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## PREPARATION OF MULTIFUNCTIONAL LAYERED OXIDE REE-CONTAINING MATERIALS

*The aim of this work was to study the processes of cooperative interactions among the structural components during the formation of the layered cation-structured perovskite-like oxide phases of rare earth and transition elements at the preparatory stages using the nitrates of elements with different electronic structure and thermal activation. Stages of such transformations and patterns of phase formation were established; factors of influence and their determinant ability were clarified; a number of physical and chemical properties of the formed intermediate phases (coordination of lanthanides nitrates) were studied.*

**Keywords:** rare earth elements, alkaline metals, ammonium, alkaline earth metals, nitrates, complex formation, water-salt systems, properties.

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## ПРИГОТУВАННЯ БАГАТОФУНКЦІОНАЛЬНИХ ШАРУВАТИХ ОКСИДНИХ РЗЕ-ВМІСНИХ МАТЕРІАЛІВ

*Метою проведення цієї роботи було дослідження кооперативних процесів взаємодії між структурними компонентами у ході формування шаруватих катіоновпорядкованих перовскітоподібних оксидних фаз рідкісноземельних і перехідних елементів у підготовчих стадіях з використанням нітратів елементів різної електронної структури і тепловою активацією. Встановлено стадійність таких перетворень і закономірності фазоутворення, з'ясовано фактори впливу та їх визначальність, вивчено низку фізико-хімічних властивостей утворюваних проміжних фаз – координаційних нітратів лантановідів.*

**Ключові слова:** рідкісноземельні елементи, лужні метали, амоній, лужноземельні метали, нітрати, комплексоутворення, водно-сольові системи, властивості.

**Introduction.** Complex layered perovskite-like oxides  $ALnTiO_4$ ,  $A_2Ln_2Ti_3O_{10}$ ,  $ALnNb_2O_7$ ,  $ALnTa_2O_7$  ( $A - Li, Na, K, Rb, Cs, H$ ;  $Ln - La, Nd$ ) are crystalline compounds where layers of the perovskite structure are alternating with layers having different type of structure. Recently, the mentioned phases have attracted significant attention due to their photo-catalytic properties [1, 2]. They can also be used as precursors to obtain other perovskite-like compounds by means of ion exchange or certain topochemical transformations. It was found that alkaline forms of such perovskites in the aqueous medium can perform replacement of cations by protons and hydration (rooting of water molecules in the interlayer space). These effects lead to substantial changes in physical and chemical properties of photo-catalysts.

The composition of layered perovskite oxides may include several different metals [1–5], and depending on their nature and stoichiometry, these objects can display a wide range of physical and chemical properties. Normally, perovskite-like oxides are semiconducting materials.

It was found that composition systems based on  $TiO_2$  due to internal photoelectric effect (in two ways: either on the electrode surface or in the suspension form) are able to perform:

– photolysis of water

$H_2O + hv \rightarrow H_2 + O_2$ , that can be used to accumulate (to converse) solar energy in the form of hydrogen, environmentally friendly fuel;

– decomposition of toxic organic impurities in solutions, gaseous media

$C_xH_yO_z + hv \rightarrow CO_2 + H_2O$ , that can be taken as a basis for purification of the latter.

The main goals of current research are the spectral action shift from the ultraviolet to the visible region and improving the quantum efficiency due to suppressing undesirable secondary processes. Besides the new materials synthesis, among the main fields of research, modification of the known photo-catalysts by means of doping and formulation of composites should also be called.

Analysis of recent sources of research and publications. Dependencies of photo-induced hydrogen release from suspensions of layered perovskite-like oxides  $A_2Ln_2Ti_3O_{10}$  and  $ALnTiO_4$  ( $A - H, Li, Na, K$ ;  $Ln - La, Nd$ ),  $ANdTa_2O_7$  ( $A - H, Li, Na, K, Rb, Cs$ ) and  $ANdNb_2O_7$  ( $A - Rb, Cs$ ) rate on cationic composition were determined [2]. It was found that the maximum activity is displayed by tantalate  $RbNdTa_2O_7$ , referring to Dion-Jacobson phases.

These layered oxides are nano-structured objects. High mobility of their interlayer cations permits wide variations in the composition of such phases and thus affects their optical properties, electronic structure and photo-catalytic activity. Some layered oxides are capable of reversible intercalation of water molecules into the interlayer space that can both cause an increase in the efficient specific surface of photo-catalyst and facilitate spatial separation of reduction-oxidation centers.

