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SODIUM OXALATOMETALLATES OF RARE EARTHS(III) (LANTHANONS)

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Abstract

On the basis of uniform methodics, oxalatometallates of rare earths(III) with sodium, were synthesized. The compounds were obtained by adding saturated solution of sodium oxalate to 1 M solutions of $Ln(NO_3)_3$ in a molar ratio $Na_2C_2O_4/Ln^{3+}$ not lower than 5. X-ray powder diffraction photographs were used for the classification of the isolated compounds into five, internally isostructural groups.

Keywords: double oxalates, rare earths (lanthanons), sodium

Introduction

This paper reports on the oxalatometallates of lanthanons(III) and sodium. $La_2(C_2O_4)_3{\cdot}Na_2C_2O_4{\cdot}xH_2O$ and $La_2(C_2O_4)_3{\cdot}2Na_2C_2O_4{\cdot}yH_2O$ [1], $NaCe(C_2O_4)_2{\cdot}3H_2O$ and $Na_4Ce_2(C_2O_4)_5{\cdot}10H_2O$ [2], $NaCe(C_2O_4)_2{\cdot}6H_2O$ [3], $NaGd(C_2O_4)_2{\cdot}3H_2O$ [4], $NaYb(C_2O_4)_2{\cdot}4H_2O$ [5], $NaSm(C_2O_4)_2{\cdot}4H_2O$ [6] and $NaSm(C_2O_4)_2{\cdot}3.5H_2O$ [7] have been synthesized and their thermal decomposition have been studied.

The present investigation were carried out in order to establish the formation of complexes of Ln(III) with sodium oxalate and to study their thermal behaviour under constant conditions over the temperature range 25–500°C. This study is a continuation of our work on the oxalates complexes of trivalent lanthanons with different monovalent cations [8–11].

Experimental

Starting substances for the synthesis of double oxalates were rare earth(III)oxides, guaranteed pure 99.9%, referring to the corresponding element from the firm Koch-Light Laboratories, Colnbrook, England, as a source for preparation of corresponding nitrates. Compounds were isolated by adding saturated solution of sodium oxalate to 1 M solutions of $Ln(NO_3)_3$, at room temperature at a pH around 6. The rare earth(III) was determined by gravimetry as rare earth(III)oxides, after precipitation as rare earth(III)oxalate and ignition [12]. The oxalate group was determined permanganometrically.

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Powder photographs with Guinier-de Wolf camera with CuK_α radiation were taken for all isolated compounds.

The conditions of thermal analysis were as follows: Mettler's thermoanalysator [13] with combined TD1 measuring head, rate of heating 4°C min^{-1}, dry air 5 l h^{-1}, mass 50 mg and α-Al_2O_3 as the reference material for DTA.

Results and discussion

The compounds in Table 1, were isolated with the molar ratio $Na_2C_2O_4/Ln^{3+}=5/l$. A survey over the table leads us to the conclusion that the stoichiometry of $NaLn(C_2O_4)_2{\cdot}nH_2O$ (where n=5.5 for Pr and Nd, n=5 for Sm–Dy and n=4.5 for Ho–Y) is principal. Larger deviations appear only in the case of the compounds with La, Ce and Lu. Another case of stoichiometry appears for La, Ce and Lu at a ratio $Ln^{3+}/C_2O_4^{2-}=2/5$. With other rare earth(III) elements the ratio $Ln^{3+}/C_2O_4^{2-}=1/2$ appears. On the basis of X-ray diffraction patterns all isolated compounds can be divided into following five isostructural groups:

1. $Na_4Ln_2(C_2O_4)_5{\cdot}11H_2O$ (*Ln*=La, Ce)
2. $NaLn(C_2O_4)_2{\cdot}5.5H_2O$ (*Ln*=Pr, Nd)
3. $NaLn(C_2O_4)_2{\cdot}5H_2O$ (*Ln*=Sm–Dy)
4. $NaLn(C_2O_4)_2{\cdot}4.5H_2O$ (*Ln*=Ho–Yb, Y)
5. $Na_4Ln_2(C_2O_4)_5{\cdot}11H_2O$ (*Ln*=Lu)

