

UDC 541.123 : 546.175 : 546.65

## Formation of multifunctional nano-layered oxide REE-containing materials using nitrate precursors

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Complex system research of the interaction of structural components in nitrate systems of rare-earth and IA, IIA elements of the periodic system – precursors of modern multicomponent oxide polyfunctional materials on their basis – established the formation of a class of lanthanides alkaline coordination nitrates. The obtained data are the basis for identifying, controlling the formed phases in the preparatory stages of processing in innovative technologies using nitrate predecessors of different electronic structures elements and various combinational methods of their activation, establishing technological and functional dependencies, controlling the modification of the synthesis products properties.

**Keywords:** alkaline coordination nitrates of lanthanides, formation conditions, crystal structure of compounds, properties.

## Формування багатofункціональних нан шаруватих оксидних РЗЕ-вмісних матеріалів з використанням нітратних прекурсорів

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Комплексним системним дослідженням взаємодії структурних компонентів у системах нітратів рідкісноземельних і ІА, ІІА елементів періодичної системи встановлено утворення цілого класу лужних координаційних нітратів лантанодів, які синтезовані в монокристалічному виді. Їхній склад, атомно-кристалічну будову, форми координаційних поліедрів Ln, типи координації лігандів, ряд їхніх властивостей досліджено з використанням комплексу фізико-хімічних методів. З'ясовані об'єктивні закономірності поведінки цього типу сполук поглиблюють розуміння про: хімічні і фізичні властивості Ln, їх комплексують здатність; можливість утворення й існування в аналогічних системах асоційованих нових фаз і їх стійкість; вплив природи лантанодів і лужних металів, магнію на структуру комплексних аніонів і сполук у цілому; індивідуальність Ln комплексів; існування ізотипних за складом і структурою груп сполук за природними рядами лантанодів і лужних металів; роль NO<sub>3</sub><sup>-</sup>-груп у стереохімії цього класу нітратів; роль води у формуванні найближчого оточення іонів Ln<sup>3+</sup>- комплексують. Одержані дані є основою для виявлення, ідентифікації, контролю утворюваних фаз, визначення елементного складу і вмісту проб, проведення аналізу і порівняння фазового стану об'єктів у підготовчих стадіях перероблення в інноваційних технологіях з використанням нітратних попередників елементів різної електронної структури і різними комбінованими способами їх активації, встановлення технологічно-функціональних залежностей, керованого модифікування властивостей продуктів синтезу. На перспективність цих прекурсорів указують існування достатньо представницького класу комплексних нітратів лантанодів, виявлення серед них ізотипних за складом і структурою груп сполук представників Y, La – Lu; Li – Cs, прояв комплексу цінних у технологічному відношенні притаманних їм властивостей.

**Ключові слова:** лужні координаційні нітрати лантанодів, умови утворення, кристалічна будова сполук, властивості.



## Introduction

The report continues the discussion and results analysis of the structural components joint behavior feature study in the precursor systems of nitrate lanthanides, alkaline, alkaline earth metals in the preparatory stages during the formation of multifunctional RE-containing oxides with the structure of perovskite, garnet using the methods of soft chemistry and thermal activation.

One of the most promising classes of complex oxide materials of rare-earth elements and titanium are nanostructured layered perovskite-like compounds (the Ruddlesden-Popper phases  $A'_2[A_{n-1}B_nO_{3n+1}]$  [1], Dion-Jacobson  $A[A_{n-1}B_nO_{3n+1}]$  [2], where  $A'$ ,  $A$  – atoms of alkaline, alkaline or rare earth metals,  $B$  – transition metal atom (most often Ti, Ta, Nb) and solid solutions on their basis. For such compounds, the alternation of perovskite layers with layers of another type is characteristic. In this case, perovskite blocks may contain one, two or more ( $n$ ) octahedron layers, with a thickness of one layer of about 0.5 nm and characterized by a different deviation from the stoichiometry of the perovskite oxygen. In their structures, the octahedra are joined by vertices and, in the ideal case, form a volumetric frame with cubic symmetry. Their structural difference lies in the orientation of the layer, separated from the perovskite sublattice, in relation to its axes and in the interlayer space.

In the elementary cell of the phases of Ruddlesden-Popper, alternation of perovskite blocks takes place  $[(A_nB_nO_{3n})]_\infty$  with balls such as rock salt  $[AO]$ . The structure of the Dion-Jacobson phases is characterized by alternation of perovskite blocks  $[(A_nB_nO_{3n})^{4+}]$  and layers of type  $[(B_2)^{4-}]$ . Such REE-containing oxide phases, revealing a set of valuable physical properties, high activity and stability, satisfy the functional, technical, technological complex of requirements for modern materials in many new applications.