There are several ways of forming perovskites [1]. By means of the high-temperature solid phase synthesis method only those phases can be obtained, whose formation is thermodynamically advantageous at a given temperature. Many layered oxides can be synthesized by means of ion exchange reactions and applying molecular and coordination precursors, including nitrate-based ones by means of «soft» chemistry methods.

**Unsolved aspects of the problem statement.** The authors are studying the possibility of forming layered perovskite-like oxides that relate to the Ruddlesden-Popper phases ( $A_2Ln_2Ti_3O_{10}$  and  $ALnTiO_4$ , where  $A - H, Li, Na, K, Rb, Cs$ ;  $Ln - La, Nd$ ) and Dion-Jacobson ( $ANdTa_2O_7$ , where  $A - H, Li, Na, K, Rb, Cs$  and  $ANdNb_2O_7$ , where  $A - Rb, Cs$ ), using nitrate coordination REE-containing precursors, whose synthesis is a difficult and extremely urgent task as of today both in the scientific and in the applied respect.

Photo-catalytic activity of the samples is under study in terms of their composition, method of obtaining, structure, nature of their interaction with water based on the results of

the available scientific information and a number of features and patterns of behavior of structural elements identified by the authors in multi-component systems at different stages of the preparatory process, in different states of aggregation, in a variety of concentrations and temperature ranges.

In the process of forming the above multifunctional materials using nitrate REE-containing precursors at the stages of preparation, performance, monitoring, at the technological schemes improvement, problems arise, related to the lack of generalized, systemic information on the rare earth elements' complexing ability. It reduces the possibility of intrinsic comprehension, interpretation of the respective chemical transformations mechanisms.

The available information is mostly relating to research of lanthanum and cerium nitrates in triple water-salt systems at low temperature (10 – 30 °C); diagrams describing  $\text{Ln}(\text{NO}_3)_3 - \text{MeNO}_3$  state within the concentration range of 30 mol. % of  $\text{Ln}(\text{NO}_3)_3$ ; studying the possibility of extracting  $\text{Ln}^{3+}$  ions from molted nitrates of elements belonging to IA, IIA groups of the periodic system, their eutectic mixtures. Preparative methods of their obtaining have acquired the most extensive use, the methods have been tested under the conditions different from those of target products synthesis. These data do not provide complete answers about the laws and features of phase formation in such systems and do not indicate ways of solving the above problem tasks.

**Aim and objectives of the study.** To assess the possibility of managing the above processes and to obtain materials with reproducible properties, it is necessary to study  $\text{Me}(\text{NO}_3)_x - \text{Ln}(\text{NO}_3)_3 - \text{H}_2\text{O}$  (25 – 100 °C) as a model system, where  $\text{Ln} - \text{Y}^{3+}, \text{La}^{3+} - \text{Lu}^{3+}; \text{Me} - \text{Li}^+ - \text{Cs}^+, \text{NH}_4^+, x = 1; \text{Mg}^{2+} - \text{Ba}^{2+}, x = 2$  – are system components that define technical specifications of the synthesis product or are used as additives to modify its physical properties.

**Experimental procedure.** The systems study is performed isothermally (at 25, 50, 65, 100 °C) using additives according to the procedure described in [6, 7]. Phase equilibrium was obtained within 1–2 days. As the source salts, hydrated and anhydrous nitrates of these elements of PA («pure for analysis») mark were used. The temperature interval selection was determined by the existence intervals of the initial components' crystalhydrate forms.

Chemical analysis of liquid, solid phases and «residues» was performed to determine the content of  $\text{Ln}^{3+}, \text{Mg}^{2+}, \text{Ca}^{2+} - \text{Ba}^{2+}$ , nitrogen ions [8]. Content of  $\text{Ln}^{3+}$  was determined by means of trilonometry;  $\text{Mg}^{2+}$  – by the volumetric method;  $\text{Ca}^{2+} - \text{Ba}^{2+}$  – using complexometry titration of the substituent in the filtrate freed from  $\text{Ln}^{3+}$  by means of ammonium buffer; nitrogen - by stripping;  $\text{Me}^+, \text{NH}_4^+$  ions – by calculation of the difference, based on the total content of nitrates and partly on the dry residue.

