

Alexander DRYUCHKO
Dmitriy STOROZHENKO
Natalia BUNYAKINA
Irina IVANYTSKA
Alexander KULCHIY
Dmitriy GOLUBATNIKOV

Poltava National Technical University Named in Honor of Yuri Kondratyuk, Ukraine

e-mail: dog.chemistry@mail.ru

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PHYSICO-CHEMICAL ASPECTS OF USING REE-CONTAINING NITRATE SYSTEMS IN FORMING MULTICOMPONENT OXIDE FUNCTIONAL MATERIALS

Abstract: *For obtaining the nanosized inorganic materials on oxides of transition and rare earth elements, the most promising is the use of methods of “soft chemistry” based on synthesis from aqueous or non-aqueous solutions at relatively low temperatures. Their key advantages are: the possibility of obtaining products with controlled composition and micromorphology, efficiency, environmental acceptance and so on.*

Keywords: *nanoscale materials, properties of bulk materials, inorganic materials on oxides.*

Statement of the problem

Considerable attention that now is being paid to the study of nanoscale materials, primarily, is due to significant differences of their properties from the properties of bulk materials of the same composition and is the result of detection by them of quantum effects.

Unfortunately, the vast majority of the currently known studies does not make it possible to formulate general principles for creation of nanomaterials possessing the assigned composition, micro- and mesostructure, functional characteristics. The main reason for this is that the mechanism of nanoparticles formation in these conditions is rather complex from physico-chemical point of view and may include parallel processes of hydration (solvation), association, complexation, formation and transformation of heterophases, laws of which are poorly understood. In this regard, one of the main challenges in the development of reproducible methods for the directed synthesis of nanodispersed materials using approaches of “soft chemistry” is a detailed study of mechanisms and dynamics of processes taking place during formation of nanoparticles. Such fundamental study envisages a systematic study of the composition and micromorphology of intermediate compounds, that in most cases determine the microstructure and structure-sensitive characteristics of the final functional nanomaterials.

Modern REE oxides-containing functional materials are extremely diverse. A common uniting point for all of them is the structure. Transition metals in structure of complex oxides coordinate oxygen polyhedra of different configurations. The structure of substances is formed by various combinations between polyhedra, which in different combinations can be united by vertices, edges, faces. In cavities formed by fragments of polyhedra rows the larger cations of alkali, alkaline earth, rare-earth elements are placed. Many properties of complex oxides depend not only on their composition and structure but also on defect structure that purposefully allows to influence their target parameters.

At present, the search of new methods and complex technologies for the synthesis of special, functional REE oxide-containing materials with a liquid multi-component nitrate systems [1-15] is being carried out. Such technological schemes are based on the production of fine powder materials by chemical homogenization of initial components in joint selection of products from the liquid phase by sequential or joint deposition followed by heat treatment in the form of their hydroxides or other insoluble compounds; the use of a thermolysis method of a solvent, ionic and molecular coordination precursors; replacement of a solvent; a spray drying; cryochemical crystallization, sol-gel processes, etc. The synthesis of nanocrystalline materials is a complex scientific and technological problem.

The information about the condition [15] and possible ways of improvement of creation technologies of REE oxide-containing functional materials is available [16], the existing requirements to their stability and reproducibility properties initiated our study.

Problem formulation and solution methods

The aim of this work is a basic research of cooperative processes proceeding upon obtaining the oxide rare earth-containing functional materials using nitrates of elements of various electronic structure and finding the possible methods of influence on liquid-phase and solid-phase systems based on thermal activation of reagents for reproducing their structure-sensitive characteristics. In the work to assess the management of these processes and to obtain materials with the desired properties as model it was studied the system $\text{KNO}_3\text{-Nd}(\text{NO}_3)_3\text{-H}_2\text{O}$, components of which specify the technical characteristics of the synthesis product or modify its physical properties. The choice for studies of neodymium nitrate (as representative of the rare earth elements of cerium subgroup) is determined by existing statistical data about the most probable changes in composition or structure of the compounds created by neodymium while passing from lanthanum to lutetium in a natural number. The choice of values for the temperature section 50°C for studying the solubility isotherms of the system is determined by instability of hexahydrate of neodymium nitrate and start point of its melting in crystalization water at 68°C , above which it is in a liquid highly viscous metastable condition.

