

STUDIES ON THERMAL DECOMPOSITION OF RARE EARTH ELEMENT COMPLEXES WITH GLYCOLIC ACID

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The rare earth complexes with glycolic acid were prepared as crystalline solids with general formula $[\text{Ln}(\text{CH}_2\text{OHCOO})_3\text{H}_2\text{O}] \cdot n\text{H}_2\text{O}$, where $n=0$ for La-Gd and $n=2$ for Y and Tb-Lu. During heating the monohydrates of La and Pr-Gd decomposed in two steps to Ln_2O_3 and Pr_6O_{11} , with intermediate formation of $\text{Ln}_2\text{O}_2\text{CO}_3$; monohydrated Ce(III) glycolate decomposed directly to CeO_2 . The trihydrated glycolates of Y and Tb-Lu first lost two water molecules and the monohydrated complexes then decomposed to Ln_2O_3 and Tb_4O_7 through $\text{Ln}_2\text{O}_2\text{CO}_3$.

The complexes of glycolic acid with rare earth elements have been prepared by adding sodium or ammonium glycolate to a hot solution of a rare earth salt [1]. Hydrated salts with a metal to ligand ratio of 1:3 crystallized out. Jantsch and Grünkraut [2-4] prepared anhydrous glycolates of La-Eu and dihydrated glycolates of yttrium and heavy lanthanides, and determined the solubilities of some glycolates in water. Powell and Farrel [5] determined the solubilities of the rare earth glycolates in water at 293 and 333 K. More recently [6], the stability constants of glycolic acid complexes with the rare earth cations (III) from La to Lu were determined by potentiometric titration. Južnič [7] determined the stability constants of the Ce(III) complexes with glycolic acid by using the radioisotope ^{141}Ce . Kostromina [8] studied the complexation reaction in the system LaCl_3 -glycolic acid by using ion-exchange at $\text{pH} \sim 3$, and confirmed the formation of neutral, anionic and cationic complexes. Petrov et al. [9] studied the IR spectra of rare earth glycolates with the general formula $\text{Ln}[\text{CH}_2(\text{OH})\text{COO}]_3$, where $\text{Ln} = \text{Pr-Gd}$, and $\text{Ln}[\text{CH}_2(\text{OH})\text{COO}]_3 \cdot 2\text{H}_2\text{O}$, where $\text{Ln} = \text{Dy, Er and Tm}$. Analysis of the IR spectra confirmed the supposition that the Ln(III) cation is coordinated by the carboxylic and hydroxylic groups of glycolate ion.

The aim of our work was to obtain complexes of rare earth elements with glycolic acid and to examine their thermal stabilities during heating in air atmosphere.

Experimental

Complexes of Y, La, Ce(III), Pr(III), Nd, Sm, Eu(III), Gd, Tb(III), Dy, Ho, Er, Tm, Yb and Lu were prepared by dissolving freshly precipitated rare earth hydroxides in an equivalent amount of glycolic acid at 333 K and crystallizing. The solids formed were heated in the mother solution for 0.5 h, then filtered off, washed with water and dried at 303 K to constant mass.

The contents of carbon and hydrogen in the complexes prepared were determined on the basis of elemental analysis, with V_2O_5 as oxidizing agent. The contents of rare earth were determined from the TG curves and by ignition of the preparations to oxides Ln_2O_3 , CeO_2 , Pr_6O_{11} and Tb_4O_7 at 1173 K. The contents of water molecules were determined from the TG curves and by heating the complexes isothermally at 473 K. The elemental analysis data are given in Table 1.

The IR spectra of the prepared glycolates and of glycolic acid were recorded over the range $4000\text{--}400\text{ cm}^{-1}$ with a UR-20 spectrophotometer. The samples were recorded as KBr discs.

X-ray diffraction patterns of the complexes were recorded on a DRON-2 diffractometer, using CuK_α radiation. The measurements were made by the Debye-Scherrer method.