In the thermal analysis, the first step is the thermal dehydration of compounds and the second exothermic oxidation of oxalate ion. Their TG, DTG and DTA are given in Fig. 1 a–n. It is seen that the dehydration begins at a temperature lower than 100°C. The complexes $Na_4La_2(C_2O_4)_5{\cdot}11H_2O$ and $Na_4Ce_2(C_2O_4)_5{\cdot}11H_2O$ lose all their water in a single stage (mass loss: calculated 19.65%, found 19.8% for La, and calculated 19.59% and found 18.81% for Ce) with an endothermic peak at 100°C (La) and at 110°C (Ce). Although the thermal decomposition are similar, therefore, the thermal decomposition should be discussed for each isostructural group. The thermal decomposition of the Pr and Nd compounds takes place only in two stages. In the first stage dehydration occurs. The Pr and Nd compounds lose water in the temperature 150°C (calc. value 22.55%, found 22.06% for Pr compound and calc. value 22.39%, found 21.60% for Nd compound). In the second stage of thermal decomposition, the decomposition of the anhydrous double salt to sodiumoxalatometallates takes place in both cases. The final product of thermal decomposition at 500°C is the corresponding basic carbonate ($Ln_2O_2{\cdot}CO_3$) and sodium carbonate in both cases (calc. value for $Na_2CO_3+Pr_2O_2{\cdot}CO_3$ is 43.66%, found 43.79%, calc. value for $Na_2CO_3+Nd_2O_2{\cdot}CO_3$ is 43.87, found 43.14%). In the DTA curve (Fig. 1c, d) for the Pr compound there is an endothermic peak at 395°C and for the Nd compound at 400°C.

In the dehydration of the double salts of Sm–Dy five moles of water are lost in two very close steps at similar temperature interval 25–200°C. In the first step of the decomposition the compounds lose four water moles, represented by the endothermic peak at 60°C (Sm, Eu), at 80°C (Tb) and at 75°C (Gd, Dy) in the DTA curves

Table 1 Analytical data of the compounds and calculated values

No.	Compound	Found/%			Calculated/%			
		Ln	C_2O_4	H_2O	*Ln*	C_2O_4	H_2O	Na
1	$Na_4La_2(C_2O_4)_5·11H_2O$	27.23	43.24	19.18	27.56	43.65	19.65	9.12
2	$Na_4Ce_2(C_2O_4)_5·11H_2O$	27.80	43.45	18.81	27.74	43.55	19.59	9.10
3	$NaPr(C_2O_4)_2·5.5H_2O$	32.70	40.16	22.06	32.10	40.10	22.55	5.25
4	$NaNd(C_2O_4)_2·5.5H_2O$	33.29	40.71	21.60	32.62	39.79	22.39	5.19
5	$NaSm(C_2O_4)_2·5H_2O$	34.51	40.08	20.50	34.23	40.05	20.48	5.23
6	$NaEu(C_2O_4)_2·5H_2O$	34.38	39.96	20.35	34.46	39.91	20.40	5.21
7	$NaGd(C_2O_4)_2·5H_2O$	35.29	40.04	19.50	35.24	39.44	20.17	5.15
8	$NaTb(C_2O_4)_2·5H_2O$	35.86	39.23	20.25	35.48	39.29	20.10	5.13
9	$NaDy(C_2O_4)_2·5H_2O$	35.27	38.98	19.59	35.99	38.98	19.93	5.09
10	$NaHo(C_2O_4)_2·4.5H_2O$	36.72	40.15	18.72	37.07	39.56	18.21	5.17
11	$NaEr(C_2O_4)_2·4.5H_2O$	35.74	37.72	17.44	35.94	37.82	17.41	4.94
12	$NaTm(C_2O_4)_2·4.5H_2O$	37.31	39.01	18.37	37.63	39.20	18.04	5.12
13	$NaYb(C_2O_4)_2·4.5H_2O$	38.19	38.85	17.82	38.38	38.15	17.44	4.70
14	$Na_4Lu_2(C_2O_4)_5·11H_2O$	31.85	40.05	18.20	32.40	40.75	18.33	8.51
15	$NaY(C_2O_4)_2·4.5H_2O$	24.54	47.39	21.77	24.09	47.71	21.96	6.23