Available information on the state and possible ways of improving technology for creating such materials; current requirements for their stability and reproducibility of properties; expansion of their use; new information on reactivity and the transformation of layered perovskite-like oxides, stabilization of photocatalytic and sensory-active crystalline modification of anatase by ions  $NO_3^-$  [3], doping  $Ln_2O_3$  [4, 5] upon receipt  $TiO_2$  from solutions [6], trends in the technical facilities development initiated the continuation of the study on this topic. And today the ways are found to control the technical parameters of the target products through the choice of composition, synthesis conditions and method of treatment.

## Review research sources and publications

Now due to the technological methods of "soft chemistry" reactions, the possibility of creating substances with various structural features, the production of metastable compounds through the sequence of low-temperature topochemical syntheses has appeared. Synthesis methods that have recently appeared are combined considering the advantages of

each used method (elements of pyrolysis and hydrolysis synthesis methods, the method of Pecuni (Fig. 1, [7]), combustion of liquid nitrate precursors (Tab. 1, [8]), sol-gel method) and use liquid nitrate precursors of different electronic structures elements.

For formation of target phases ion exchange [9], intercalation and deintercalation [10], various processes of substitution and condensation [11], splitting processes [12] and mutual transformations of one structure into another [13] (for example, transition from the phases of Ruddlesden-Popper in the Dion-Jacobson phase; transition within one type of phase with an increase or decrease in the number of layers).

The most common reactions of "soft" chemistry include reactions of ion exchange, during which there is the replacement of weakly bound cations of the interlayer space, while perovskite layers are sufficiently stable mainly due to covalent bonds of metal-oxygen and act as carcass in a layered structure. It enables to substitute some interlayer cations to other, without affecting the basic structure of the layered oxide. Such reactions can be used to obtain a wide range of new perovskite-like structures.

So layered oxides with Dion-Jacobson phases in solutions [14] and the Ruddlesden-Popper phases in the melt [9,15] of the corresponding nitrates salts are subjected to ionic substitution reactions of larger-dimensional interlayer cations such as  $Cs^+$ ,  $Rb^+$  i  $K^+$ , on cations of smaller size –  $Li^+$ ,  $Na^+$ ,  $NH_4^+$ . For the Ruddlesden-Popper phases, it is also characteristic to replace two monovalent interlayer cations with one bivalent cation ( $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Si^{2+}$ ,  $Ba^{2+}$ ;  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  and others) with the transformation in the Dion-Jacobson phase (shown in the scheme of such ionic transformations, Fig. 2).

Now, to increase the effectiveness of these reactions and reduce the time expenditures, methods of physical influence on reactionary systems, such as microwave heating [16] and ultrasound treatment [17], have become more commonly used.

For technological reception of active phases of perovskite type, leading manufacturers use immersion (impregnation) of structured carriers of cellular or ball-like type in aqueous solutions of precursors - salts of nitrates of a given composition (possible spray application or other) in the absence of any additives or in the presence of chelating agents [18] (for example, citric acid (Pecuni method)), enabling to obtain bulk-linked (polymerized) high-concentrated homogeneous solutions of nitrate precursors. Thus, there is subsequent two stage heat treatment - drying in a conventional furnace (80–200 °C) or in a microwave oven (it prevents the redistribution of active components and ensures their good distribution on the substrate) and there is subsequent calcination at 700–1100 °C – converts predecessors into given oxide of the perovskite type [19]. Generally, phase-clear materials are obtained. Their active phase layer, 2–160  $\mu m$  thick, covering the walls of a structured carrier, demonstrates high productivity through good accessibility to its active sites.