The thermal stabilities of the complexes were studied by means of TG, DTG and DTA techniques (Figs 3-7). The measurements were made with an OD-102

Table 1 Analytical data

Complex	Ln, %		C, %		H, %		Solubility $\text{mol}\cdot\text{dm}^{-3}\cdot 10^{-3}$
	calcd.	found	calcd.	found	calcd.	found	
Y[CH ₂ (OH)COO] ₃ ·3H ₂ O	24.16	24.20	19.57	19.60	4.07	0.05	5.60
La[CH ₂ (OH)COO] ₃ ·H ₂ O	36.37	36.40	18.85	18.88	2.88	2.90	7.60
Ce[CH ₂ (OH)COO] ₃ ·H ₂ O	36.57	36.50	18.79	18.80	2.86	2.90	9.01
Pr[CH ₂ (OH)COO] ₃ ·H ₂ O	36.70	36.75	18.75	18.70	2.86	2.88	10.03
Nd[CH ₂ (OH)COO] ₃ ·H ₂ O	37.25	37.20	18.59	18.60	2.84	2.85	11.30
Sm[CH ₂ (OH)COO] ₃ ·H ₂ O	38.55	38.60	18.46	18.55	2.82	2.84	20.82
Eu[CH ₂ (OH)COO] ₃ ·H ₂ O	38.48	38.50	18.23	18.30	2.78	2.80	20.34
Gd[CH ₂ (OH)COO] ₃ ·H ₂ O	39.28	39.30	17.99	18.00	2.75	2.70	22.28
Tb[CH ₂ (OH)COO] ₃ ·3H ₂ O	36.29	36.30	16.44	16.50	3.42	3.40	9.89
Dy[CH ₂ (OH)COO] ₃ ·3H ₂ O	36.80	36.85	16.30	1.30	3.39	3.40	6.54
Ho[CH ₂ (OH)COO] ₃ ·3H ₂ O	37.15	37.20	16.21	16.20	3.37	3.35	4.60
Er[CH ₂ (OH)COO] ₃ ·3H ₂ O	37.48	37.50	16.13	16.15	3.36	3.35	3.35
Tm[CH ₂ (OH)COO] ₃ ·3H ₂ O	37.77	37.80	16.05	16.10	3.34	3.35	2.27
Yb[CH ₂ (OH)COO] ₃ ·3H ₂ O	38.27	38.30	15.92	16.00	3.32	3.33	1.82
Lu[CH ₂ (OH)COO] ₃ ·3H ₂ O	38.54	38.60	15.86	15.90	3.30	3.32	0.50

derivatograph with a sensitivity $TG = 100$ mg. The samples were heated in ceramic crucibles in air atmosphere to 1273 K at a rate of $9 \text{ deg} \cdot \text{min}^{-1}$. The thermal curves were also recorded for the glycolates of heavy lanthanides heated isothermally at 473 K. The analysis and identification of the solid products were performed on the basis of the IR spectra. From the thermal curves, the thermal decomposition data of the prepared complexes were evaluated; they are presented in Table 2.

Results and discussion

The glycolates of Y, La and lanthanides from Ce(III) to Lu were prepared as crystalline solids. The complexes of Y, La, Ce(III), Sm, Eu(III), Gd, Tb, Dy, Tm, Yb and Lu were white, that of Pr green, and those of Nd and Er pink. They were hydrated compounds with a metal to ligand ratio of 1 : 3. The glycolates of La and the light lanthanides from Ce(III) to Gd were prepared as monohydrates, and those of Y and the heavy lanthanides from Tb to Lu as trihydrates (Table 1). The complexes prepared were characterized by a higher degree of hydration than those described in the literature [2-4, 9].

The IR spectra of the studied complexes are similar to one another. Analysis of the IR spectra confirms the suggested compositions of the complexes. When the acid is converted into a salt, the COOH group absorption band at 1720 cm^{-1} disappears, and two bands arising from symmetric and asymmetric vibrations of COO^- appear at $1600\text{--}1590 \text{ cm}^{-1}$ and $1410\text{--}1390 \text{ cm}^{-1}$, respectively. In the IR spectra of the prepared glycolates, the absorption bands of the alcoholic OH group appear at $1230\text{--}1220 \text{ cm}^{-1}$ and $1270\text{--}1260 \text{ cm}^{-1}$, the broad absorption band indicating the presence of crystallization water with max. at 3100 cm^{-1} and $3250\text{--}3200 \text{ cm}^{-1}$, the absorption bands of C—O at $1005\text{--}990 \text{ cm}^{-1}$ and $1080\text{--}1050 \text{ cm}^{-1}$, and the bands to the metal-oxygen bonds at $520\text{--}510$ and $560\text{--}530 \text{ cm}^{-1}$. In the IR spectra of the prepared glycolates, the absorption bands of $\nu\text{C—O}$ are displaced to lower frequencies and the bands of δOH to higher frequencies with respect to those for the free acid. The shifts in $\nu\text{C—O}$ are $10\text{--}40 \text{ cm}^{-1}$, and those in δOH are $10\text{--}20 \text{ cm}^{-1}$. These facts confirm the participation of the OH group in the formation of a coordination bond with the Ln(III) ion. The shifts are larger for the complexes of Y and heavy lanthanides than those for La and light lanthanides. The larger shifts for the heavy lanthanides glycolates may be connected with the higher ionic potential of the Ln(III) cation and the higher degree of hydration. The existence of hydrogen-bonds between the H_2O molecules and the glycolate ligand is confirmed by the absorption bands with maximum over the range $3100\text{--}3250 \text{ cm}^{-1}$. The obtained results confirm the suggestion of Petrov et al. [9] that the glycolate ligand