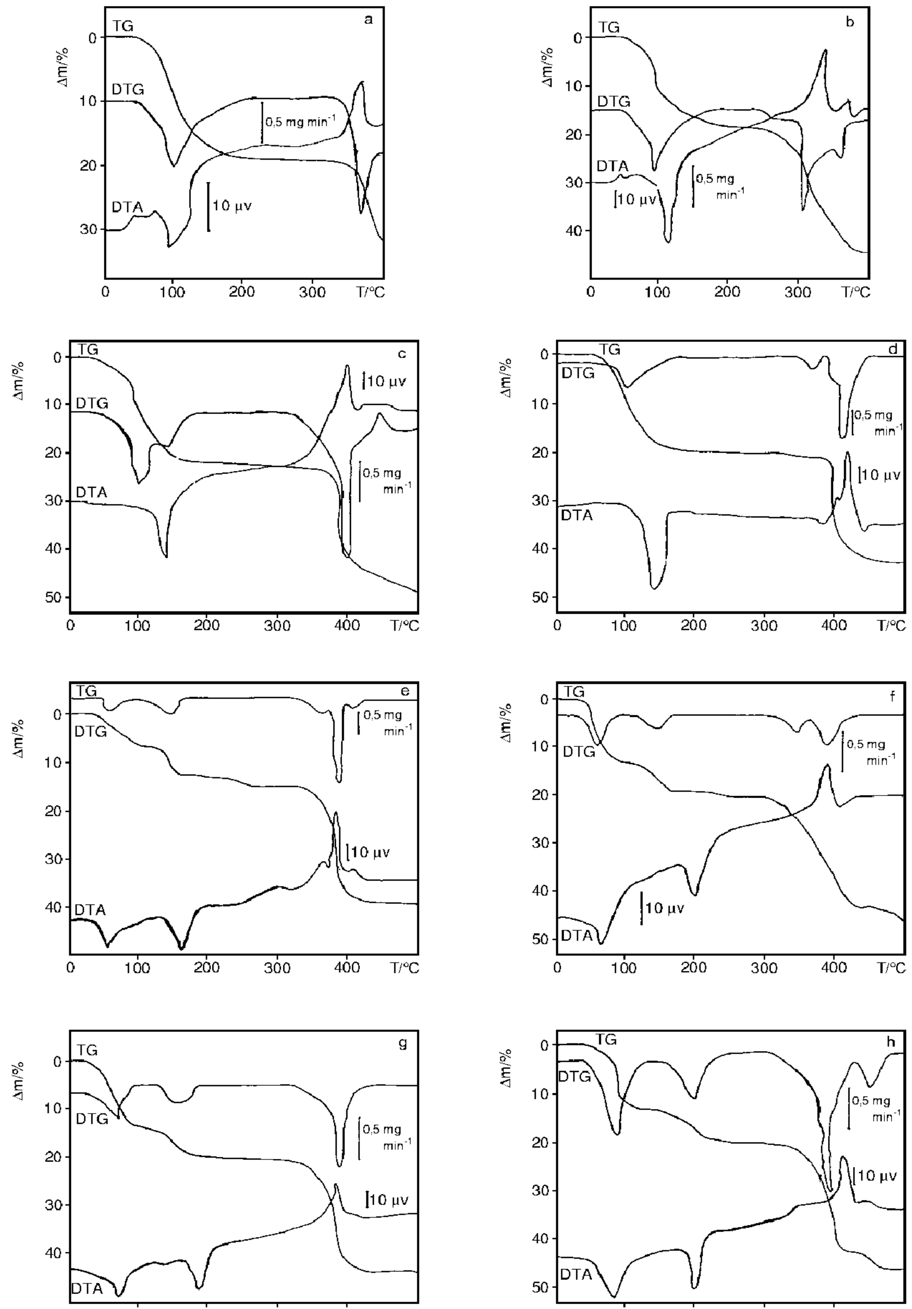

Fig. 1 TG, DTG and DTA curves of $Na_4Ln_2(C_2O_4)_5\cdot 11H_2O$: a – La; b – Ce; $NaLn(C_2O_4)_5\cdot 5.5H_2O$: c – Pr; d – Nd; $NaLn(C_2O_4)_2\cdot 5H_2O$: e – Sm; f – Eu; g – Gd; h – Tb

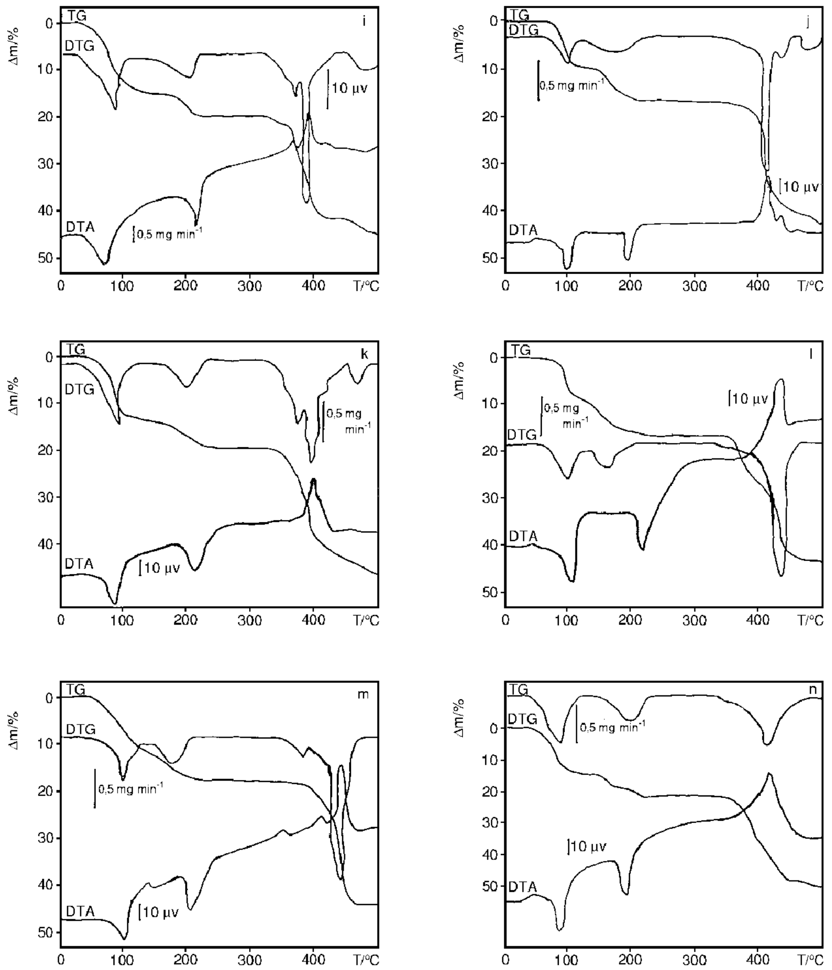

Fig. 1 Continued: TG, DTG and DTA curves of $Na_4Ln_2(C_2O_4)_5{\cdot}11H_2O$: i – Dy; $NaLn(C_2O_4)_2{\cdot}4.5H_2O$: j – Ho; k – Er; e – Tm; m – Yb; n – Y

(Fig. 1e–i). In the second step of the dehydration the compounds lose one water mole which is followed by an endothermic peak at 180°C (Sm), 195°C (Gd), 200°C (Eu, Tb) and at 225°C (Dy). Here, the isolation of monohydrates would probably be possible. Exothermic oxidation of oxalate occurs at the temperature 400±15°C regardless of the rare earth. The final product of thermal decomposition up to 500°C was the corresponding a mixture of sodium carbonate and either the basic carbonate ($Ln_2O_2{\cdot}CO_3$) for the double oxalates from Sm to Dy.