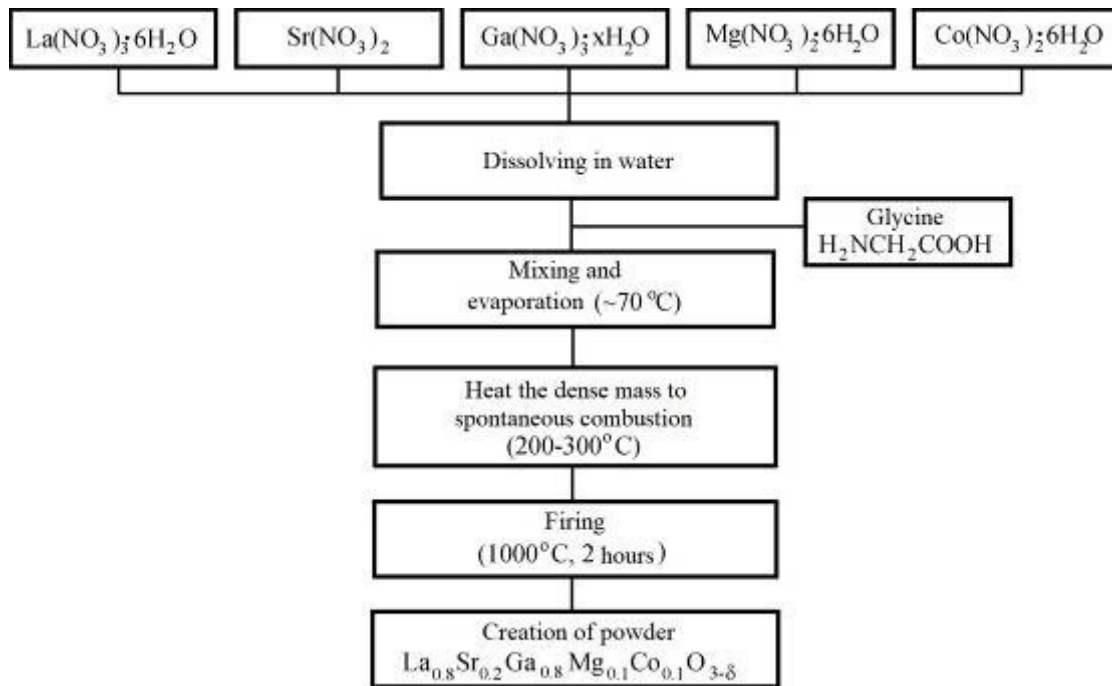


Figure 1 – The sequence of operations of formation of perovskite-like oxide phases  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.1}\text{Co}_{0.1}\text{O}_{3-\delta}$  glycine-nitrate method [7]

Table 1 – Components that are most often used in the preparatory stages during the formation of multicomponent REE-containing oxide phases by burning liquid nitrate precursors [8]

Oxidizer	Fuel	Solvent
metal nitrates or their hydrates: $\text{Me}^v(\text{NO}_3)_v \cdot n\text{H}_2\text{O}$ , $v$ - valence of metal	urea ( $\text{CH}_4\text{N}_2\text{O}$ ) glycine ( $\text{C}_2\text{H}_5\text{NO}_2$ ) saccharose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ )	water ( $\text{H}_2\text{O}$ ) kerosene benzene ( $\text{C}_6\text{H}_6$ ) alcohols: ethanol ( $\text{C}_2\text{H}_6\text{O}$ ) methanol ( $\text{CH}_4\text{O}$ )
ammonium nitrate ( $\text{NH}_4\text{NO}_3$ )	fuels based on hydrazine: carbohydrazide ( $\text{CH}_6\text{N}_4\text{O}$ ) oxalyl dihydrazide ( $\text{C}_2\text{H}_6\text{N}_4\text{O}_2$ )	furfuryl alcohol ( $\text{C}_5\text{H}_6\text{O}_2$ ) 2- methoxyethanol ( $\text{C}_3\text{H}_8\text{O}_2$ )
nitric acid ( $\text{HNO}_3$ )	hexamethylenetetramine ( $\text{C}_6\text{H}_{12}\text{N}_4$ ) acetylacetone ( $\text{C}_5\text{H}_8\text{O}_2$ )	formaldehyde ( $\text{CH}_2\text{O}$ )

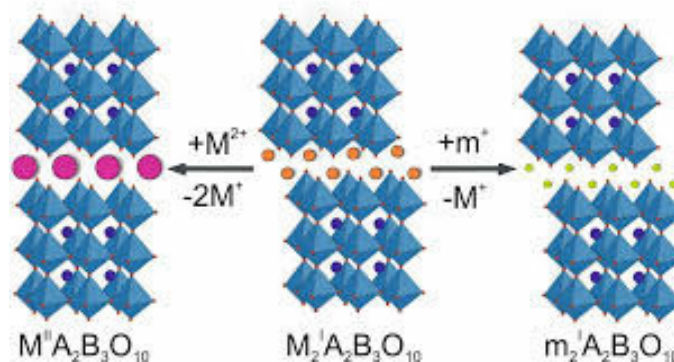


Figure 2 – Ion exchange of phases in Ruddlesden-Popper

A good alternative to the procedures that have been described previously is synthesis by the method of burning the solution [8]. It enables to receive a porous well-fixed perovskite layer with a smaller number of technological steps. After immersion in an aqueous solution containing precursors - nitrates of the relevant elements (oxidants), urea, glycine (fuel) and ammonium nitrate (combustion accelerator), the structured carrier is subjected to heated initiation to self-ignition of the system. For several minutes, the heat released during combustion of fuel (glycine), enables to convert the precursors of nitrates into a phase of pure perovskite type oxide. The removal of large quantities of gaseous products over a very short period of time during combustion gives a thick, porous and spongy coating of 40–100  $\mu\text{m}$  in thickness with a high specific surface area ( $4\text{--}30\text{ m}^2 \cdot \text{g}^{-1}$ ). Such a structure minimizes the drop in the pressure of the gas stream and improves the mass transfer. Coatings obtained by this procedure, show excellent adhesion. Their thermal aging at temperatures up to 850  $^{\circ}\text{C}$  in the presence of  $\text{SO}_2$  or water does not cause significant deactivation.