Table 2 Data on thermal decompositions of Y, La and lanthanide glycolates

Complex	Temperature range of dehydration, K.	Loss of weight, %		No. of H ₂ O molecules lost	Temperature range of decomposition, K	Loss of weight, %		Temperature of oxide formation, K
		calcd.	found			calcd.	found	
Y[CH ₂ (OH)COO] ₃ ·3H ₂ O	433-483	9.79	10.0	2	523-993	65.95	66.0	993
La[CH ₂ (OH)COO] ₃ ·H ₂ O	—	—	—	—	593-1093	57.32	57.5	1093
Ce[CH ₂ (OH)COO] ₃ ·H ₂ O	—	—	—	—	573-913	55.36	55.5	913
Pr[CH ₂ (OH)COO] ₃ ·H ₂ O	—	—	—	—	593-1033	55.63	55.5	1033
Nd[CH ₂ (OH)COO] ₃ ·H ₂ O	—	—	—	—	583-1093	56.61	57.0	1093
Sm[CH ₂ (OH)COO] ₃ ·H ₂ O	—	—	—	—	593-1053	55.80	55.0	1053
Eu[CH ₂ (OH)COO] ₃ ·H ₂ O	—	—	—	—	593-913	55.45	55.5	913
Gd[CH ₂ (OH)COO] ₃ ·H ₂ O	—	—	—	—	593-1053	54.75	54.5	1053
Tb[CH ₂ (OH)COO] ₃ ·3H ₂ O	413-493	8.22	8.5	2	523-1093	53.50	53.0	1093
Dy[CH ₂ (OH)COO] ₃ ·3H ₂ O	433-493	8.15	8.5	2	513-1033	54.00	54.0	1033
Ho[CH ₂ (OH)COO] ₃ ·3H ₂ O	433-493	8.10	8.5	2	513-1073	53.68	54.0	1073
Er[CH ₂ (OH)COO] ₃ ·H ₂ O	413-473	8.06	8.2	2	513-1043	53.38	53.3	1043
Tm[CH ₂ (OH)COO] ₃ ·3H ₂ O	433-493	8.00	8.3	2	533-993	53.15	53.5	993
Yb[CH ₂ (OH)COO] ₃ ·3H ₂ O	433-503	7.96	8.5	2	543-1003	52.65	52.5	1003
Lu[CH ₂ (OH)COO] ₃ ·3H ₂ O	423-493	7.93	8.0	2	553-1023	51.32	51.3	1023