The data obtained was offset against the salt content for individual ions and according to the correspondence principle was applied to the solubility diagram. Graphical display of solid phases, formed in the system, was performed according to Schreinemakers [7]. Their identity was confirmed by chemical, crystal optical, X-ray phase, X-ray structural, infrared spectroscopic, laser SHG, thermographic analysis and other methods.

**Results and discussion.** Experimental data of the studied systems are generalized and summarized in table 1. They permitted to build the relevant polythermal spatial solubility diagrams for ternary systems. On their basis, the following was established: nature of interaction between the structural components of the systems; quantity, composition, solubility nature, temperature and concentration limits of starting materials and new phases formation; eutonic and transition points structure; in the areas of phase coexistence the positions of divariant equilibria lines were defined; the choice of optimal conditions for coordination nitrates synthesis was made, their crystals growth forms were studied. The obtained data permit to identify phases, to make quantitative calculations in the processes of evaporation and crystallization for similar objects.

Most systems at 25 – 100 °C (under conditions of the solutions existence) are characterized by the formation of new coordination compounds of REE. The compositions of non-variant points of the relevant solubility isotherms correspond to concentration limits of saturated solutions which complex nitrates are extracted from. Difficulty of transformations in nitrate precursors of cerium subgroup elements (La – Sm),  $\text{Li}^+ - \text{Cs}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$  during thermal activation was found in our previous studies [8–10, 5] and by the results of X-ray diffraction study of REE coordination nitrates [11, 12] and, as an example, are vividly illustrated by the data of rubidium solubility polytherm (Fig. 1) and by the data of X-R lanthanide complex compounds (table 2).

All the newly-detected phases are synthesized in the mono-crystal form. They have an isometric shape, sizing 4 – 30 mm. Their composition, atomic crystal structure, forms of coordination Ln polyhedrons, types of ligands coordination, a number of their properties are investigated using the set of the above physical and chemical methods. The experimental data are consistent with the results of the previous X-ray studies of potassium lanthanum nitrates, as well as praseodymium, lanthanum-magnesium nitrate [13] studied by means of neutron diffraction analysis.

The performed study permitted to integrate data on the nature and patterns of structural components' chemical interaction, heterogeneous equilibrium (25 – 100 °C) in water-salt systems of lanthanide nitrates, yttrium and elements belonging to IA, IIA groups of the periodic system, ammonium, existing types of compounds, conditions of their formation, it permitted to submit their formulas in an integrated form; to set limits of their stoichiometry and schemes of composition and structure transfer in natural series  $\text{Y}^{3+}$ ,  $\text{La}^{3+} - \text{Lu}^{3+}$ ;  $\text{Li}^+ - \text{Cs}^+$ ,  $\text{NH}_4^+$ ;  $\text{Mg}^{2+} - \text{Ba}^{2+}$ ; the decisive role of the central Ln atom's nonmonotonic change of Ln properties in the process of complexing was defined.

The greatest number of compounds is formed by cerium subgroup elements  $\text{Na}_2[\text{Ln}(\text{NO}_3)_5] \cdot \text{H}_2\text{O}$  (Ln – La – Sm),  $\text{Me}_2[\text{Ln}(\text{NO}_3)_5(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$  (Me – K Ln – La – Nd  $n=0$ ; Me – Rb Ln – La, Ce  $n=0$ ; Me – Cs Ln – La – Nd  $n=0$ ; Me –  $\text{NH}_4^+$  Ln – La  $n=1, 2$ ),  $\text{Rb}_5[\text{Ln}_2(\text{NO}_3)_{11}] \cdot \text{H}_2\text{O}$  (Ln – Pr – Sm),  $\text{Me}_3[\text{Ln}_2(\text{NO}_3)_9] \cdot n\text{H}_2\text{O}$  (Me – Li  $n=3$ , Me – K, Rb,  $\text{NH}_4^+$   $n=0, 1$  Ln – La – Sm),  $\text{Cs}[\text{Ln}(\text{NO}_3)_4(\text{H}_2\text{O})_3]$  (Ln – Pr – Sm).