To solve this problem, our research were focused on:

- solid analytical literature review of the available scientific information on the subject of the work;
- the choice of methods and means of physico-chemical studies of a model system;
- mastering the methods and techniques of preparation and conduct of the experiment;
- experimental study of chemical interaction of components, heterogeneous equilibria in water-salt system $\text{KNO}_3\text{-Nd}(\text{NO}_3)_3\text{-H}_2\text{O}$ (50°C) with the application of complex physico-chemical methods;
- building the isothermal solubility chart system. Determination of concentration limits of original compounds crystallization and identified of complex salts in the system;
- identification of optimal growth conditions and performing the synthesis of coordinating neodymium nitrates and potassium examination of their properties and confirmation of identity;
- thermographic study of solid phases produced in the system of neodymium nitrate and potassium from solutions, solutions – melts, melts;
- clarification the nature and peculiarities of sequential thermal transitions in the rare earth-containing nitrate multicomponent systems in different aggregate states during the heat treatment;
- using the acquired knowledge to justify the preparatory processes in the production of REE-containing functional materials for various purposes, development of possible ways to control them.

To clarify the nature of chemical interactions and phases equilibria in water-salt system of the studied nitrates (precursors of multicomponent oxide functional materials) in full concentration ratios in a temperature range of solutions existence the method of solubility, described in [17, 18], was used.

The method allows to find the limits of self-development, to which in specific conditions in equilibrium state the isolated system of this composition aims.

The transformations nature of solid phases, crystallizing in the investigated ternary system was studied using the method of thermal analysis on derivatograph Q – 1500 D, the developed thermoanalytical complex, as well as methods of elemental and X-ray analysis.

The experimental part

In this work as source salts there were used hydrated and anhydrous nitrates of these elements of the brand „p.f.a.”, additionally purified by recrystallization.

Heterogeneous equilibria in aqueous system of nitrate salts was studied isothermally at 50°C in dry air thermostat, with continuous mixing using the mixing electromagnetic multi-device. The equilibrium of phases was established within 1-2 days. Sampling of liquid and solid phases of the investigated mixtures for preventing crystallization and maximum separation of mother mix were carried out by a special samplers in the same isothermal conditions using the forvacuum pump.

The chemical analysis of liquid and solid phases, the „leftovers”, were tested on the content of Nd^{3+} ions, they were determined trigonometrically; ions K^+ were calculated according to the difference concerning the total content of nitrates in dry residue. The obtained experimental data from the studied system for individual ions were calculated according to their salt content, generalized, summarized in Table 1 and according to the correspondent principles were applied to the solubility chart (Fig. 1). Graphical display of composition of solid phases formed in the system was carried out according to Schreinemakers [17, 18]. Their identity was confirmed by chemical, X-ray phase, thermal and other methods of analysis.

The study of mutual behavior of structural components in a liquid phase and phase of equilibria in the system of potassium nitrate-neodymium nitrate-water, the building of its solubility isotherms allow to determine the concentration boundaries of separation into the solid phase of potassium coordinating neodymium nitrates. The obtained data allowed to make the choice of optimal conditions of separation of complex nitrates and carry out their synthesis by isothermal evaporation of the solvent. In slightly supersaturated mother mixture isometric crystals of binary potassium nitrates were obtained. The habitus of crystals $\text{K}_2[\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$ (Fig. 2a), $\text{K}_3[\text{Nd}_2(\text{NO}_3)_9]\cdot\text{H}_2\text{O}$ (Fig. 2b) is determined by the composition of compounds, the nature and content of their constituent cations, conditions of crystallization and is their diagnostic sign.