The thermal decomposition of the Ho–Yb and Y compound is very similar to that of Sm–Dy compounds. In the temperature range 25–200°C the compound lose 4.5 water moles in two steps. In the DTA curves (Fig. 1 j–n) there are two endothermic peaks. In the temperature 100°C (Ho, Tm, Yb) and 85°C (Er, Y) compounds lose four water moles. In the second step of dehydration the compounds lose the remaining 0.5 water moles. The first and the second steps for the compounds from Ho–Yb correspond to the formation of sesquihydrates. The final product of thermal decomposition up to 500°C was corresponding a mixture of sodium carbonate and either the basic carbonate ($Ln_2O_2{\cdot}CO_3$) in all cases, as concluded from the X-ray powder diffraction patterns of the residues, and also from the calculated and experimentally found values. An exception is the cerium compound where CeO_2 and Na_2CO_3 were obtained (calculated value for Na_2CO_3+CeO_2 is 44.93%, found 44.04%). The DTA maximal for the Ce compound is reached at 300°C, probably because of formation of CeO_2.

The X-ray powder diffraction patterns showed that the double oxalates of $NaLn(C_2O_4){\cdot}5H_2O$ and $KLn(C_2O_4)_2{\cdot}4H_2O$ [10] (*Ln*=Sm–Dy) are isomorphous. The TG and DTA curves (Fig. 1 e–i) and (Fig. 1 d, e) [10] are similar, indicating in general two stages of thermal decomposition in the temperature range 25–500°C. In the first stage dehydration occurs, and in the second stage of thermal decomposition the anhydrous double oxalate decomposes. The dehydration takes place in the temperature interval 75±10–200°C with different velocities. In the first step of the decomposition the Na compounds lose 4.5, and K compounds lose 3.5 water moles. The first and the second steps for the Na and K complexes at Sm–Dy correspond to the formation of sesquihydrates. The second stage of thermal decomposition of the sodium compounds is too very similar to that of the potassium compounds. The DTA maximal for the sodium and for the potassium compounds are at 400±10°C caused by the oxidation of oxalate ion. The final product of thermal decomposition up to 500°C was the corresponding mixture sodium or potassium carbonate and either basic earth(III)carbonate ($Ln_2O_2{\cdot}CO_3$ where *Ln*=Sm–Dy).

Thermal decomposition at higher temperature was not examined because of great possibility of corrosion of platinum vessels. The compounds of this type present a potential for the synthesis of the binary oxides of sodium or potassium and elements of rare earths.

All the samples were extremely dispersive and therefore Guinier diagrams were not very sharp. For more details, single crystal structures of the representatives of all Na and K compounds will be needed.

We had a lot of experiments to obtain the macrocrystals, suitable for the X-ray structural analysis. Unfortunately, without success, for now. According to the found structural data for the compounds: $NH_4Y(C_2O_4)_2{\cdot}H_2O$ [14], $K_3LnOX_3{\cdot}nH_2O$ (*Ln*=La–Tb), $K_8LnOX_7{\cdot}14H_2O$ (*Ln*=Tb–Yb, Y) [15], $K_3(LnOX_3{\cdot}H_2O){\cdot}H_2O$ (*Ln*=Nd, Sm, Gd, Tb) [16], the coordinate number of the lanthanon cation is 9 (nine). Because of this, we suppose that some parts of the water are coordinatively linked and probably some other parts of the water, are bridging ligands, as well as the oxalate ions.

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