Peculiarities of Tansformations in Systems of Coordination of Nitrate Precursors of REE and Alkali Metals During Formation of Polyfunctional Layered Oxide Materials

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Abstract The information on alkaline coordination nitrates of rare-earth elements of the cerium subgroup - precursors of promising modern multifunctional materials - on the conditions of their formation and existence, nature of chemical bonding, composition, structure, shape of Ln coordination polyhedra, type of ligand coordination, existence of isotype series is generalized. on stoichiometry of structure, structure, the found out characteristic properties. The obtained data (as primary information) are the basis for detection, identification, control of the phase state of processing objects in the preparatory stages, selection of compatibility criteria of components in the formation of single-layer and layered nanostructured oxide composite systems of lanthanides and transition elements with catalytic activity and photocatalyst., a coating capable of self-cleaning with hydrophilic properties; development of various combined methods of their activation and establishment of technological and functional dependencies; controlled modification of the properties of the obtained target products. To increase the photocatalytic activity of coating samples based on highly dispersed TiO_2 anatase modification, a methodology for chemical modification of oxidation centers in their surface layer with heat treatment in contact with thermolysis products of alkaline coordination nitrates of lanthanides is proposed. The effective test photocatalytic destruction of vapors of organic substrates on the example of ethanol is revealed.

Keywords Alkaline coordination nitrates of lanthanides · Formation conditions · Crystal structure of compounds · Characteristic properties · Transformations with physical activation

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1 Introduction

Currently, the search for methods and complex technologies to create new and improve existing regulations for the production of perfect multifunctional oxide materials of transition and rare earth elements with the structure of defective perovskite, garnet with reproducible properties by low-temperature methods of "soft chemistry" and precursors. They have a complex structure and in scientific and technological terms are difficult objects that are intensively studied [1–9], including with the participation of authors [see, 10]. Therefore, modern materials science, which is based on them, requires regulatory solutions simple in configuration, low-speed, energy efficient, characterized by scale, with the ability to reproduce products with a given homogeneity, stability, a set of predefined characteristics.

There are many methods for the synthesis of these oxide multicomponent materials [2–12], based on different physical and chemical principles. The main ones are:

- high-temperature method of solid-phase chemical reactions;
- condensation liquid-phase methods for obtaining nanosized oxide materials based on:

- various variants of mixing of initial components (chemical precipitation (coprecipitation); sol – gel; hydrothermal; complexonate homogenization; solvent replacement; synthesis under the action of microwave radiation);
- rapid thermal decomposition of precursors in solution (spray drying; rapid expansion of supercritical fluid solutions; cryochemical);
- self-igniting (glycine-nitrate; Pechini method; cellulose (fabric, paper) technology; pyrolysis of polymer-salt films).

The choice of using a particular method depends on the chemical nature of the obtained compounds, the size and morphological characteristics of the particles of the synthesis products, the conditions and method of formation of the latter; the material and condition of the surface, the shape of the samples on which the coating is applied; capabilities of available technical equipment, etc. These methods are used both independently of each other and in combination.

Recently, titanium dioxide has attracted special attention due to new unique prospects for its use in the form of nanostructured materials and nanocomposites with controlled morphological, physicochemical and optical properties. TiO_2, which has high chemical and thermal stability, as well as impurity levels in the electronic structure of the material, created by a given type of doping, is unique for building on its basis new effective functional materials used in photocatalysis and photovoltaics, sensory, catalysis, for liquid chromatography and other areas.

The essence of the FC properties of TiO_2 is that in the volume of a semiconductor particle under the influence of electromagnetic radiation, electron - hole pairs are generated, which, upon reaching the surface of a TiO_2 particle, enter redox reactions with adsorbed molecules. For titanium dioxide, the process is as follows:

$$(Ox_1)_{ads} + (Red_1)_{ads} \frac{TiO_2}{hv > E_g} \rightarrow Ox_2 + Red_2$$

In this case, part of the electrons and holes can undergo recombination in the bulk or on the surface of TiO_2. For the effective occurrence of photocatalytic processes, it is necessary that redox reactions involving an electron–hole pair be more effective than recombination processes.

The advantages of the photocatalytic method of purification are well known: 1) the ability to oxidize almost any organic matter and also a number of inorganic, such as CO, H_2S, HCN, NH_3, NO_x, etc.; 2) the method works at room temperature and atmospheric pressure; 3) it is possible to oxidize even small concentrations of pollutants, cleaning of which by other methods is economically unprofitable; 4) for the implementation of the method of photocatalytic purification does not require additional reagents, because the oxidant is oxygen.

However, for the photocatalytic method of air purification, a number of disadvantages are known, such as: 1) a relatively low purification rate; 2) the need to use ultraviolet light sources in the case where the photocatalyst is titanium dioxide; 3) low adsorption capacity of most simple photocatalysts; 4) the possibility of formation of intermediate products during the oxidation of high concentrations of pollutants. Therefore, the development of new photocatalytic systems that would overcome these shortcomings is the subject of an urgent series of modern studies.

When creating and heat treatment of materials based on titanium dioxide, it is necessary to take into account the possibility of surface and bulk defects of the TiO_2 crystal lattice (due to the existence of phase diversity in the range of O/Ti < 2 ratios on the phase diagram of the Ti - O system [13]) and detection their significant effect on the photochemical properties and photoinduced hydrophilic ability of the synthesis products [14].

Available information on the state and possible directions of improvement of technologies for creating such materials, current requirements for their stability and reproducibility of properties, expansion of their use [1–14], manifestation of high activity of low-crystallized particles of structural components formed by solvent thermolysis [15], new information on reactivity and transformation of layered perovskite-like oxides [16], stabilization of photocatalytic and sensory-active crystalline modification of anatase due to NO_3^- ions [17], doping of Ln_2O_3 [18, 19] in obtaining TiO_2 from solutions [20] initiated the continuation of our study. Today, ways to control the technical parameters of the target products through the choice of composition, synthesis conditions and method of processing.