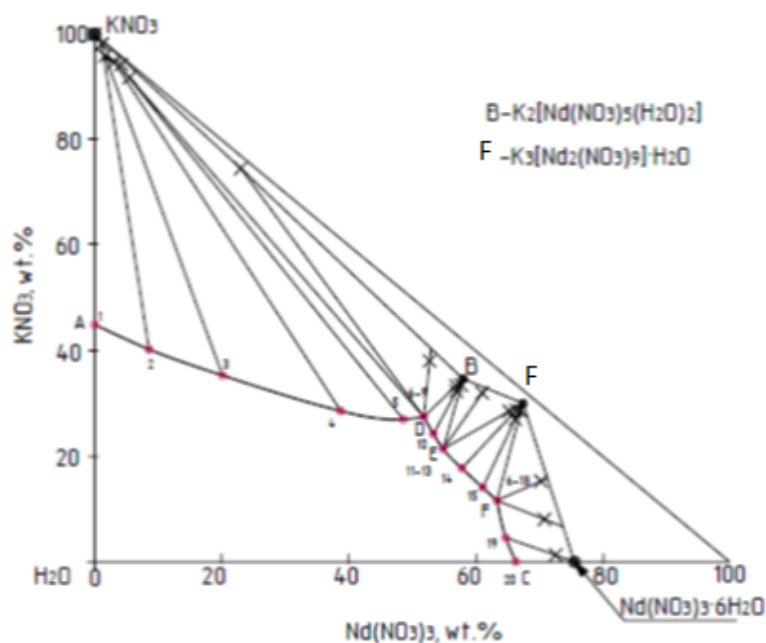


FIGURE 1. Solubility system isotherm $\text{KNO}_3\text{-Nd}(\text{NO}_3)_3\text{-H}_2\text{O}$ at 50°C

TABLE 1. Data of phase equilibria study in the system KNO_3 - $Nd(NO_3)_3$ - H_2O at $50^\circ C$

Points of composition	Saturated solution				Composition of "leftovers", wt. %		Solid phases*
	Composition, wt. %		Properties		KNO_3	$Nd(NO_3)_3$	
	KNO_3	$Nd(NO_3)_3$	$d \cdot 10^3$ kg/m^3	n			
1	2	3	4	5	6	7	8
1 A	44.88	0.00	1.223	1.3748	100.00	0.00	A
2	40.12	8.67	1.391	1.3862	97.93	1.25	Also
3	35.21	20.31	1.514	1.4014	95.68	1.72	-
4	28.46	38.81	1.602	1.4406	94.51	3.22	-
5	26.80	48.65	1.858	1.4659	94.03	4.36	-
6					91.54	5.56	-
7					74.51	23.07	A + B
8 D	27.26	51.82	2.092	1.4781	37.95	52.73	Also
9					33.84	56.49	B
10	24.08	53.28	2.064	1.4764	34.07	57.16	Also
11					34.58	57.29	-
12 E	21.34	54.91	2.068	1.4791	31.95	60.97	B + F
13					29.82	65.46	F
14	17.03	57.09	1.960	1.4772	30.12	66.91	Also
15	13.94	61.08	1.969	1.4778	29.23	66.65	-
16					29.61	67.07	-
17 F	11.49	63.31	2.124	1.4822	15.17	70.18	F + G
18					8.01	70.76	Also
19	4.44	66.02	1.964	1.4726	1.76	72.49	G
20 C	0.00	66.16	1.974	1.4667	0.00	75.28	-

* A - KNO_3 ; G - $Nd(NO_3)_3 \cdot 6H_2O$; B - $K_2[Nd(NO_3)_5(H_2O)_2]$; F - $K_3[Nd_2(NO_3)_9] \cdot H_2O$.

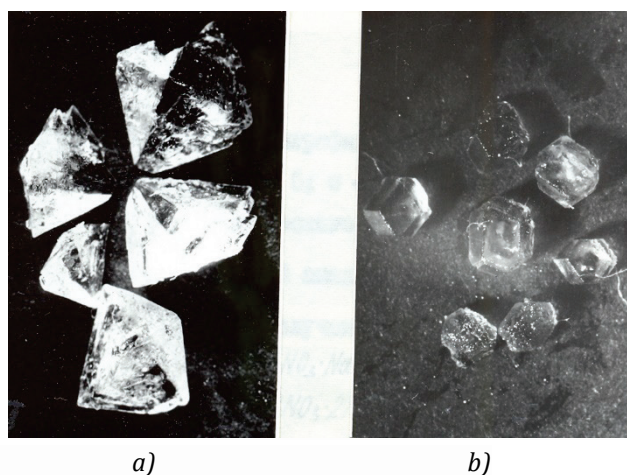


FIGURE 2. Microphotoes of crystals: a) $K_2[Nd(NO_3)_5(H_2O)_2]$; b) $K_3[Nd_2(NO_3)_9] \cdot H_2O$

The chemical analysis of the synthesized compounds confirms the mass ratio of elements in the above formulas. The conducted X-ray phase analysis of samples indicates that the compounds are characterized by individual set, position and intensity of lines in the diffraction charts (see Fig. 3) and it confirms their individuality. Thermographic examination of initial nitrates KNO_3 , $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; solid phases formed in the system of neodymium nitrates and potassium; synthesized potassium coordinating nitrates of REE were conducted on the developed thermoanalytical complex for differential thermal analysis and on derivatograph of F. Paulik, I. Paulik, L. Erdei Q – 1500 D system.