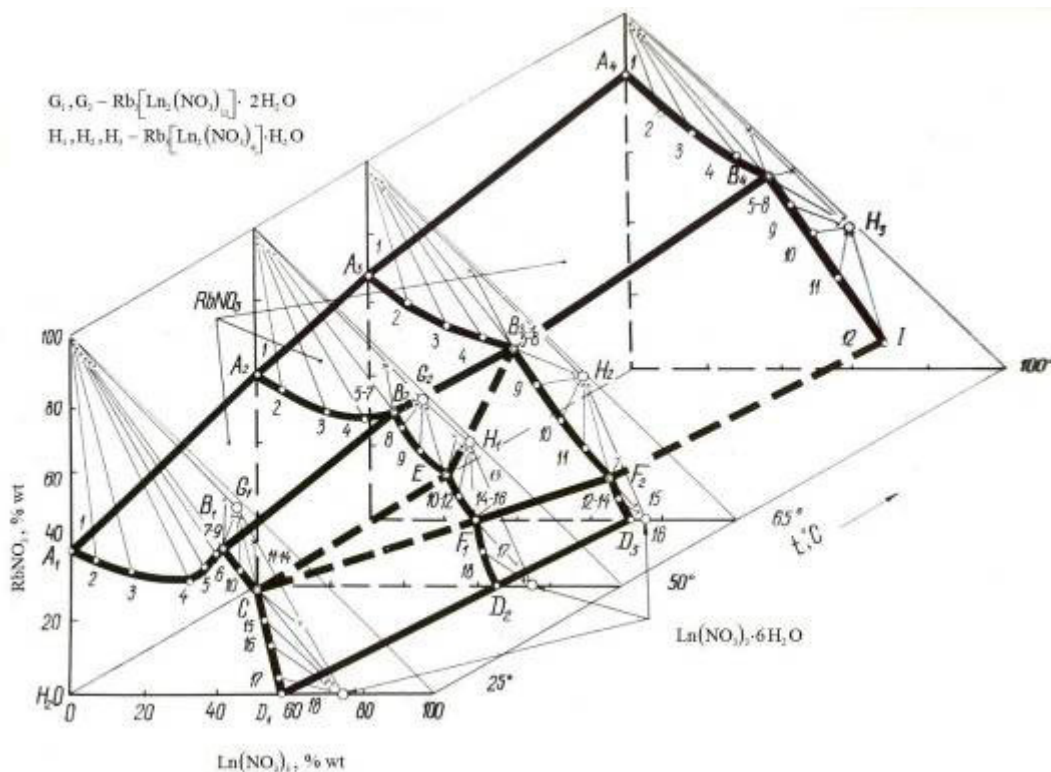
In the temperature interval 25 – 100 °C yttrium subgroup elements only form compounds with  $\text{KNO}_3$ ,  $\text{RbNO}_3$ ,  $\text{CsNO}_3$ ,  $\text{NH}_4\text{NO}_3 - \text{K}[\text{Ln}(\text{NO}_3)_4(\text{H}_2\text{O})_2]$  (Ln – Y, Gd – Lu),  $\text{M}[\text{Ln}(\text{NO}_3)_4(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (Me – Rb, Cs,  $\text{NH}_4^+$ ; Ln – Y, Gd – Lu).

Information on the nature of the interaction in the systems of cerium subgroup elements nitrates and Mg, Ca, Sr, Ba indicates that only in magnesium systems in the range of the studied temperatures congruently soluble  $[\text{Mg}(\text{H}_2\text{O})_6]_3[\text{Ln}(\text{NO}_3)_6]_2 \cdot 6\text{H}_2\text{O}$  [5] are formed. In other systems new solid phases are not formed (eutonic type systems).

In the studied water-salt systems complexing mechanism can be explained from the standpoint of competitive substitution of water molecules in the immediate vicinity of  $\text{Ln}^{3+}$  for  $\text{NO}_3^-$ -groups. The degree of substitution completeness depends on the nature of  $\text{Ln}^{3+}$ , the impact of disordering effect on these processes, on the solutions structure of the available single- and double-charged cations  $\text{Li}^+ - \text{Cs}^+$ ,  $\text{NH}_4^+$ ;  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ , the nature of the structural components' thermal motion, properties of electron donor oxygen atoms and spatial structure of the ligand, concentration of anions, amount of solvent. Significant influence of heat factor on these processes and their stages is revealed. The presence of certain temperature values at the beginning of complex compounds evolution into the solid phase indicates the existence of an energy barrier and the necessity for some extra energy to make such transformations possible.