One of the most promising classes of complex oxide materials of rare earth elements and titanium are nanostructured layered perovskite-like compounds and solid solutions based on them. Depending on the composition and structure, they have a wide range of physicochemical properties. Presented in this paper perovskite-like layered titanates belong to the homologous series $(Me, Ln)_{n+1} Ti_nO_{3n+1}$, where Ln - La – Nd, Me - Li – Cs, n is the number of nanolayers of perovskite (Ruddlesden-Popper phases; with a thickness of approximately one layer 0.5 nm). Accordingly, $MeLnTiO_4$ in its structure contains one nanolayer of perovskite, $Me_2Ln_2Ti_3O_{10}$ -

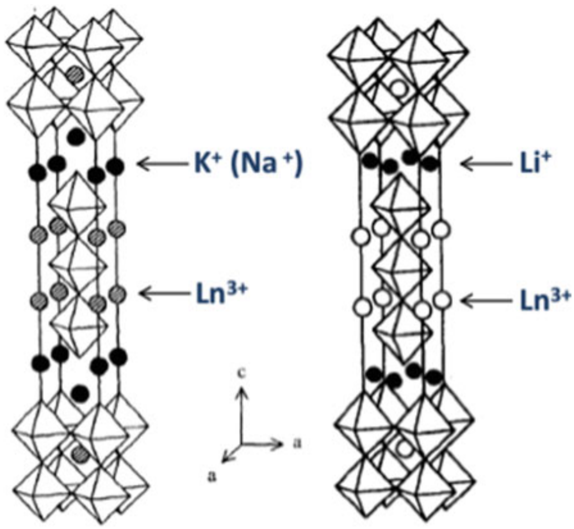

Fig. 1 Extended elementary cells of Ruddlesden-Popper phases

three. Perovskite-like nanolayered titanates were obtained and studied by the authors of [21–24]. Figure 1 shows an extended unit cell for $Me_2Ln_2Ti_3O_{10}$ (Ln - La, Nd; Me - Li, K) [23] and $Na_2Ln_2Ti_3O_{10}$ [24].

So oxides of $K_2Nd_2Ti_3O_{10}$ (as an example) crystallize in a tetragonal structure. The spatial group for these compounds is defined as I4/mmm. The thickness of layered oxides of this type is characterized by three titanium-oxygen octahedra [$Nd_2Ti_3O_{10}$], alternating with each other and separated by alkali metal cations, in this case potassium cations, between the layers. The lattice parameter c (≈30 Å) indicates the displacement of adjacent perovskite layers by ½. The neodymium cation is located in the center of the perovskite lattice and is characterized by a 12-coordinated oxygen environment. The alkali metal cation is located in the interlayer space and is usually 9-coordinated [25].

The layered structure, consisting of lamellar particles, is stored by the product when kept in humid air and confirmed by scanning electron microscopy [26]. The identified stability of the systems recommends them as promising photocatalysts in conditions close to their use and is important for other innovative areas of their applications.

Analysis of recent publications shows that titanium dioxide is mainly used in thin film form, which most effectively implements its properties necessary for photocatalysis, solar energy, sensors, self-cleaning coatings and more.

And the practical implementation of modern technologies of the already proposed variant of the composite photocatalyst [27], the structure of the granules of which is represented by three layers: adsorbent, silicon dioxide and photocatalyst - titanium dioxide anatase modification, will simultaneously solve problems: 1) effective adsorption of both polar and nonpolar (for example, pollutants); 2) exclusion of the influence of the electrically conductive properties of the sorbent on the recombination of photogenerated electron–hole pairs; 3) to ensure complete absorption of incident light by the particles of the photocatalyst, not the adsorbent; 4) detection of photocatalytic activity under visible light.

Today, thanks to the technological methods of reactions of "soft chemistry", it is possible to create substances with various structural features, to obtain metastable compounds by a sequence of low-temperature topochemical syntheses. Such reactions with a change in the structure and morphology of the particles take place at low temperatures while maintaining the basic structural features in perovskite-like layered oxide compounds. Depending on the nature and stoichiometry of their cations, they can exhibit a variety of physical and chemical properties: superconductivity, colossal magnetoresistance, ferroelectricity, catalytic and photocatalytic activity, the ability to ion exchange in solutions and melts, and the ability to hydrate.. Therefore, the study of the peculiarities of transformations of intermediate precursors - alkaline coordination nitrates of REE, their reactivity during the synthesis of layered perovskite-like oxide phases directly affects the possible areas of further application of the latter.

For layered perovskite-like compounds, such researchers include, in particular, ion exchange [25], intercalation and deintercalation [28], various substitution and condensation processes [29], fission processes [30], and mutual transformations of one structure into another [31] (for example, the transition from Ruddlesden-Popper phases to Dion-Jacobson phases; transition within one type of phase with increasing or decreasing number of layers).

The most common reactions of "soft" chemistry are ion exchange reactions, during which the weakly bound cations of the interlayer space are replaced, while the perovskite layers are quite stable mainly due to metal–oxygen covalent bonds and play the role of a framework in the layered structure.. This allows the substitution reactions of some interlayer cations to others, without affecting the basic structure of the layered oxide. Such reactions can be used to obtain a wide range of new perovskite-like structures.

For effective management of properties of the received products deep understanding of physical and chemical processes, the phenomena occurring during their formation is necessary. And their complex research with application of modern physical and chemical methods allows to improve our knowledge of characteristic features of fast-moving processes, stages of evolution of structure and microstructure of technological objects.

The Purpose and Tasks of the Study. To study the cooperative processes of interaction between structural components in the systems of nitrate precursors of REE representatives of the cerium subgroup and elements of IA subgroup of the periodic table (Li, Na, K) in conditions similar to the regulations for creating multifunctional oxide materials for various purposes using photocatalytically active TiO_2 to form reliable ideas and obtaining objective knowledge about the features of transformations and the total behavior of the constituent elements in the preparatory stages of processing of technological objects with thermal activation (25–1000 °C), necessary for improving and developing methodologies and regulations of modern manufacturing technologies.