#### **Definition of unsolved aspects of the problem**

It should be noted that the synthesis of nanosized oxide materials by combustion of solutions (or modification of the method) is a complex exothermic chemical process that self-sustains and propagates in the aqueous or sol-gel medium of precursor components. Such transformations are fleeting multi-stage; begin with the dehydration and thermal decomposition of liquid systems of initial precursors and include a series of thermally coupled exothermic reactions that lead to the formation of a solid product and a large amount of gas. Due to the variability of the source constituents nature, the conduction conditions, the activation methods, the course nonequilibrium, the actions of other specific factors of the target products formation in the aspect of knowledge of their mechanisms, the clarification of the phase transformations features, it is not simple scientific and technological object, which is now intensively investigated. Such attention to the method is explained by the ease of its implementation technology, the versatility of the approach and the impressive number of important applications: new materials for energy technologies – accumulators, super-capacitors, fuel and solar cells, efficient devices for mutual conversion and energy conservation; heterogeneous catalysts – for reforming hydrocarbons, cleaning from organic pollutants of solutions and air, oxidation and treatment of exhaust gases of cars / diesel engines; semiconductor and optical materials for photo catalytic and optical applications; thin films for the development of special types of transistors and electronic structures; nanoceramics (electro-, magneto-, bio-) and others.

Synthesis of solution combustion also positively differs from other varieties of self-propagating high-temperature synthesis, namely: 1) mixing of the initial components in an aqueous solution at the molecular level (ion sizes, ligands in solution 0.1–1 nm, size of

solid powder particles by ceramic technology 102–105 nm); 2) the reaction responsible for the formation of a solid product may differ from the transformation of self-sustaining combustion; 3) a large amount of gaseous by-products leads to a substantial expansion of the solid product, a rapid drop in the temperature of the system after the reaction, which makes the solid product porous and slightly dispersed (it plays the main role in the synthesis of nanosized powder).

And modern studies are aimed at studying the thermodynamics and kinetics of reactive technological systems used in innovative solutions; the role of the process parameters responsible for self-sustaining combustion speed; the basic principles of composition management; physico-chemical characterization of composition, size, structure and microstructure, properties of both intermediate and final transformation products; elucidation of the influence factors, their degree of importance on the processes of formation and regulation of the size and morphology of nanosized phases, characteristics of target materials, etc.

#### **Problem statement**

The purpose of this work is to study cooperative processes of interaction between structural components during the formation of perovskite-like oxide phases of rare-earth and transitional elements in the preparatory stages using nitrates of different electronic structures elements and finding possible methods of influence on rare-phase and solid-phase systems based on the reagents thermal activation, from purpose of their structural-sensitive characteristics reproduction.

The most recent data on the results of such studies are far from unequal, in some cases they are due to large experimental constraints, sometimes contradictory and do not give a complete picture of the complexing ability of rare-earth elements in such objects. The unambiguous interpretation of the flow above these processes is often hindered also by the incongruous nature of the solubility (melting) of the intermediate phases formed, the simultaneous coexistence of several metastable forms of thermolysis product; the formation of heterophases, the dependence of their form on the prehistory of the process itself (the possible amorphous or poorly crystallized state of precursors [20]), the complexity of processes occurring on the boundaries of grains in polycrystalline systems, which are determined by the peculiarities of the chemical interaction of system components, the unevenness of the occurrence of transformations and the presence limiting their stages and other existing factors. The need for a deeper understanding of the above-mentioned features and the effective use of the possibilities of specific technological schemes for the formation of perovskite-like oxide phases, which nowadays become widely used, led to the study continuation.

### Basic material and results

To evaluate the possibility of controlling the synthesis processes in the multistage production of products by iso- and hetero-valent replacement of components and thermal processing; the study of the water-salt systems of nitrates has been studied as the modeling of the mechanisms of phase formation as a model using a complex of physico-chemical methods  $\text{Me}^{\text{I}}\text{NO}_3 - \text{Me}^{\text{II}}(\text{NO}_3)_2 - \text{Ln}(\text{NO}_3)_3 - \text{H}_2\text{O}$ , ( $\text{Me}^{\text{I}} - \text{K}$ ;  $\text{Me}^{\text{II}} - \text{Mg, Ca; Ln} - \text{Nd}$ ). The choice of the research objects, temperature sections are determined by a number of factors. Among the elements of the rare-earth series, the higher complex-forming ability is found by representatives of the cerium subgroup; among them the greatest changes in composition, structure, properties of their compounds - elements of its middle, Pr and Nd. Selected system components specify the specifications of the target product or modifiers of its properties. And the presence of large quantities for the use of potential electronic analogues (representatives of natural rows of rare earth, alkaline, alkaline-earth elements) causes a considerable variation and breadth of the range of modification of their characteristics. The temperature cross sections are due to the domains of the crystalline hydrate forms of the initial components.

