33	17.12	3.30	3.33
$Eu_2(C_4H_4O_5)_3 \cdot 8H_2O$	35.98	36.01	17.26	17.06	3.52	3.31
$Gd_2(C_4H_4O_5)_3 \cdot 8H_2O$	36.70	36.74	16.88	16.85	3.20	3.27

Analysis of the IR spectra confirms the elemental analysis data.

The thermal stabilities of the prepared complexes were studied by the use of TG, DTA and DTG techniques. The measurements were made with the OD-102 derivatograph at a heating rate of 9°/min.

The recorded TG, DTG and DTA curves are given in Figs 1–7. From the thermal curves of the diglycolates, the temperatures of thermal decomposition were evaluated and are presented in Table 2, where:

ΔT_1 = temperature range (K) corresponding to the endothermic loss of a given number of crystallization water molecules;

ΔT_2 = temperature range (K) corresponding to the decomposition of the anhydrous salt and deflagration of the carbon residue until the formation of oxides;

ΔT_{min} = temperature (K) corresponding to the minimum in the DTA curve;

ΔT_k = temperature of oxide formation.

The results indicate that the diglycolates of Ce(III), Pr, Eu and Gd decompose in two stages.

Table 2

Temperature data on thermal decompositions of La and light lanthanide diglycolates

Compound	ΔT_1, K	ΔT_2, K	T_{min}, K	T_K, K
$La_2(C_4H_4O_5)_3 \cdot 9H_2O$	323–563	593–1073	458	1093
$Ce_2(C_4H_4O_5)_3 \cdot 9H_2O$	303–553	573– 863	463	923
$Pr_2(C_4H_4O_5)_3 \cdot 8H_2O$	333–493	633–1023	463	1073
$Nd_2(C_4H_4O_5)_3 \cdot 8H_2O$	313–533	588–1083	463	1123
$Sm_2(C_4H_4O_5)_3 \cdot 8H_2O$	333–493	633–1053	463	1103
$Eu_2(C_4H_4O_5)_3 \cdot 8H_2O$	313–473	543– 963	453	1073
$Gd_2(C_4H_4O_5)_3 \cdot 8H_2O$	323–503	633–1023	463	1113

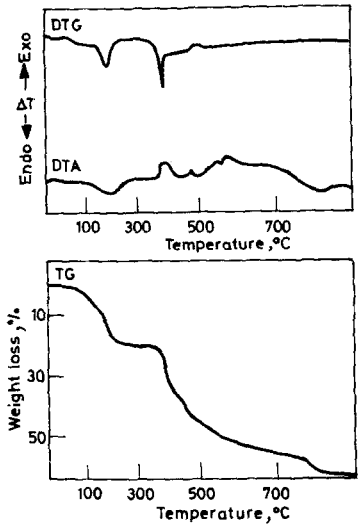

Fig. 1. TG, DTG and DTA curves of $La_2(C_4H_4O_5)_3 \cdot 9H_2O$

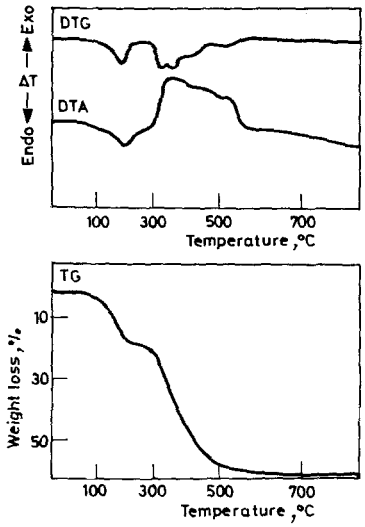

Fig. 2. TG, DTG and DTA curves of $Ce_2(C_4H_4O_5)_3 \cdot 9H_2O$

In the first stage, at 303–553 K, the diglycolates undergo dehydration with an accompanying strong endothermic effect, and the anhydrous complexes are then decomposed to oxides in the temperature range 923–1113 K. The diglycolates of La, Nd and Sm are found to decompose in three steps.