To achieve this goal, the following tasks were gradually solved in the work:

1) study of the mechanisms of transformations in the systems of coordination nitrate precursors of REE and alkali metals during the formation of multifunctional photocatalytically active layered oxide materials;
2) development of methodology and production of samples of photocatalysts based on TiO_2 anatase modification and composite with the structure of three-layer titanate $K_2Ln_2Ti_3O_{10}$ with their two-stage application and molding on structured metal carriers;
3) study of the kinetic patterns of reactions of test photocatalytic oxidation of vapors of organic substances (for example, ethanol) in a static reactor;
4) establishment of technological and functional dependencies; controlled modification of the properties of the obtained target products.

Experiment Methodology. To evaluate the possibility of controlling the processes of multistage formation of complex oxide compositions with multifunctional properties and substantiation of phase formation mechanisms as a model using a set of physicochemical methods, water-salt nitrate systems $MeNO_3$ - Ln $(NO_3)_3$ - H_2O, (Me - Li, Na, K; Ln - La-Sm) at 25–100 °C. The choice of the composition of the objects of study, temperature sections are determined by a number of factors.

First, among the elements of the rare earth series, the highest complexing ability is found by representatives of the cerium subgroup; among them the largest changes in the composition, structure, and properties of their compounds are the elements of its middle, Pr and Nd. The selected components of the systems specify the technical characteristics of the target product or are modifiers of its properties. And the presence of a large number for the use of potential electronic analogues (representatives of natural series of rare earth, alkaline elements) causes significant variability and breadth of the range of modification of their characteristics. Temperature cross sections are due to the areas of existence of crystal hydrate forms of the source components.

Secondly, according to the research of the authors [32], three layered potassium titanates $K_2Ln_2Ti_3O_{10}$ (Ln - La, Nd) of the above components, obtained by ceramic technology, in suspension form in aqueous-alcoholic solutions under the action of UV radiation show the highest among known species phases photo catalytic activity for the decomposition of H_2O and the release of hydrogen. This fact is associated with the morphology of their particles and the ability to reversibly intercalate water molecules in the interlayer space, which can lead to both an increase in the effective specific surface area of the photocatalyst and contribute to the spatial distribution of redox centers.

To determine the nature of chemical interaction and phase equilibria in water-salt systems of the studied nitrates (precursors of multicomponent oxide polyfunctional materials) in full concentration ratios in the temperature range of solutions used the method of additives described in [33, 34] and based on the study of solutions one of the properties of the most "sensitive" to the detection of phase transformations in systems, which is both a parameter of their state, and also simple experimental methods currently available. The method allows to find the limits of self-development to which the isolated system of the set structure goes in concrete conditions in an equilibrium state.

The equilibrium of the phases was reached within 2–3 days. Hydrated and anhydrous nitrates of these "c.f.a". elements were used as starting salts.

Chemical analysis of liquid and solid phases, "residues" was performed on the content of Ln^{3+} and nitrogen. The Ln^{3+} content was determined trilonometrically in the presence of xylenol orange as an indicator (acetate buffer solution, pH = 5–6) [35]; nitrogen - by distillation [36]; Me^{+} ions - calculated by the difference, based on the total nitrate content and partly on the dry residue.

The obtained data for individual ions were converted into salt content and plotted on the solubility diagrams according to the principle of conformity. Graphical representation of the composition of solid phases formed in the system was performed according to Screenmakers [33, 36], confirmation of their individuality and characterization - chemical, crystal-optical, X-ray phase, X-ray structural, IR spectroscopic, thermographic, and other methods.

Crystal-optical determinations of the compounds were performed by the immersion method using a MIN-8 microscope. Phase analysis was performed on a DRON-3 M diffractometer (Cu Kα radiation, Ni filter) by the "powder" method. Diffractograms were deciphered from the PDF file JCPDS. Determination of symmetry, parameters of unit cells and measurement of the intensity of diffraction reflections from single crystals was performed on an automatic X-ray single crystal diffractometer CAD - 4F "Enraf - Nonius" (Mo Kα - radiation, graphite monochromator; ω/2θ - method). All calculations for the determination and refinement of atomic structures were performed using complexes of crystallographic programs SHELX, XTL – SM, AREN. The IR absorption spectra of the synthesized compounds in the region of 400–4000 cm^{-1} were recorded on a UR – 20 spectrophotometer using a standard vaseline oil suspension technique. Thermograviometric analysis was performed on a Q – 1500 D derivatograph at temperatures from 293 to 1273 K in air with a heating rate of 10°/min and the developed device for DTA.

At the stage of research of photocatalytic oxidation of vapors of organic substrates for formation of samples of composite photocatalysts was used Titanium Oxide Micro Powder (TiO_2, Anatase, 1500 nm, 99,9%) US Research Nanomaterials, Inc.

To study the effect of the formed samples-photocatalysts on the kinetics of formation of gaseous intermediates, the study of photocatalytic oxidation of organic vapors (on the example of ethanol) by static method in a developed sealed chamber-container equipped with replaceable hinged sample holder small and volley doses of injections of substrates, a fan - a mixer of the internal gas environment, an additional internal heater, a sensor for measuring the concentration of CO_2, hinged investigated "passive" plates-adsorbers, lighting system.

A portable multifunctional electronic gas analyzer AZ 7755 (AZ Instrument Corp., Taiwan) was used to measure the CO_2 concentration in the study medium, which allows simultaneous measurement of temperature, relative humidity and has the ability to connect to an external interface.

The following were used as illuminators: a low-pressure fluorescent lamp with a power of 8 W and a bactericidal lamp of the same power with a wavelength of 254 nm.