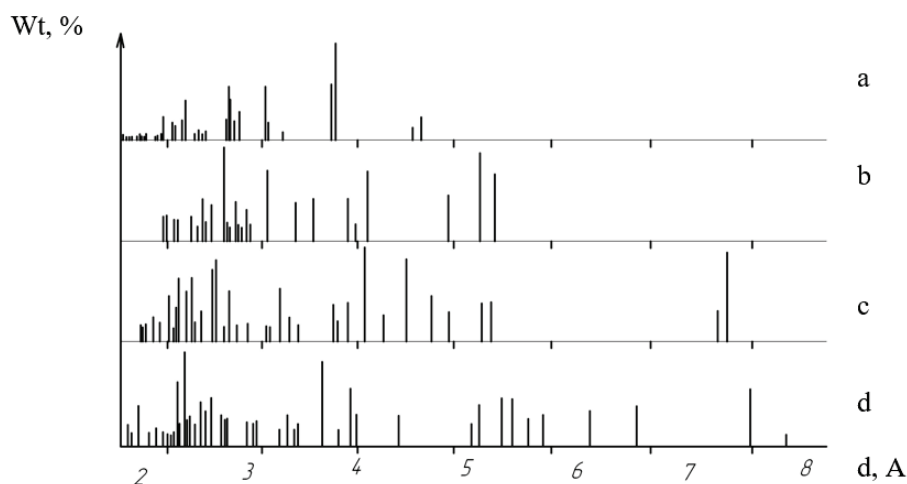


FIGURE 3. A stroke X-ray chart of initial salts of nitrates: a) potassium, b) neodymium and identified coordination compounds, c) $\text{K}_2[\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$; d) $\text{K}_3[\text{Nd}_2(\text{NO}_3)_9] \cdot \text{H}_2\text{O}$

The used tools made it possible to investigate physical and chemical transformations in the resulting compounds under the influence of heat and confirmed their identity.

The results of the research

By physical and chemical methods in water-salt system of neodymium nitrates and potassium at 50°C between structural components there were found the exchange interactions with the formation of 2 new anionic coordination compounds. The number, composition, concentration limits of crystallization phases coexisting in the system, the nature of their solubility were studied. The phase diagram of solubility was built. Concentration limits of saturated solutions from which the complex nitrates appear coincide with compositions of nonvariant points of solubility isotherms. All possible types of compounds were found. They are all synthesized in a single crystal form. The systematic study of some of their properties was carried out.

In the studied water-salt systems with the increase of the activation energy of heating the complexometric ability of Ln increases. Competing processes of substitution of H_2O molecules on NO_3^- group in presence of Ln^{3+} create conditions for formation of corresponding high symmetric complexes. The different ways of their spatial packing with other structural elements in the crystallization process leads to separation from a liquid phase of anionic coordination compounds of definite composition and structure. The processes of complex formation are affected by the nature of the central atom-complexformer, directed effect on the solutions structure of available singly charged cations (e.g., K^+), the concentration and character of thermal motion of structural elements. A significant effect of the temperature factors, the need for some activation energy for such transformations and their staging were found. The found peculiarities of the aggregate behavior of structural elements in the studied system indicate that the leaky competing reactions are strong technological factors significantly affecting the changes of the lanthanides structural forms activity.

The authors have also studied thermography of the solid phases formed in the system of neodymium nitrates and potassium to explain some regularities that occur in the studied processes of synthesis of

oxide rare earth-containing functional materials, as well as for comparison characteristics that confirms the identity of the received new coordination compounds. The given information of KNO_3 behavior is based on references data [19-22]; $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Fig. 4), $\text{K}_2[\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$, $\text{K}_3[\text{Nd}_2(\text{NO}_3)_9\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$ – on data from our own studies (Fig. 5, Tables 2, 3).