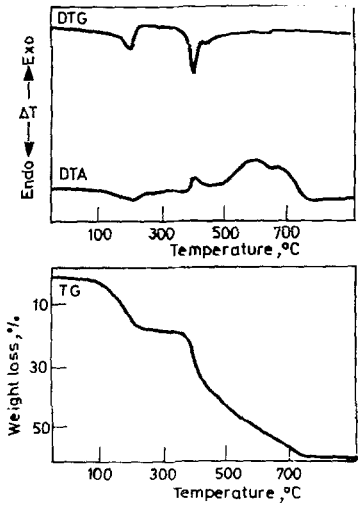

Fig. 3. TG, DTG and DTA curves of $Pr_2(C_4H_4O_5)_3 \cdot 8H_2O$

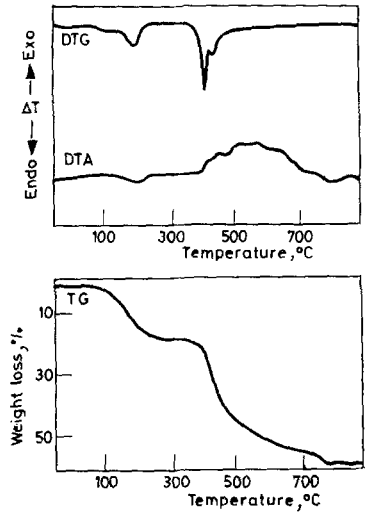

Fig. 4. TG, DTG and DTA curves of $Nd_2(C_4H_4O_5)_3 \cdot 8H_2O$

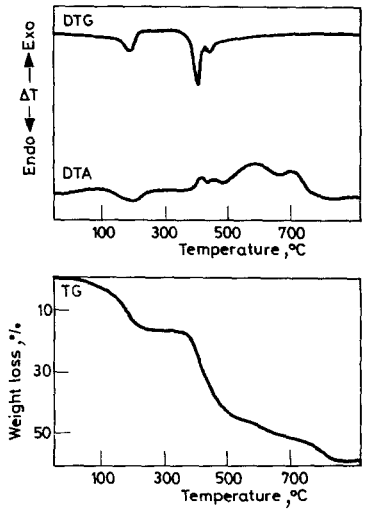

Fig. 5. TG, DTG and DTA curves of $Sm_2(C_4H_4O_5)_3 \cdot 8H_2O$

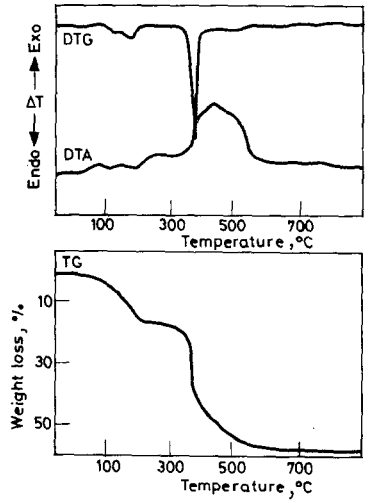

Fig. 6. TG, DTG and DTA curves of $Eu_2(C_4H_4O_5)_3 \cdot 8H_2O$

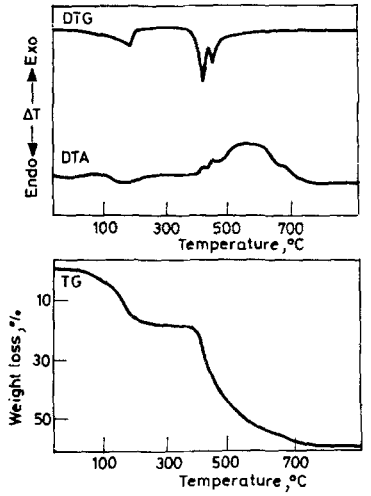

Fig. 7. TG, DTG and DTA curves of $Gd_2(C_4H_4O_5)_3 \cdot 8H_2O$

On heating, the hydrated complexes undergo dehydration, forming the anhydrous salts, which are ultimately decomposed to Ln_2O_3 with intermediate formation of $Ln_2O_2CO_3$. The thermal decomposition of $Ln_2O_2CO_3$ to Ln_2O_3 is accompanied by an endothermic effect.

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RÉSUMÉ — La décomposition thermique des diglycolates de La, Ce(III), Pr, Nd, Sm, Eu et Gd a été étudiée. Les diglycolates de Ce(III), Pr, Eu et Gd perdent leur eau de cristallisation par chauffage et fournissent des sels anhydres qui se transforment ensuite en oxydes.

Les diglycolates de La, Nd et Sm se décomposent en trois étapes, avec formation successive du sel anhydre, de $Ln_2O_2CO_3$ et de Ln_2O_3.

ZUSAMMENFASSUNG — Die Bedingungen der thermischen Zersetzung von La-, Ce(III)-, Pr-, Nd-, Sm-, Eu(III)- und Gd-Diglykolaten wurden untersucht. Die wasserhaltigen Diglykolate von Ce(III), Pr- und Eu(III) gehen beim Erhitzen in wasserfreie Salze über, die später zu Oxiden zersetzt werden. Die Zersetzung der La-, Nd- und Sm-Diglykolate ist dreistufig. Erst gehen die Hydrate in wasserfreie Salze über. Dann erfolgt die Zersetzung dieser Salze über die Oxycarbonate in die Oxide.

Резюме — Исследованы условия термического разложения дигликоятов La, Ce(III), Pr, Nd, Sm, Eu и Gd. Дигликоляты Ce(III), Pr, Eu и Gd теряют кристаллизационную воду, давая безводные соли, которые затем превращаются до окисей. Дигликоляты La, Nd и Sm разлагаются в три стадии. Сначала они подвергаются процессу дегидратации, образуя безводные соли, разлагающиеся затем до $Ln_2O_2CO_3$. Конечной стадией является разложение $Ln_2O_2CO_3$ до Ln_2O_3, сопровождающееся эндотермическим эффектом.