2 Results of the Research and Their Discussion

2.1 Mechanisms of Transformations in Systems of Coordination Nitrate Precursors of REE And Alkali Metals Accompanying Formation of Polyfunctional Photocatalytically Active Layered Oxide Materials

Generalized and important for practical use information on alkaline coordination nitrates of rare earth elements of the cerium subgroup - precursors of promising modern multifunctional materials - on the conditions of their formation and existence, nature of chemical bond, composition, structure, type of ligand coordination, existence of isotype series on stoichiometry, composition the structures of the revealed properties are systematized by authors [10] and in the most obvious form are resulted in Tables 1, 2, 3 and 4. The choice of this form of data presentation is the most informative and useful in the development of innovative projects allows to predict the causal fundamental patterns of behavior of structural components in similar production processes, to choose the right modes, stages, methods of forming and obtaining target products with reproducible structurally sensitive characteristics.

The revealed regularities in the nature of the behavior of structural components in rubidium, cesium nitrate systems La - Sm, in objects based on REE of the yttrium subgroup (Y, Gd - Lu) indicate the possibility of only limited or special application of the latter predecessors in the study area. There are a number of objective and economic reasons for this. These are the features of the electronic structure of their atoms, lower manifestation of chemical activity and complex-forming ability of these Ln^{3+} in comparison with the elements of the cerium subgroup, weaker effect of the considered influencing factors on the studied processes. To clarify the general patterns and build a holistic objective picture of the behavior of such technological precursors, the authors studied the systems of natural series Y, La - Lu, Li - Cs. Analysis of the results of the study was published in previous works of the authors [10, 37, 38].

In ternary REE-containing nitrate precursor systems, which are integral components of more complex multicomponent systems, exchange transformations begin from the moment the components are dissolved in water. It was found that the Ln^{3+} cerium subgroup in the studied conditions are active complexing agents, form anionic coordination compounds of Me^{+} of all alkali metals, and their stability and complex of inherent properties are potent technological factors that significantly affect the

Table 1 Isothermal concentration limits of crystallization of alkaline coordination nitrates of neodymium from solutions of water-salt systems $MeNO_3 - Nd(NO_3)_3 - H_2O$ (Me – Li, Na, K)

The composition of the compounds	t, °C	Compositions of saturated solutions corresponding to transition and eutonic points, wt. %		The nature of solubility
		$MeNO_3$	$Nd(NO_3)_3$	
$Li_3[Nd_2(NO_3)_9]·3H_2O$	65	19,32 13,95	59,61 65,63	Incongruent
	100	24,03 9,68	54,68 72,51	Congruent
$Na_2[Nd(NO_3)_5]·H_2O$	50	16,55 8,60	51,62 62,58	Incongruent
	65	20,44 3,03	50,40 70,17	Incongruent
	100	25,27 4,15	47,28 76,96	Incongruent
$K_2[Nd(NO_3)_5 (H_2O)_2]$	50	27,26 21,34	51,62 54,91	Incongruent
$K_3[Nd_2(NO_3)_9]·H_2O$	50	21,34 11,49	54,91 63,31	Incongruent
	65	32,57 8,67	47,88 70,44	Congruent
	100	40,15 3,39	45,02 76,44	Congruent

nature of transformations in systems as intermediates. and the results of processes in general.

The obtained information allows to model the behavior of structural components at the preparatory stages of formation of modern multifunctional photocatalytically active materials according to innovative technological regulations with the use of nitrate REE-containing precursors.

The available identified trends in phase formation in the model systems studied are thermodynamically the most probable limits of transformations in technological objects in the conditions of formation and production of target products. And possible real deviations in such systems are caused by inhomogeneity of the reaction medium in composition, content of reacting components, conditions of their location, finiteness of transformations, diffusion features, heat capacity, viscosity, nature of transformations at the boundaries of formed hetero phases, using their applied principles and methods. activation and other specific factors. And the identified processes of complexation in aqueous solutions of nitrates contribute to the homogenization of systems of structural components at the molecular level in complex or combined processing.

The analysis of the obtained data indicates the flow of competing processes of replacement of water molecules by nitrate ions in the systems in the immediate

Table 2 Radiographic data of neodymium lithium, sodium, potassium coordination nitrates

$Li_3[Nd_2(NO_3)_9]\cdot 3H_2O$				$Na_2[Nd(NO_3)_5]\cdot H_2O$		$K_2[Nd(NO_3)_5\ (H_2O)_2]$				$K_3[Nd_2(NO_3)_9]\cdot H_2O$			
d, Å	I/I_0,%	d, Å	I/I_0, %	d, Å	I/I_0, %	d, Å	I/I_0, %	d, Å	I/I_0, %	d, Å	I/I_0, %	d, Å	I/I_0, %
8,36	30	2,013	19	7,84	63	5,42	66	2,056	24	9,48	85	2,281	21
7,64	77	1,979	19	7,54	47	5,27	90	1,993	27	7,74	92	2,249	69
6,68	13	1,944	28	7,07	73	4,94	45	1,947	26	7,65	32	2,189	54
6,00	38	1,931	26	5,18	27	4,11	72	1,777	11	5,36	39	2,108	68
5,75	79	1,855	15	4,23	100	3,88	15			5,27	40	2,082	37
5,42	98	1,778	15	3,80	57	3,80	42			4,94	30	2,058	15
5,26	74	1,726	28	3,15	23	3,66	12			4,76	46	2,012	49
4,76	51	1,708	34	3,09	67	3,53	42			4,49	87	1,909	21
4,64	100			3,02	86	3,35	38			4,26	27	1,837	27
4,35	43			2,629	20	3,18	13			4,06	100	1,757	19
4,19	47			2,391	17	3,05	73			3,89	40	1,729	16
3,94	51			2,346	17	2,873	17			3,78	22	1,714	18
3,90	40			2,307	8	2,843	33			3,73	39		
3,56	26			2,234	13	2,783	14			3,36	19		
3,32	19			2,178	27	2,750	17			3,27	26		
3,22	47			1,979	13	2,724	40			3,18	55		
2,978	34					2,664	14			3,07	16		
2,772	19					2,639	19			3,04	17		
2,617	28					2,594	100			2,844	20		
2,545	43					2,463	37			2,755	12		

(continued)

Table 2 (continued)