Thermal decomposition of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ is of a complex character (Fig. 4).

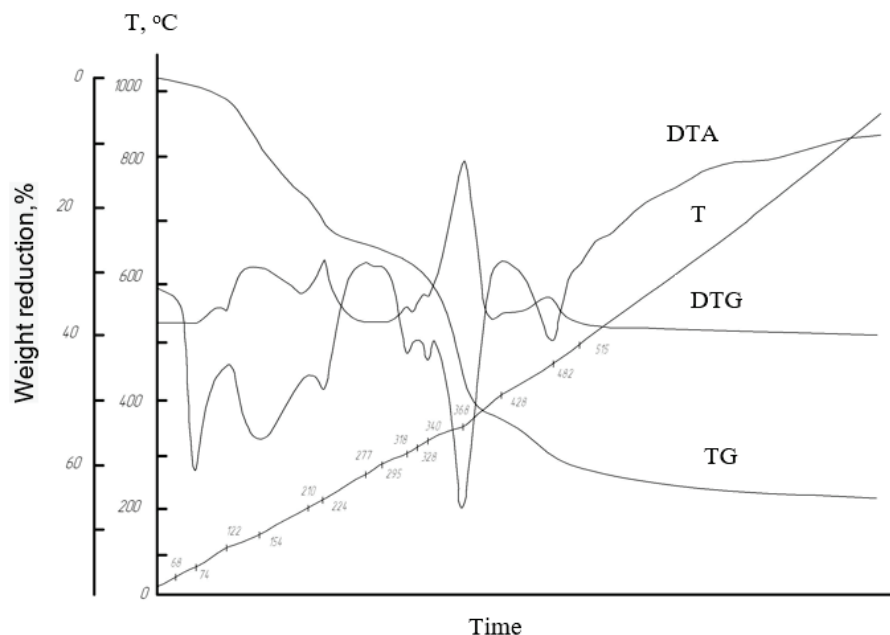
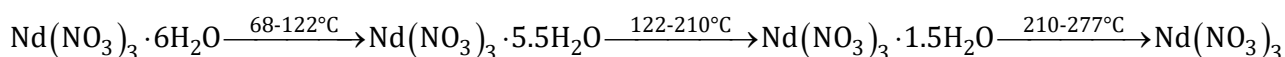


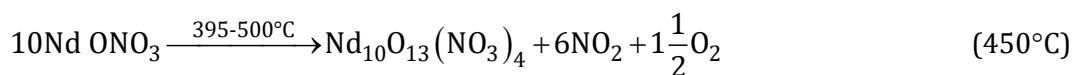
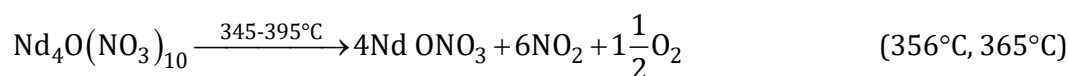
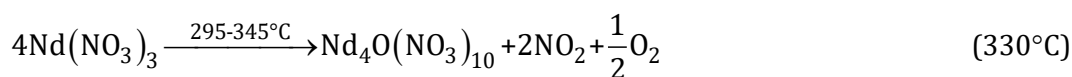
FIGURE 4. Derivatograph $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$

The obtained results are consistent with the data given in a work [23]. At 74°C $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ it melts in crystallization water (start melting point is 68°C). In temperature range of $74\text{--}224^\circ\text{C}$ conversions happen in viscous liquid metastable phase, due to instability of its crystallohydrate forms. The peaks on the curves DTA, DTG with extremes 154°C , 224°C correspond to end effects that overlap and are linked with dehydration of a sample according to the scheme:



Anhydrous neodymium nitrate exists in the temperature interval $277\text{--}295^\circ\text{C}$. This is indicated by the dominance of relations Nd-ONO_2 in the melt crystallohydrate forms of neodymium nitrate in spectroscopic studies [24] and clear stoichiometry and composition of complex oxynitrates formed at later stages of decomposition.