To find out the nature of the chemical interaction and phase equilibrium in the water-salt systems of the investigated nitrates (precursors of multicomponent oxide polyfunctional materials) in the full concentration ratios in the temperature range of the existence of solutions, the method of additives described in [21, 22] has been used. It is based on the solubility study as one of the properties that are most "sensitive" to the detection of phase transformations in systems that are both a parameter of their state, and moreover, the simple available experiment now thorough methods. The method enables to find the limits of self-development, to which, in specific conditions, an isolated system of a given composition goes in an equilibrium state. In order to increase the reliability of the data obtained, a simultaneous comprehensive study of the system components solubility, density and relative refractive index of light of their solutions is used. Good coherence of the obtained results is revealed.

Phase equilibrium has been achieved within 2–3 days. The starting salts used hydrated and anhydrous nitrates of the specified elements of the brand «ch.d.a.».

Chemical analysis of liquid and solid phases, "residues" has been carried out on the ion content  $\text{Nd}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , nitrogen. Contents  $\text{Ln}^{3+}$  have been determined trilonometrically;  $\text{Mg}^{2+}$  – volumetric method;  $\text{Ca}^{2+}$  – complexometric titration of the substituent in the filtrate liberated from  $\text{Ln}^{3+}$  ammonium buffer; nitrogen – the method of distillation; ion  $\text{K}^+$  – calculation of the difference, based on the total content of nitrates and partly on the dry residue.

The obtained data for individual ions have been transferred to the salt content and, according to the principle of compliance; have been applied to the solubility graph. The graphic representation of the solid phase composition formed in the system was carried out by Skreinemakers [21, 22]. Their individuality has been confirmed, in addition to chemical, X-ray, crystalloptical, thermographic, IR-spectroscopic, etc. methods of analysis.

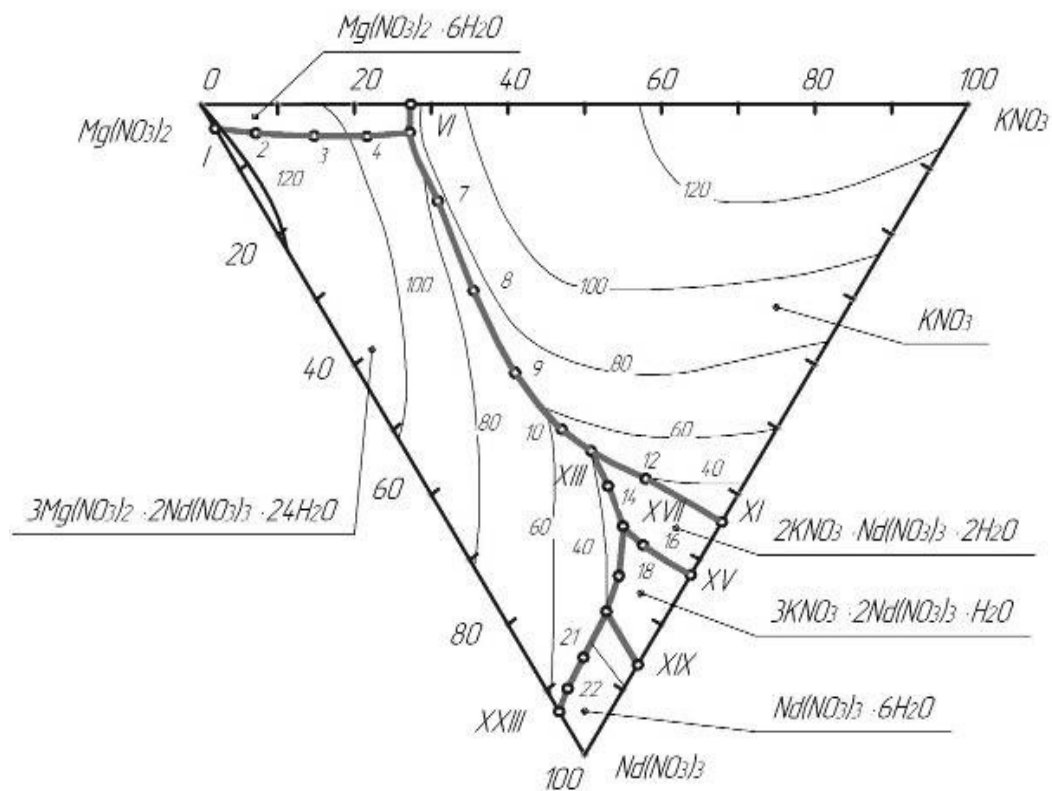
The experimental data from the study of systems are obtained  $\text{KNO}_3 - \text{Me}^{\text{II}}(\text{NO}_3)_2 - \text{Nd}(\text{NO}_3)_3 - \text{H}_2\text{O}$ , ( $\text{Me}^{\text{II}} - \text{Mg, Ca}$ ) and summarized in the table. The complexity of transformations in the objects of the study clearly demonstrates the presented horizontal projections of their corresponding spatial isotherms of solubility (Fig. 1, 2).