$Li_3[Nd_2(NO_3)_9]\cdot 3H_2O$				$Na_2[Nd(NO_3)_5]\cdot H_2O$		$K_2[Nd(NO_3)_5\ (H_2O)_2]$				$K_3[Nd_2(NO_3)_9]\cdot H_2O$			
d, Å	I/I_0,%	d, Å	I/I_0, %	d, Å	I/I_0, %	d, Å	I/I_0, %	d, Å	I/I_0, %	d, Å	I/I_0, %	d, Å	I/I_0, %
2,385	21					2,392	19			2,730	18		
2,328	17					2,374	44			2,647	55		
2,305	23					2,314	15			2,592	16		
2,226	19					2,235	25			2,508	87		
2,135	49					2,188	10			2,468	78		
2,111	43					2,099	21			2,349	32		

Note: d, Å - interplanar distances; I/I_0,% - the relative intensities of the reflexes

Table 3 Coordination polyhedra of Ln atoms in alkaline rare earth nitrates

Compound	D_1	D_2	D_3	C. N.	Polyhedron type, its symmetry
$Li_3[La_2(NO_3)_9]\cdot 3H_2O$		2,66 2,65	2,66 2,65	12 12	Ic $4L_33L_2$ Ic L_33L_2
$Li_3[Nd_2(NO_3)_9]\cdot 3H_2O$		2,61 2,60	2,61 2,60	12 12	Ic $4L_33L_2$ Ic L_33L_2
$Na_2[Nd(NO_3)_5]\cdot H_2O$		2,62 2,61 2,61	2,62 2,61 2,61	12 12 12	Ic L_33L_2 Ic L_33L_2 Ic L_33L_2
$K_2[La(NO_3)_5\ (H_2O)_2]$	2,70	2,68	2,68	12	Ic L_2
$K_2[Nd(NO_3)_5\ (H_2O)_2]$	2,62	2,61	2,61	12	Ic L_2
$K_3[Pr_2(NO_3)_9]$		2,63	2,63	12	Ic L_33L_2
$K_3[Nd_2(NO_3)_9]$		2,61	2,61	12	Ic L_33L_2
$(NH_4)_2[La(NO_3)_5\ (H_2O)_2]\cdot H_2O$ $(NH_4)_2[La(NO_3)_5\ (H_2O)_2]\cdot 2H_2O$	2,54 2,59	2,70 2,70	2,67 2,68	12 12	Ic L_35L_2 Ic L_35L_2
$(NH_4)_2[Pr(NO_3)_5\ (H_2O)_2]\cdot 2H_2O$	2,54	2,66	2,64	12	Ic L_35L_2

D_1, D_2, D_3 – average distance (Å) ‹Ln–O $_{H2O}$›, ‹Ln–O $_{NO3}$›, ‹Ln–O›; Ic – icosahedron.

vicinity of the Ln^{3+} complexing agent. The degree of completeness of substitution depends on the nature of Ln^{3+}, the presence of Me^+, the properties of electron-donor oxygen atoms and the spatial structure of ligands, the concentration of anions, the amount of solvent. A significant influence of temperature factor on these processes is revealed. There are differences in the complexing ability of the elements of cerium and yttrium subgroups, Y, as well as among REE in the middle of the first subgroup. The obtained results indicate the gradual processes of complexation. The presence of certain values of the temperature of the beginning of the release into the solid phase of complex compounds - the existence of an energy barrier and the need for some activation energy to carry out such transformations. In the formation of nitrate complexes, the requirements of symmetry are largely met, and the planar small-sized ligand NO_3^- is "convenient" for the formation of a highly symmetric environment of the Ln_3^+ ion. Lanthanides have a tendency to form three types of NO_3^- ligand coordination. This leads to the formation of both isolated complexes and their polymerization into dual-core, chains, frameworks.

All established coordination compounds were synthesized in single crystal form and characterized by a set of physicochemical methods. Table 2 shows the X-ray diffraction characteristics of the newly formed phases for the possibility of their identification and detection during processing.

The authors conducted a crystal chemical analysis of alkaline rare earth nitrate compounds, which is based on the results of our own research [38] and on literature data [39]. Particular attention is paid to the structure of coordination polyhedra Ln, which largely determines the basic properties of the corresponding compounds.

Table 4 The temperature values of the detected effects during the heat treatment of the representatives of the established groups of alkali coordination nitrates REE

Compounds; spatial group of crystals	Representatives	Temperature interval of formation, °C	The nature of solubility	Dehydration	Melting in crystallization water	Polymorphic transitions	Melting anhydrous form	The composition of the products of conversion at 980 °C
$Li_3[Ln_2(NO_3)_9]\cdot 3H_2O$ cubic.; $P2_13$	La –Sm	65–100	Congr.	65 183 216	183	–	274	$LiLnO_2$
$Na_2[Ln(NO_3)_5]\cdot H_2O$ monocl.; $P2_1/a$	La –Sm	50–100	Congr.	81 148 236	–	271	328	$NaLnO_2$
$K_2[Ln(NO_3)_5\ (H_2O)_2]$ rhomb.; Fdd2	La – Nd	50–100	Incongr.	95,111	95	219	314	$KLnO_2$, Ln_2O_3
$K_3[Ln_2(NO_3)_9]\cdot H_2O$ cubic.; $P4_332$	La –Sm	50	Congr.	126	–	–	347	Ln_2O_3
$K[Ln(NO_3)_4(H_2O)_2]$ prim. rhomb.; $P2_1cn$	Y, Gd - Lu	50–100	Congr.	138,172	138	–	–	Ln_2O_3

Analyzing the shape, symmetry and other properties of polyhedra (see Table 3), we get the opportunity to approach the understanding of the individual features of REE.