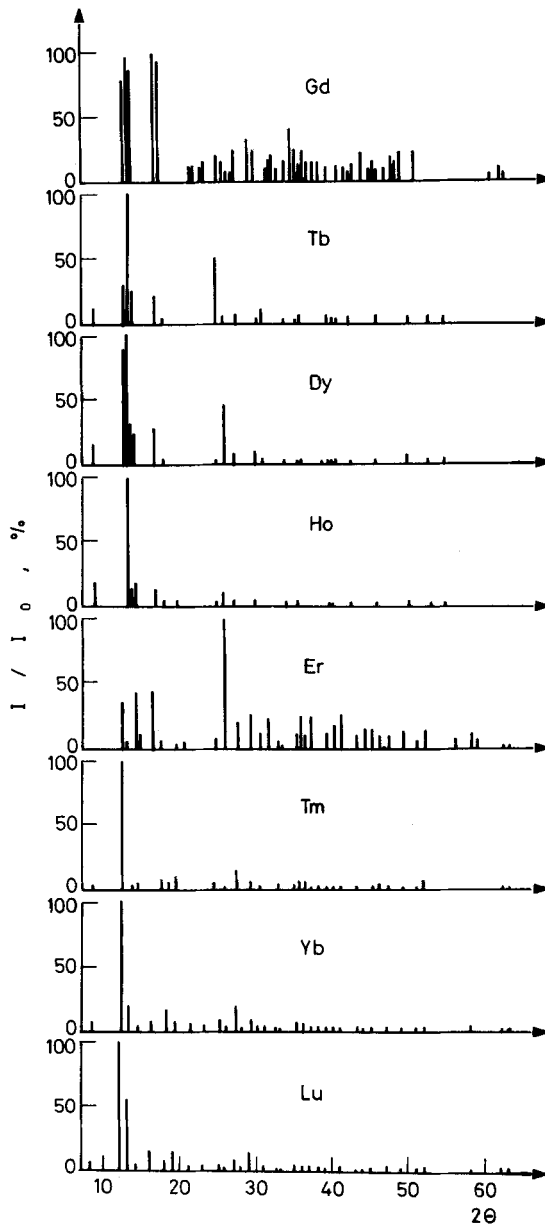


Fig. 1 X-ray spectra of Y, La and light lanthanide glycolates

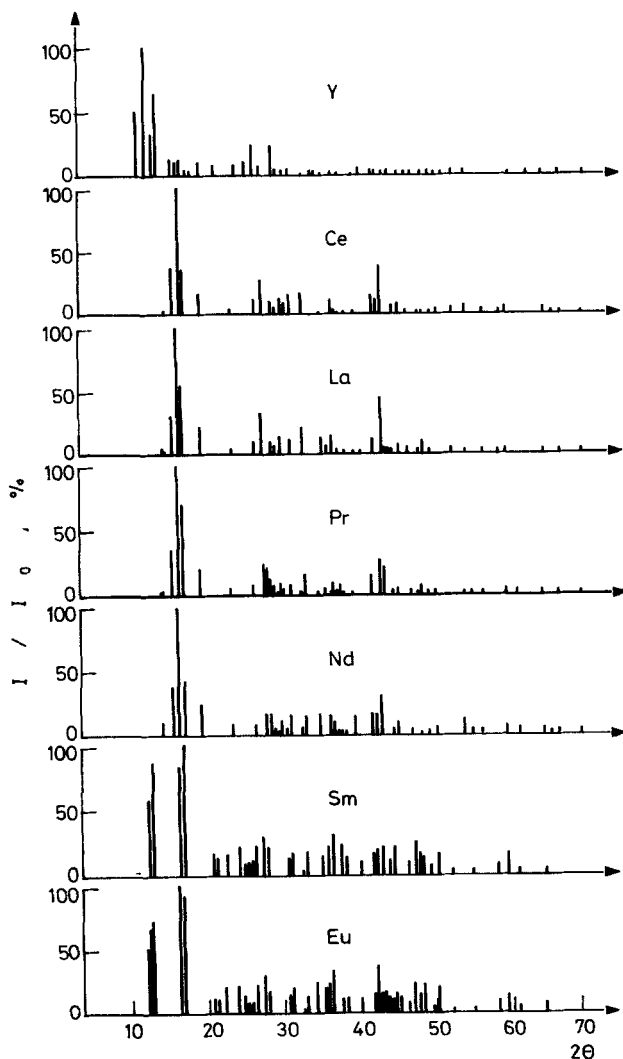


Fig. 2 X-ray spectra of heavy lanthanide glycolates

coordinates Ln ions via both carboxylate and alcoholic groups, forming chelate complexes.

From the recorded X-ray spectra (Figs 1 and 2), the glycolates of the rare earths were found to be crystalline compounds of low symmetry and large unit cells. They form groups of isostructural complexes: La–Nd, Sm–Eu, Tb–Ho and Tm–Lu.

By analysis of the thermal curves recorded on the prepared complexes, the data

and products of thermal decomposition were evaluated (Table 2). The data are presented in Figs 3–7.