The fact of existence of $\text{Nd}(\text{NO}_3)_3$ simplifies elemental analysis of studied samples and allows to do analytical determinations according to dry residue. In [23] on the base of data from chemical, thermal analyses the scheme of further decomposition of $\text{Nd}(\text{NO}_3)_3$ is proposed:



According to our data, Nd_2O_3 is formed above 515°C . Thermal transformations identified in water-salt system of potassium coordination compounds of neodymium (representative of the cerium subgroup) and terbium (representative of yttrium subgroup) [25] were studied up to 1000°C and shown in (Fig. 5).

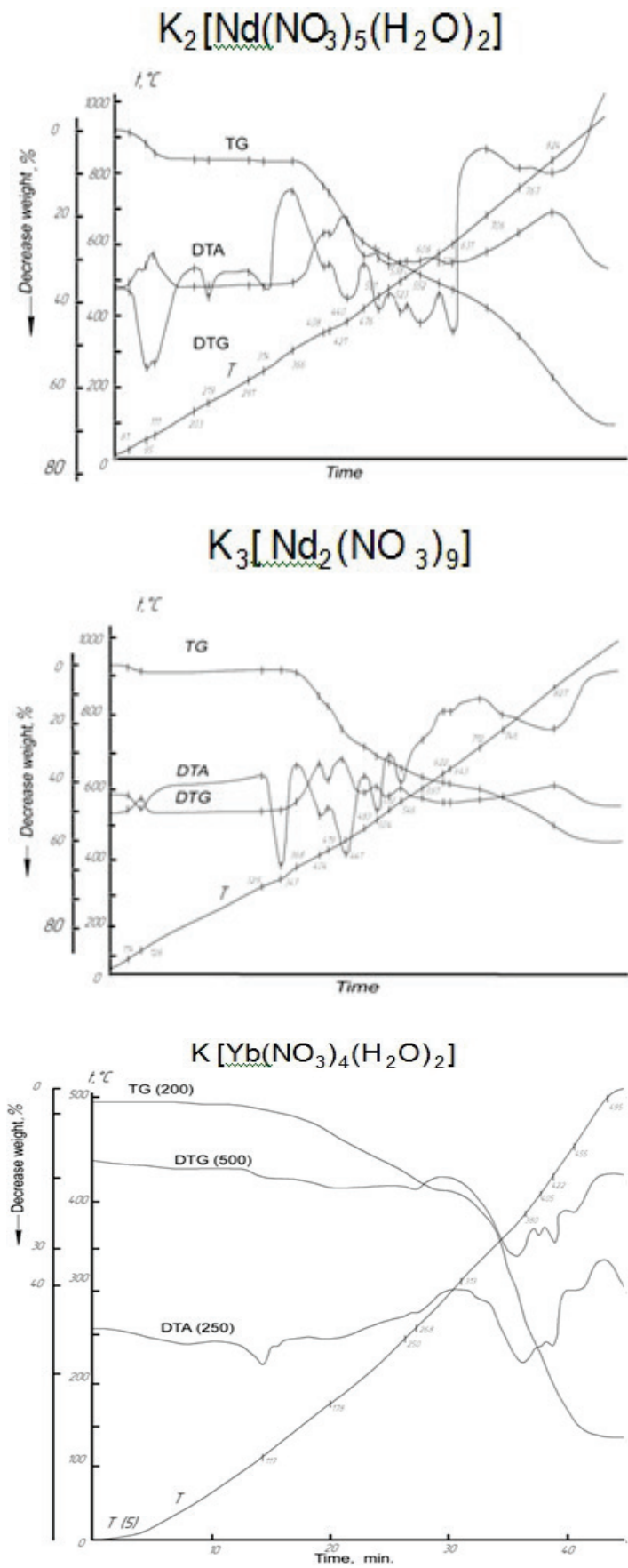


FIGURE 5. Derivatograph chart of potassium coordination nitrates of neodymium and terbium

The temperature values of the identified effects, their character and nature are systematized and summarized in Tables 2, 3. The obtained data allow the identification of phases. A number of characteristics and laws was found. Their justification from the positions of competing processes is being done.