Data on average Ln - O distances in rare earth nitrates of alkaline cations discussed in this paper are in good agreement with the expected tendency to decrease

Ln - O distances according to lanthanide compression and to increase these distances with increasing coordination number for fixed REE ion. The distances Ln - O (H_2O), as a rule, are among the shortest contacts in polyhedra. This fact can be explained on the basis of the presence of competing interactions with bonds of the type Ln - O (NO_3^-). Coordination polyhedra are composed, as a rule, of oxygen atoms of bidentate coordinated nitrate groups, less often in combination with oxygen atoms of water molecules. In all considered compounds coordination numbers of representatives of lanthanides of cerium subgroup 12.

When summarizing the structural data of alkaline coordination nitrates, REE draws attention to the extremely limited range of coordination polyhedra for such high CN REEs. In Fig. 2 shows a general view of the identified types of icosahedrons found in the structures of the studied compounds. In cases where water is not part of the coordination sphere of the Ln atom, the polyhedra are constructed in exactly the same way (Fig. 2a). Their equivalence is that the shortened O – O ribs (common to NO_3^- – ligands) occupy the same positions. Exceptions are one of the 2 independent polyhedra Ln in two isostructural compounds $Li_3[Ln_2(NO_3)_9]{\cdot}3H_2O$ (Ln - La, Nd) (Fig. 2b). If the coordination saturation occurs with the participation of water molecules, the shape of the 12-vertices changes slightly. Topologically, it is still the same icosahedron. However, the distribution of shortened ribs in this case is different (Fig. 2c).

The analysis of the Ln-polyhedra considered by us gives grounds to note the tendency of REE in this class of compounds to the organization of a symmetric coordination environment. In some cases, despite the fact that Ln^{3+} ions are

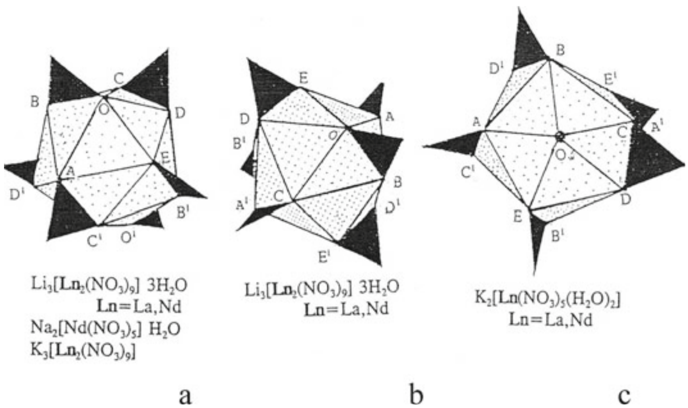

Fig. 2 Schematic representation and general view of Ln-icosahedrons found in the structures of the REEs of the cerium subgroup and lithium, sodium, and potassium

located in common positions, their coordination polyhedra have at least one noncrystallographic axis of symmetry 2 (see Table 3).

The following data from the thermographic study of lithium, sodium, potassium coordination nitrates of rare earth elements of the cerium subgroup (Fig. 3, Table 4) clarify the nature and patterns of thermal transformations of these compounds in the temperature range 25–1000 °C, establish their heat resistance, intervals, staged processes, phase formation depending on the composition, content, nature of the components, the method of packing coordination polyhedra in spatial construction, conditions and method of processing, etc. This makes it possible to predict the behavior of the applied potential predecessors in real technological systems in similar conditions. For comparison and analysis there is information about the low

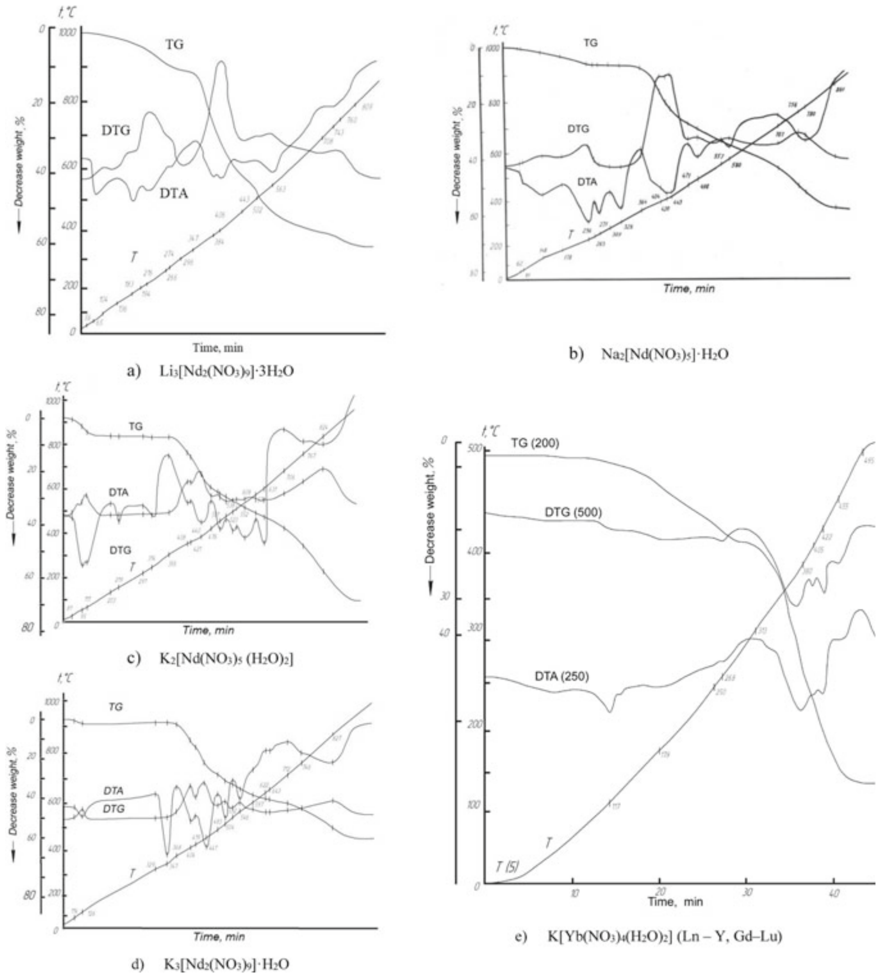

Fig. 3 Derivatograms of compounds

stability and heat resistance of potassium coordination nitrates Y, Gd - Lu composition $K[Ln(NO_3)_4(H_2O)_2]$, which leads to limitations in the use of this type of precursors in technological transformations to modify the properties target products.