For these systems, in the regions of phases coexistence, the positions of the quasi-equilibrium equations lines, the composition of the electron and transition points are determined in isothermal conditions; the quantity, composition, the nature of solubility, temperature and concentration limits of the phases formation of phases; regularities and features of complex formation, heterogeneous equilibria are established. Isothermal horizontal and frontal projections of their multidimensional solubility charts are constructed. Lines of equal water content are drawn. The relative sizes of the crystallization fields of all formed phases are established.

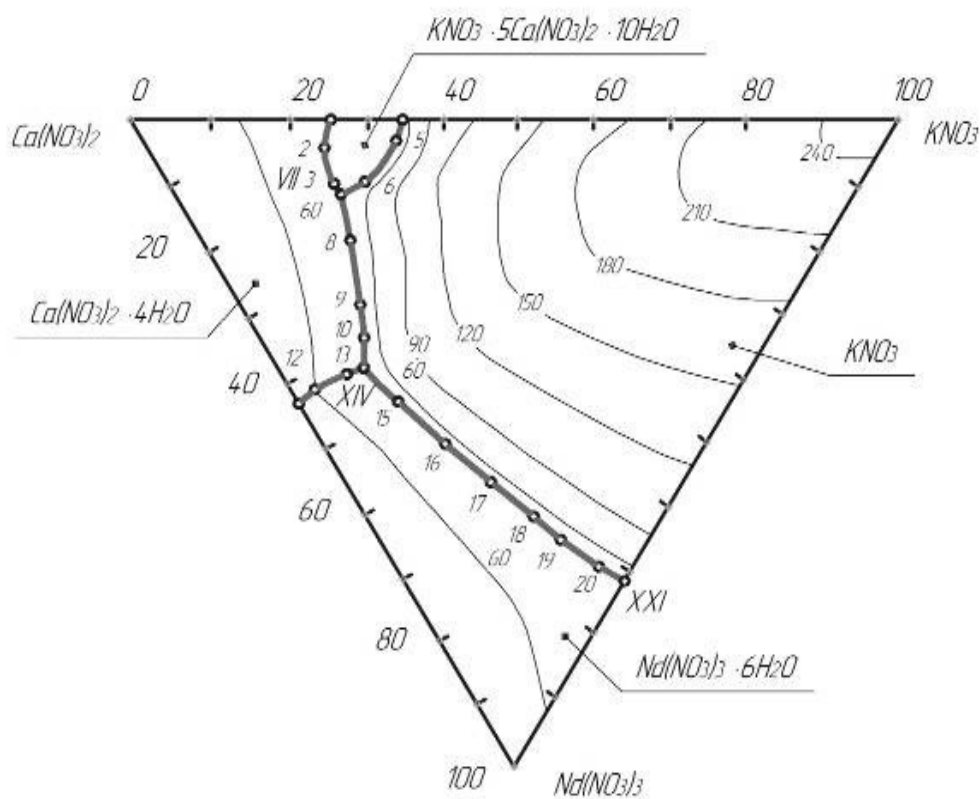
Triple systems, which are part of the quaternary magnesium-containing system,  $\text{KNO}_3 - \text{Nd}(\text{NO}_3)_3 - \text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 - \text{Nd}(\text{NO}_3)_3 - \text{H}_2\text{O}$  at 50 °C have been studied by the authors and described in previous publications [23–25]. The first system is characterized by the formation of incongruently soluble compounds of the composition  $\text{K}_2[\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$  and  $\text{K}_3[\text{Nd}(\text{NO}_3)_9]$ ; The second is a congruent soluble complex nitrate  $[\text{Mg}(\text{H}_2\text{O})_6]_3[\text{Nd}(\text{NO}_3)_6]_2 \cdot 6\text{H}_2\text{O}$ . In the system  $\text{KNO}_3 - \text{Mg}(\text{NO}_3)_2 - \text{H}_2\text{O}$  the limits of the crystallization of only the initial salts have been established [26].

Isotherm solubility of the system at 25 °C has 4 crystallization fields  $\text{KNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $[\text{Mg}(\text{H}_2\text{O})_6]_3[\text{Nd}(\text{NO}_3)_6]_2 \cdot 6\text{H}_2\text{O}$ . As the temperature rises, the nature of the interaction between the structural components of the system is greatly complicated. And with 50°C the solubility isotherm of the system, in addition to the crystallization fields of the initial salts, contains 2 more solid-phase separation fields  $\text{K}_2[\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$  and  $\text{K}_3[\text{Nd}(\text{NO}_3)_9]$ . In the system, the largest area in horizontal projections is potassium nitrate. To carry out quantitative calculations of evaporation, crystallization, its front water projections are constructed; On horizontal projections, an insulating net of equal water content is applied. The smallest contents of water are solutions saturated with coordination nitrates  $\text{K}_2[\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$ ,  $\text{K}_3[\text{Nd}(\text{NO}_3)_9]$ .