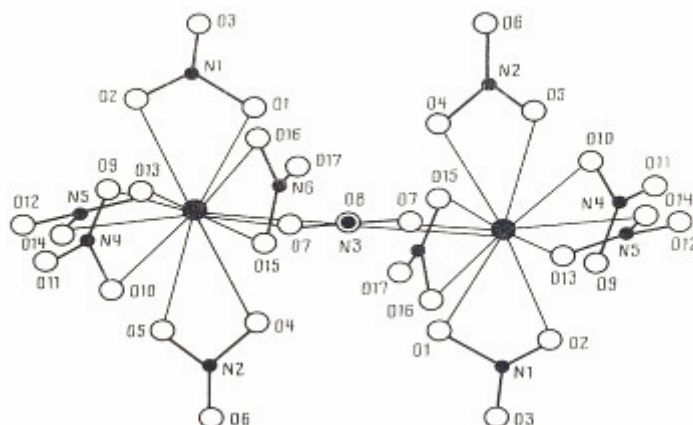
**Table 1 – Phase balance and coordination compounds in ternary nitrate water-salt systems of alkaline metals and neodymium at 25 – 100 °C**

Systems of $\text{MeNO}_3 - \text{Nd}(\text{NO}_3)_3 - \text{H}_2\text{O}$			
Me – alkaline metals	Complex nitrate composition	Temperature interval of crystallization, °C	Nature of complex nitrate solubility
Li	Eutonic type system at 25 – 50 °C		
	$\text{Li}_3[\text{Nd}_2(\text{NO}_3)_9] \cdot 3\text{H}_2\text{O}$	65	incongruent
		100	congruent
Na	Eutonic type system at 25 °C		
	$\text{Na}_2[\text{Nd}(\text{NO}_3)_5] \cdot \text{H}_2\text{O}$	50–100	incongruent
K	Eutonic type system at 25 °C		
	$\text{K}_2[\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$	50	incongruent
	$\text{K}_3[\text{Nd}_2(\text{NO}_3)_9] \cdot \text{H}_2\text{O}$	50	incongruent
	$\text{K}_3[\text{Nd}_2(\text{NO}_3)_9] \cdot \text{H}_2\text{O}$	65–100	congruent
Rb	$\text{Rb}_5[\text{Nd}_2(\text{NO}_3)_{11}] \cdot \text{H}_2\text{O}$	25	incongruent
		50	congruent
	$\text{Rb}_3[\text{Nd}_2(\text{NO}_3)_9] \cdot \text{H}_2\text{O}$	50	incongruent
	$\text{Rb}_3[\text{Nd}_2(\text{NO}_3)_9] \cdot \text{H}_2\text{O}$	65–100	congruent
Cs	$\text{Cs}_2[\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$	25–65	incongruent
	$\text{Cs}_2[\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$	100	incongruent
	$\text{Cs}[\text{Nd}(\text{NO}_3)_4(\text{H}_2\text{O})_3]$	50–65	incongruent

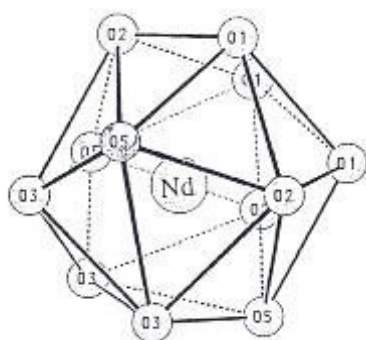


**Figure 1– Solubility polytherm of  $\text{RbNO}_3 - \text{Ln}(\text{NO}_3)_3 - \text{H}_2\text{O}$  ( $\text{Ln} - \text{Pr} \div \text{Sm}$ ) system**

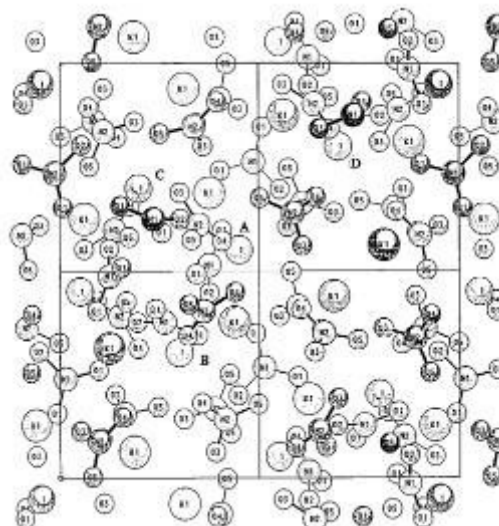
**Table 2 – X-ray data on the structure of the newly formed coordination alkaline nitrates of Nd**