It was found that the coordination numbers of the Ln^{3+} cerium subgroup - 12, found in low-temperature associated forms, remain unchanged until the formation of stable high-temperature multicomponent oxide phases $MeLnO_2$, $Me_2Ln_2Ti_3O_{10}$. This indicates the feasibility of using alkaline coordination nitrate REE-containing precursors in such technological innovative solutions.

2.2 Influence of Formed Samples-Photocatalysts (with Structure of Three-Layer Titanate $Me_2Ln_2Ti_3O_{10}$ (Me - K; Ln - Nd) on Kinetics of Oxidation of Vapors of Organic Substances (on an Example of Ethanol)

The logical practical application and testing of the obtained set of empirical knowledge about the combined behavior and properties of constituent components in the studied systems was the development of one of the possible ways of applying and forming composite photocatalytically active coatings on structured metal carriers (to minimize the contribution of adsorption component). submicron sizes of the anatase phase of TiO_2 and similar particles with modified properties of their surface layer and subsequent comparative test for activity in the processes of photodestruction of vapors of organic substances (for example, ethanol) in the air under the influence of UV radiation. Modification of the activity of oxidation centers of objects was carried out by two-stage heat treatment of samples with separate stages of processes: application and fixing of coatings on the basis of water-suspension systems TiO_2 and soluble nitrate precursors Ln and alkali metals taken in given ratios; formation of diffusion flows at the interfacial boundaries of the components of heterogeneous composite systems and regulation of the composition and processing conditions of nitrate precursor melts (in order to create favorable conditions for the association of titanates with a layered structure of $Me_2Ln_2Ti_3O_{10}$). Such composite systems are crystallization-condensed curing structures.

(Requirements for structured functionally active such coatings, their preparation procedures and characteristics are discussed in several review articles [40, 41]).

In the preparatory stages of heat treatment of the original water-suspension systems with refueling of the component composition of soluble nitrate precursors in a ratio corresponding to the formation of a three-layer perovskite-like titanate $Me_2Nd_2Ti_3O_{10}$ (Me_2O $Nd_2O_3{\cdot}3TiO_2$, Me – Li, Na, K; Ln – La–Nd) the solvent is removed from the supersaturated dispersion medium, and according to the studied polythermal solubility diagram [11] (transformation in the region of concentration congruence), the alkaline crystals of alkaline coordination nitrates Ln are gradually isolated. Further heating of these intermediate newly formed phases leads to their melting and subsequent decomposition with the release of oxides of nitrogen and oxygen.

In [42] it was found that the transition of submicron titanium dioxide powder from anatase to rutile occurs at 750–850 °C, and the role of primary structural elements in such dispersed objects is played by powder particles.

TiO_2 (anatase) in the studied multicomponent heterogeneous system behaves chemically indifferent with respect to the constituent structural components until the moment of nucleation in the products of melt thermolysis of nitrate coordination precursors of weakly crystallized chemically active particles of double oxides $MeLnO_2$ ($Me_2O{\cdot}Ln_2O_3$) [15]. With increasing activation energy of the system (t > 520 °C) and, accordingly, the energy of thermal motion of structural elements there is a possibility of their convergence at shorter distances, there is a strengthening of the coordination chemical bond between the constituent cations of the corresponding metals and oxygen anions with the formation of perovski or to some extent, cation-ordered three-layer oxide structures of $Me_2Ln_2Ti_3O_{10}$ with a set of inherent properties.

In the study of the photocatalytic activity of the synthesized materials was performed on the example of the test reaction of ethanol vapor oxidation in a static reactor. The process occurs with the formation in the gas phase of an intermediate product - acetaldehyde, which is eventually completely oxidized to CO_2. For the formed composite photocatalysts, an increase in the oxidation rate of the substrate was observed in comparison with pure TiO_2 (see Fig. 4). As a result, this led to a decrease in the time of removal of the substrate and the intermediate from the gas phase and a decrease in the maximum concentration of acetaldehyde in the latter.

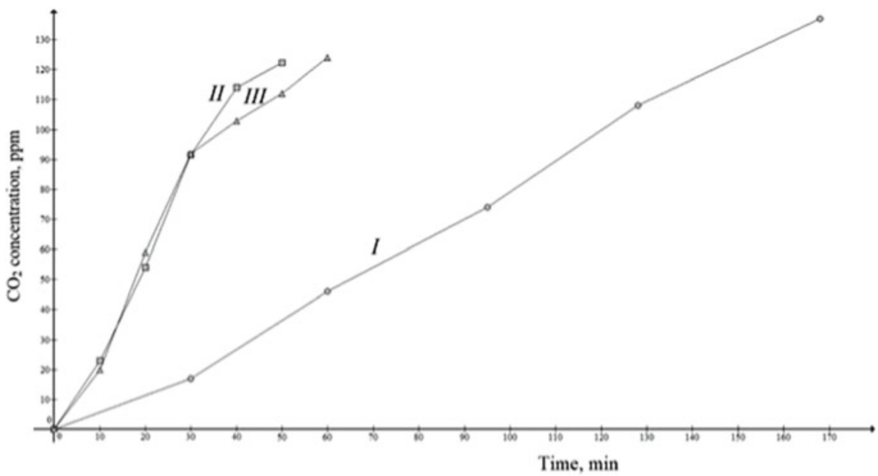

Fig. 4 Kinetics of ethanol vapor oxidation processes under ultraviolet irradiation of titanium dioxide (anatase) (I) photocatalysts and compositions (II, III) modified with the structure of layered perovskite-like oxides $K_2Nd_2Ti_3O_{10}$

The rate of oxidation of the substrate depended on the method of coating, the nature of the applied property modifiers, the sequence of stages and modes of processing, the compatibility of the coating and the base material and the nature of its preparation, the applied composition and content of impregnating systems. To be able to compare the activity of the developed photocatalysts, the portion of the mass of TiO_2 in the original refueling of water-suspension systems samples with pure titanium dioxide and samples with applied modified compositions took the same.