The results demonstrated that the glycolates of the rare earth decompose in various ways. The monohydrates of the La, Ce(III), Pr(III), Nd, Sm, Eu(III) and Gd salts are stable up 593 K, and then lose crystallization water and simultaneously

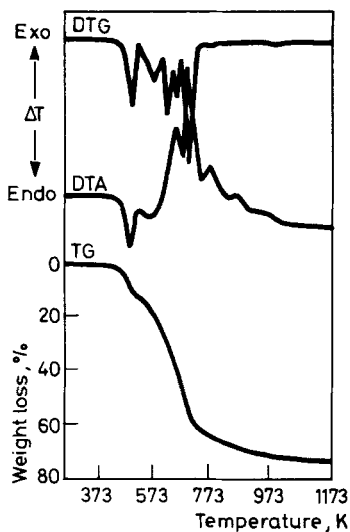


Fig. 3 Tg, DTG and DTA curves of $Y(CH_2OHCOO)_3 \cdot 3H_2O$

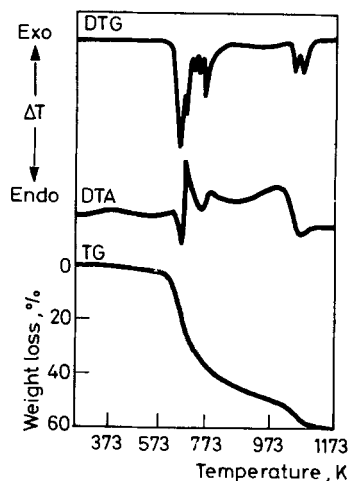


Fig. 4 TG, DTG and DTA curves of $La(CH_2OHCOO)_3 \cdot H_2O$

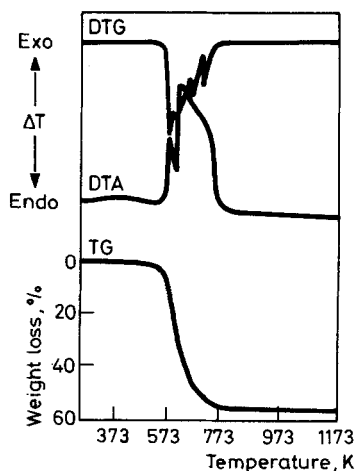


Fig. 5 TG, DTG and DTA curves of $Ce(CH_2OHCOO)_3 \cdot H_2O$

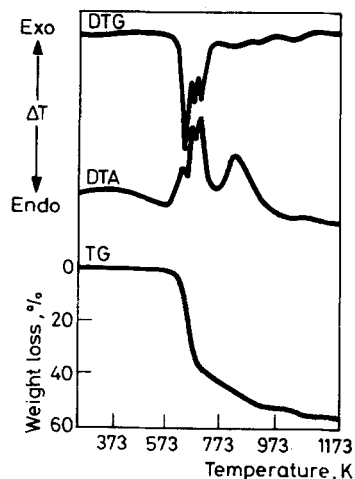


Fig. 6 TG, DTG and DTA curves of $Gd(CH_2OHCOO)_3 \cdot H_2O$

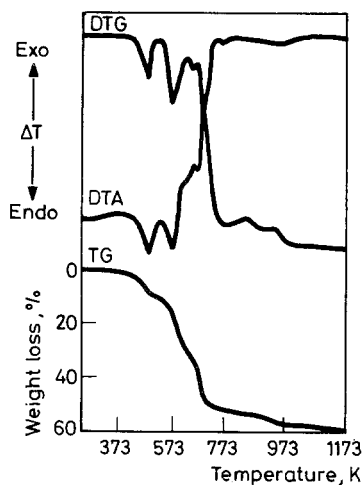


Fig. 7 TG, DTG and DTA curves of $\text{Tm}(\text{CH}_2\text{OHCOO})_3 \cdot 3\text{H}_2\text{O}$

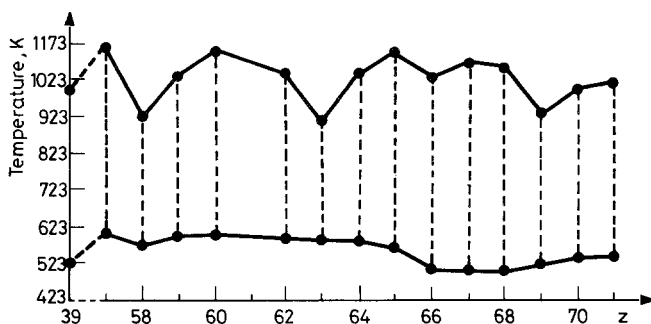
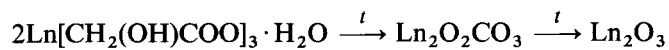
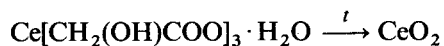
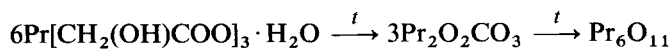