TABLE 2. Temperature of representatives transformations of the coordinating group of REE nitrates

Compounds	Representatives	Dehydration	Melting in crystallization water	Polymorph transfer	Melting of anhydrous form	Note
$K_2[Ln(NO_3)_5(H_2O)_2]$	La-Nd	95.111	95	219	314	cerium subgroup, values for coord. compounds Nd
$K_3[Ln_2(NO_3)_9] \cdot H_2O$	La-Sm	126	-	-	347	cerium subgroup, values for coord. compounds Nd
$K[Ln(NO_3)_4(H_2O)_2]$	Y, Gd-Lu	138.172	138	-	-	yttrium subgroup, values for coord. compounds Yb

TABLE 3. The composition of thermolysis products (air, 980°C) of coordination nitrates REE, Y and potassium according to the XRD

Compounds	Representatives	Composition of transfer products
$K_2[Ln(NO_3)_5(H_2O)_2]$	La-Nd	$KLnO_2, Ln_2O_3$
$K_3[Ln_2(NO_3)_9] \cdot H_2O$	La-Sm	Ln_2O_3
$K[Ln(NO_3)_4(H_2O)_2]$	Y, Gd-Lu	Ln_2O_3

Based on the characteristics of obtaining process of oxide REE-containing functional materials there is an interest to limits of concentration ratios of components to which in phase diagrams the crystallization fields of initial nitrates of rare-earth elements, coordination compounds and their mixtures correspond.

The results of thermal transformations studies of new solid phases found in the model system (see Fig. 5, Tables 2, 3) indicate the different nature of the processes of transformation of compounds of rare-earth elements of cerium and yttrium groups, low and high – temperature of compounds forms of “light lanthanides”. Thermograms of elements compounds in the first subgroup are characterized by the formation of anhydrous nitrates. Among compounds with the same name and outer sphere cation the nitrates with a high content of lanthanotus are more heat resistant.

The fact of existence of polymorphism in crystals of composition $K_2[Ln(NO_3)_5(H_2O)_2]$ (Ln-La-Nd) was found. This phenomenon can be explained by the fact that in crystals the disorder occurs due to implementation availability of several distinctive orientations of ions NO_3^- . This kind of disorder is possible due to symmetry of flat NO_3^- -ligand, the way of coordinating them by central atom (Ln^{3+} – complexing agents), as well as the method of packing complexes into spatial structure.

The temperature properties of yttrium subgroup compounds are characterized by the absence of stable anhydrous forms of nitrates, low melting temperatures, dehydration from the molten state, the formation of Ln_2O_3 (980°C).

The composition of thermal conversion products (about 980°C) compounds of cerium subgroup depends on the composition of initial nitrates, the degree of volatility of oxides of corresponding alkali metals. In products of thermolysis the compounds $\text{K}_2[\text{Ln}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$, except oxides K_2O , contain also their dioxolanthanides KLnO_2 .

Analysis of the research results with the study of model systems and system analysis of information obtained from scientific publications on the topic of this paper evidents that a positive feature of the use of these REE-containing nitrate systems compared to other soluble systems of chlorides, oxalates is in that, that competing ion exchange interaction leads to easy formation of a whole class of anionic coordination compounds Ln^{3+} with oxygen atoms (electron donors) NO_3^- -groups (ligands) of the entire natural range of rare earth elements with all cations of alkali metals, and still stable both in solutions and melts. This allows to carry out technological transformations with a low energy cost (due to low activation energy of the processes of complexation Ln^{3+} with planar small NO_3^- -groups). Complex compounds are fusible, little aggressive, elements of cerium subgroup are non-volatile. It allows to work at lower temperatures, the temperature range of stability of complex particles increases.

Conclusions

The results of the study indicate that processes of obtaining REE oxide-containing structural and functional materials for various purposes using nitrates with various elements of electronic structure by chemical mixing the initial components in joint selection of products from the liquid phase by sequential or joint deposition followed by heat treatment happen stage by stage through the formation of several intermediate phases. Their structure, content and behaviour, in each case, require systematic empirical knowledge about their joint behavior in full concentration ratios in a given temperature interval.

The differences in the behavior of structural components in systems lanthanides of cerium and yttrium subgroups, the nature of interaction, stages, characteristics and regularities of flow were found.

New knowledges are the basis for search of ways of increasing the activity of Ln-forms; clarification of the nature of serial thermal transformations of nitrate REE containing multicomponent systems of different aggregate states in the course of their thermal treatment; conditions of formation and existence, properties of intermediate phases; influencing factors; possible methods of control; for creation of modern, perfect low-cost technologies for the synthesis of functional various purposes materials with reproducible properties.

Conflicts of Interest: The author declares no conflict of interest.

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