Investigation of phase equilibria in a four-component system  $\text{KNO}_3 - \text{Ca}(\text{NO}_3)_2 - \text{Nd}(\text{NO}_3)_3 - \text{H}_2\text{O}$  preceded the study of heterogeneous equilibrium



**Figure 3 – Horizontal projection of the solubility spatial isotherm of the system  $\text{KNO}_3 - \text{Mg}(\text{NO}_3)_2 - \text{Nd}(\text{NO}_3)_3 - \text{H}_2\text{O}$  at  $50^\circ\text{C}$ .**



**Figure 4 – Horizontal projection of the solubility spatial isotherm of the system  $\text{KNO}_3 - \text{Ca}(\text{NO}_3)_2 - \text{Nd}(\text{NO}_3)_3 - \text{H}_2\text{O}$  at  $25^\circ\text{C}$ .**

in systems  $\text{KNO}_3 - \text{Nd}(\text{NO}_3)_3 - \text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2 - \text{Nd}(\text{NO}_3)_3 - \text{H}_2\text{O}$ ,  $\text{KNO}_3 - \text{Ca}(\text{NO}_3)_2 - \text{H}_2\text{O}$  for the possibility of preparing refills of triple systems with saturated solutions corresponding to the contents of non-invariant points. Data from the study of the authors of the first two systems were discussed earlier in [23]. Existing system information  $\text{KNO}_3 - \text{Ca}(\text{NO}_3)_2 - \text{H}_2\text{O}$  are controversial, so it has neeb studied again. On the diagram of this system solubility (25 °C) there are separated fields of crystallization of the source components  $\text{KNO}_3$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and incongruously soluble compound  $\text{KNO}_3 \cdot 5\text{Ca}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$ ; certain warehouses of electron and transition points. Synthesis is carried out with double nitrate, its chemical analysis confirms the ratio of components in the formula above.

Isotherm solubility of this four-component system at 25 °C has 4 crystallization fields  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{KNO}_3$ ,  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{KNO}_3 \cdot 5\text{Ca}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$ . The increase in the temperature of the study narrows and, to this end, a limited number of the quantities ratios of the liquid and solid phase, which corresponds to the possibility of the system being in the given conditions in an equilibrium two-phase state, complicates the dehydration processes of the structural components, and the system near the non-invariant points passes into a metastable, syrup state.

All of these complex nitrates are synthesized in a monocrystalline form, their optimal conditions of formation and forms of growth are studied. The research of their atomic-crystalline structure, forms of coordination polyhedrons, type of coordination of ligands, a number of physical properties by chemical, X-ray diffraction, X-ray structural, IR-spectroscopic, crystalloptic, thermographic, GDG laser radiation and other methods have been carried out.

The conducted multidimensional studies using a set of indicated methods enabled to determine the tendencies of the joint behavior of structural components in the system of nitrate precursors of REE and elements of IA, IIA groups of the periodic system. It was established that in the studied water-salt systems of nitrate precursors, which are integral components of more complex multicomponent systems; exchange chemical transformations starts in the liquid phase, from the moment dissolution of the components in water – a strong polar solvent. The mechanism of complex formation can be explained from the positions of competing substitutions of water molecules in the immediate environment  $\text{Ln}^{3+}$  for  $\text{NO}_3^-$  groups, disordering the structure of solutions by introducing one - ( $\text{Li}^+ - \text{Cs}^+$ ) and two-charge ( $\text{Mg}^{2+} - \text{Ba}^{2+}$ ) cations, influence of temperature factor. The degree of completeness of substitution depends on nature  $\text{Ln}^{3+}$ , present cations  $\text{Me}^+$ ,  $\text{Me}^{2+}$ , the properties of the electron donor oxygen atoms and the spatial structure of the ligands, the concentration of the electrolytes and temperature. Significant influence on these processes of the thermal factor and their stage is revealed. The presence of certain values of isolation start temperature in the solid phase of complex compounds indicates the existence of an energy

barrier and the need to provide some additional energy to the system for the possibility of such transformations.

According to the results of previous studies [23] and available scientific data, there are differences in the complexing cerium and yttrium subgroups elements ability, Y, as well as among RHES within the first subgroup. In the formation of nitrate complexes to a large extent, the requirements of symmetry are fulfilled, and planar small-sized ligands  $\text{NO}_3^-$  is "convenient" for the formation of a high-symmetric environment of ions  $\text{Ln}^{3+}$ . The structure of such compounds is based on rare-earth coordination polyhedrons, which are somehow connected in space [28]. The influence of nature is revealed  $\text{Me}^+$ ,  $\text{Mg}^{2+}$  on the form of coordination polyhedrons, a way of packing complexes into a spatial structure, properties of compounds.