Fig. 8 Relationship between temperatures of complex decomposition and oxide formation and Z

decompose according to the scheme:



(Ln = La, Nd, Sm, Eu and Gd)



The dehydration and simultaneous decomposition are connected with a strong endothermic effect, and the ignition of the organic ligand with an exothermic one.

The trihydrated complexes of Y, Tb(III), Dy, Ho, Er, Tm, Yb and Lu decompose in three steps. In the first step, at 433 K, they lose two water molecules and then decompose to the oxides Ln_2O_3 or Tb_4O_7 through $\text{Ln}_2\text{O}_2\text{CO}_3$.

Three endothermic effects are observed in the DTA curves. The first is connected with the loss of two water molecules, the second with dehydration and simultaneous decomposition of glycolate, and the third with decomposition of $\text{Ln}_2\text{O}_2\text{CO}_3$. Ignition of the organic ligand is connected with a strong exothermic effect.

The X-ray spectra recorded when the heavy lanthanide glycolates are heated isothermally at 473 K are of the same form as those for the monohydrates of the light lanthanides. They are very stable up to 513–593 K.

The results indicate that the crystallization water in the monohydrates is inner sphere water, while the water molecules in the trihydrates are bound in various ways. Two water molecules, relatively weakly bonded, are outer sphere water, whereas the water molecule lost during the decomposition process is inner sphere water. From these results it is possible to suggest the following formula for the prepared complexes:



where $n=0$ for La–Y and $n=2$ for Y and Tb–Lu.

The temperatures of glycolates decomposition and oxide formation vs. lanthanide atomic number Z are presented in Fig. 8. The temperature of oxide formation varies periodically with increasing Z and ionic potential in the rare earth series. The double–double effect is observed. The temperatures of decomposition of the complexes are lower for the heavy rare earths than for the light ones, which is caused by the higher degree of hydration and the difference in the bonding of the water molecules.

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Zusammenfassung — Komplexe der Seltenerden mit Glykolsäure wurden in Form von kristallinen Substanzen mit der allgemeinen Formel $[\text{Ln}(\text{CH}_2\text{OHCOO})_3 \cdot \text{H}_2\text{O}] \cdot n\text{H}_2\text{O}$ mit $n=0$ für La–Gd und $n=2$ für Y und Tb–Lu dargestellt. Die Monohydrate von La und Pr–Gd zersetzen sich beim Erhitzen in zwei Stufen über die Zwischenstufe $\text{Ln}_2\text{O}_2\text{CO}_3$ in Ln_2O_3 und Pr_6O_{11} . Das Monohydrat von Ce(III) glykolat zerfiel direkt in CeO_2 . Die Trihydrate der Glykolate von Y und Tb–Lu gaben zunächst zwei Moleküle Wasser ab und die so entstandenen Monohydratkomplexe zersetzen sich dann über $\text{Ln}_2\text{O}_2\text{CO}_3$ in Ln_2O_3 bzw. Tb_4O_7 .

Резюме — Получены кристаллические комплексы редкоземельных элементов с гликолевой кислотой общей формулы $[\text{Ln}(\text{CH}_2\text{OHCOO})_3 \cdot \text{H}_2\text{O}] \cdot n\text{H}_2\text{O}$, где $n=0$ для La–Gd и $n=2$ для иттрия и Tb–Lu. При нагревании моногидраты лантана и Pr–Gd разлагаются в две стадии до соответствующих окислов Ln_2O_3 и Pr_6O_{11} с образованием промежуточного продукта $\text{Ln}_2\text{O}_2\text{CO}_3$. Моногидрат гликолята трехвалентного церия разлагается прямо до CeO_2 . Тригидраты гликолятов иттрия и Tb–Lu сначала теряют две молекулы воды, а образующиеся моногидраты затем разлагаются до Ln_2O_3 и Tb_4O_7 через промежуточную стадию образования $\text{Ln}_2\text{O}_2\text{CO}_3$.