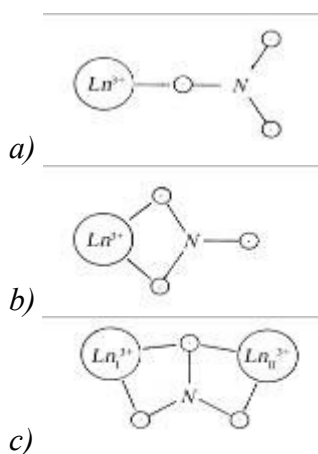
**Figure 2 – Binuclear complexes  $[\text{Nd}_2(\text{NO}_3)_{11}]^{5-}$  in the structure of  $\text{Rb}_5[\text{Nd}_2(\text{NO}_3)_{11}] \cdot \text{H}_2\text{O}$**



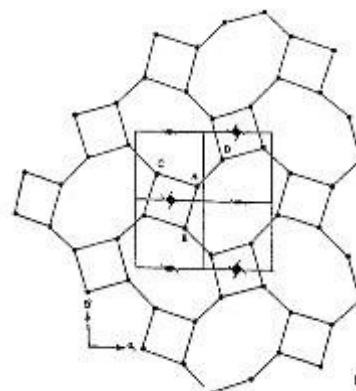
**Figure 3 – Coordination Nd polyhedron in the structure of  $\text{Rb}_3[\text{Nd}_2(\text{NO}_3)_9] \cdot \text{H}_2\text{O}$**



a)



**Figure 4 – Three types of coordinating by nitrate groups lanthanides in coordination nitrates structures:**  
 a – monodentate;  
 b – symmetrical bidentate;  
 c – symmetrical bridge bidentate



b)

**Figure 5 – Structure projection of  $\text{Me}_3[\text{Nd}_2(\text{NO}_3)_9] \cdot \text{H}_2\text{O}$  (Me –  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Rb}^+$ ) in xy plane (a) and its schematic diagram (b)**

Differences are determined in the complexing ability of cerium and yttrium subgroups elements, Y, and REE in the middle of the first subgroup. In the formation of nitrate complexes the requirements of symmetry are largely carried out, and small sized planar ligand  $\text{NO}_3^-$  is «convenient» for the formation of high-symmetric environment of  $\text{Ln}^{3+}$  ions (Fig. 2). The basis of the compounds structure is presented by rare earth coordination polyhedrons (Fig. 3) that are somehow or other linked in space [11, 12]. Water plays an important role, coordinately saturating complexing ions, and providing additional contacts between the complexes in the structure due to hydrogen bonds. For  $\text{Ln}^{3+}$  complexing ions the tendency is revealed to form a limited number of coordination polyhedrons types, three types of  $\text{NO}_3^-$ -ligands coordination (Fig. 4). This leads to the formation of both isolated complexes and their polymerization into the dual-core ones, chains, frames (Fig. 5).

The benefits of using this type of precursors are indicated by the existence of sufficiently representative segment (a whole class) of coordination REE-containing nitrate compounds of alkaline metals [8] and magnesium [5], identifying among them compounds groups, isotype by composition and structure, that are relevant representatives of lanthanides series, a series of alkaline metals, manifesting a set of technologically valuable properties: a) high solubility and compatibility with most components; b) sufficiently broad temperature range of the complex nitrates existence; c) congruent nature of transformations for most compounds of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Rb}^+$ ,  $\text{Mg}^{2+}$  both in solution and in the molten state; d) detection of their high activity by reactive particles obtained by means of the solvent thermolysis, and also nanoscale and uniform in size and morphology; e) existence of a wide range of ways, methods and technical means to activate these processes. Attention should be paid to the fact that now combined transformation methods with special requirements have acquired more widespread together with rapid synthesis methods with combined ways of activating systems and mass production.

**Conclusion.** Comprehensive study provides a reliable picture of tendencies in compatible behavior of nitrate REE precursors' components, alkaline, alkaline-earth metals at the preparatory stages of layered perovskite-like phase formation with thermal activation. Stages of such transformations and patterns of phase formation were revealed, factors of influence and their paramount importance were clarified, a number of physical and chemical properties of the intermediate phases formed, coordination lanthanide nitrates, was studied. The integrated data allow finding out the mechanisms, kinetics of structural components transformations in similar technological objects, and enabling translating the obtained set of knowledge into the procedure of controlled synthesis of new schemes for obtaining oxide REE-containing multifunctional materials with renewable structure-sensitive performance.

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