Cation-ordered three-layer composite materials $K_2Nd_2Ti_3O_{10}$ under appropriate conditions can act as alternatives to TiO_2 anatase modification, the relative specific activity of which is 6,2 times higher compared to this characteristic of titanium dioxide.

The obtained information allows to optimize the conditions of formation of cation-ordered layered titanates; find out the conditions and identify the temperature range of application of this class of compounds. The obtained own and literary physicochemical, thermochemical and structural data, as well as the results of their interpretation are a stage in the development of experimental and theoretical scientific databases on layered compounds and processes with their participation.

(Note. Test oxidation of substrates of vapors of organic substances (for example, ethanol) formed by photocatalysts was carried out by irradiation with a bactericidal lamp (254 nm, 8 W) by static method in the laboratory chamber V chamber = 40 dm^3; at T = 292 K, respectively: a) with the introduction of a large simulated dose of C_2H_5OH 2 ml (experiment I) in the presence of TiO_2 anatase modification applied to a structured nonwoven base and b) small doses of 0,1 ml (experiment II), 0,2 ml (experiment III) C_2H_5OH followed by evaporation, in the presence of a functionally active composition $K_2Nd_2Ti_3O_{10}$, applied to steel sheets and moistened with H_2O.

In Experiment I, the coating was formed by drying the anatase modification applied to the structured nonwoven base of an aqueous submicron dispersion of TiO_2; in experiments II, III composite coatings with the structure $K_2Nd_2Ti_3O_{10}$ are formed on sheet steel carriers by a two-stage procedure of application and fixation of precursors and subsequent slow heating of systems at a rate of 3–5 °/min. up to 550 °C and exposure for 4 h).

The studied class of layered compounds is a promising basis for creating functional materials with unique properties, which are determined by the two-dimensional nature of the interlayer space, distortion of the structure of titanium-oxygen octahedra of the perovskite layer and high mobility of alkali metal cations. Such their properties can be used in innovative fields of science, technology, energy, electronics, ecology (see Fig. 4, Table 5).

Table 5 Evaluation of the conditional activity of photocatalyst samples: I sample - based on TiO_2 (anatase) and II sample - based on the composition of the three-layer oxide $K_2Nd_2Ti_3O_{10}$ in the decomposition of ethanol (Fig. 4, for areas with proportional trends)

Cation ordered three-layer $K_2Nd_2Ti_3O_{10}$	TiO_2 (modification of anatase)
$S = 218$ cm^2	$S = 395$ cм^2
$t = 18{,}8$ °C	$t = 19{,}0$ °C
$\tau_\Sigma = 40$ min	$\tau_\Sigma = 128$ min
$\Delta CO_2 = 114$ ppm	$\Delta CO_2 = 108$ ppm
$v_{avg.} = 2{,}85$ ppm/min	$v_{avg.} = 0{,}84$ ppm/min
$v_{avg.\ act.} = 13{,}1 \cdot 10^{-3}$ ppm/cm^2·min	$v_{avg.\ act.} = 2{,}1 \cdot 10^{-3}$ ppm/cm^2·min

3 Scientific Novelty

A comprehensive systematic study of the interaction of structural components in systems of rare earth nitrates and IA groups of elements of the periodic table - precursors of modern multicomponent oxide functional materials based on them - established the formation of a wide class of alkaline coordination nitrates of lanthanides. The identified objective patterns have a fundamental and applied value, deepen the understanding of:

- chemical and physical properties of Ln, their complexing ability,
- possibility of formation and existence in similar systems of associated new phases, their atomic-crystalline structure, stability and stability,
- the influence of the nature of lanthanides and alkali metals on the structure of complex anions and compounds in general,
- individuality of Ln complexes,
- existence of isotypic in composition and structure of groups of compounds in the natural series of lanthanides and alkali metals,
- the role of NO_3^- - groups in the stereochemistry of this class of nitrates,
- the role of water in the formation of the immediate environment of Ln^{3+} ions-complexing agents.

4 Practical Significance

The obtained system of knowledge about transformation processes in REE-containing nitrate precursor systems and crystal chemical properties of Ln coordination nitrate samples acquires special value in the formation of nanostructured layered perovskite-like compounds of lanthanides and transition elements (including titanium, described in [7, 8, 11, 32, 43–51], others), solid solutions based on them; in establishing technological and functional dependencies between the method of preparation, variability of the method of activation of technological systems, methodology of manufacturing the target product and its phase composition, lattice parameters, specific surface area, morphology of constituent particles, activity of self-cleaning compositions with photocatalytic and hydrophilic properties. and special structural elements; in the practical implementation of innovative projects of water decomposition for the purposes of hydrogen production (as an alternative fuel), decomposition of toxic organic substances in solutions and air, incomplete oxidation of carbohydrates; in obtaining other perovskite-like phases by ion exchange reactions and in other areas.

5 Conclusions

1. The results of the study show that the processes of obtaining oxide REE-containing structural and functional materials for different purposes using nitrates of elements of different electronic structure by chemical mixing of the source components in the joint separation of products from the liquid phase by sequential or co-precipitation followed by heat treatment. Data on their composition, content and behavior in each case require prior systemic empirical knowledge in full concentration ratios in a given temperature range.
2. Differences in the behavior of structural components in the systems of lanthanides of cerium and yttrium subgroups, in their nature of interaction, stages, features and patterns of flow.
3. The new knowledge is the basis for:

   – finding ways to increase the activity of Ln-forms;
   – elucidation of the nature of successive thermal transformations in nitrate REE-containing multicomponent systems of different aggregate states during their heat treatment; conditions of formation and existence, properties of intermediate phases; influencing factors; possible ways to control the receipt of the target product;
   – in case of creation of modern perfect low-cost technologies of formation of functional materials of various function with reproducible properties.

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