The publication also summarizes the systematized information provided by the authors (see Table 2) on the peculiarities of internal organization and physico-chemical characterization of tumors [29] – coordination nitrates of REE for the possibility of combining and directing modern scientific, technological and technical efforts to solve urgent tasks. on the formation of perfect multicomponent oxide polyfunctional materials with mixed electronic and oxygen conductivity, rapid ion transport for systems of mutual transformation p ofthem forms of energy, oxygen-conducting materials in the conversion of natural gas, fuel cells, many catalytic and magnetic systems, oxygen membranes, high-electrodes, heating elements in gas sensors and others.

## Conclusions

The empirical data obtained by the authors as for the atomic-crystalline structure formation and existence conditions. its features and patterns, the inherent properties, mechanisms and kinetics of thermal transformations (25–1000 °C) of the representatives of alkaline anionic coordination nitrates of lanthanides play an important role in optimizing the development of technologies for the production of new nanosized multicomponent oxide materials with the structure of perovskite, pomegranate in the form of powders, thin films, bulk ceramics, and components of composite systems. They help to clarify the relationship between the method of formation, the variability of the systems activation methods, the methodology of manufacturing and phase composition, lattice parameters, the magnitude of the specific surface, the morphology of the particles, the catalytic activity of the samples in the photoinduced reactions of water decomposition for the purpose of obtaining hydrogen (as an alternative species fuel), decomposition of toxic organic substances, incomplete oxidation of carbohydrates; when receiving other perovskite-like phases through ion exchange reactions, which can significantly simplify the procedures for the target products synthesis.

**Table 2 – Characteristic properties of the representatives of isoslast groups of coordination nitrates of rare earth, yttrium (°C)**

Compounds; spatial group of crystals	Representatives	Dehydration	Melting in crystallization water	Polymorphic transitions	Melting anhydrous form	Note
$\text{Li}_3[\text{Ln}_2(\text{NO}_3)_9 \cdot 3\text{H}_2\text{O}]$ cubic.; $P2_13$	La–Sm	65 183 216	183	–	274	Temperature data for the coordination compound Nd
$\text{Na}_2[\text{Ln}(\text{NO}_3)_5] \cdot \text{H}_2\text{O}$ monocl.; $P2_1/a$	La–Sm	81 148 236	–	271	328	Temperature data for the coordination compound Nd
$\text{K}_2[\text{Ln}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$ rhomb.; $Fdd2$	La–Sm	95 111	95	219	314	Temperature data for the coordination compound Nd
$\text{K}_3[\text{Ln}_2(\text{NO}_3)_9] \cdot \text{H}_2\text{O}$ cubic.; $P4_332$	La–Sm	126	–	–	347	Temperature data for the coordination compound Nd
$\text{K}[\text{Ln}(\text{NO}_3)_4(\text{H}_2\text{O})_2]$ prim. rhomb.; $P2_1cn$	Y, Gd–Lu	138 172	138	–	–	Temperature data for the coordination compound Gd
$\text{Rb}_2[\text{Ln}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$ monocl.; $Cc$	La, Ce	93 144	93	–	327	Temperature data for the coordination compound La
$\text{Rb}_5[\text{Ln}_2(\text{NO}_3)_{11}] \cdot \text{H}_2\text{O}$ monocl.; $C2/c$	Pr–Sm	172	172	–	–	Temperature data for the coordination compound Nd
$\text{Rb}_3[\text{Ln}_2(\text{NO}_3)_9] \cdot \text{H}_2\text{O}$ cubic.; $P4_332$	La–Sm	136	–	–	302	Temperature data for the coordination compound Nd
$\text{Rb}[\text{Ln}(\text{NO}_3)_4(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ monocl.; $P2_1/n$	Y, Gd–Lu	98 165 231	98	–	–	Temperature data for the coordination compound Yb
$\text{Cs}_2[\text{Ln}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$ monocl.; $12/a$	La	99 148	148	–	263	Temperature data for the coordination compound La
$\text{Cs}_2[\text{Ln}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$ monocl.; $C2/c$	Ce–Nd	122 156	156	–	235	Temperature data for the coordination compound Nd
$\text{Cs}[\text{Ln}(\text{NO}_3)_4(\text{H}_2\text{O})_3]$ threecl.; $P\bar{1}$	Pr–Sm	62 90 162	162	–	355	Temperature data for the coordination compound Nd
$\text{Cs}[\text{Ln}(\text{NO}_3)_4(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ monocl.; $P2_1/n$	Y, Gd–Lu	155 175 252	155	–	–	Temperature data for the coordination compound Yb
$[\text{Mg}(\text{H}_2\text{O})_6]_3[\text{Nd}(\text{NO}_3)_6]_2 \cdot 6\text{H}_2\text{O}$ hexagon.	La–Sm	109	109	–	–	Temperature data for the coordination compound Nd



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