

Formation of multifunctional perovskite-like layered oxide materials using precursors based on coordinated nitrates of alkali and rare-earth metals

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The results of the research summarize important information about alkaline coordination nitrates of rare earth elements of the cerium subgroup. They are used as precursors for promising modern multifunctional materials. Using a complex of physicochemical methods, the conditions of their formation and existence, the nature of chemical bonding, composition, structure, coordination polyhedra Ln, and ligand coordination type have been elucidated. The existence of a few isotopic series has been revealed based on the stoichiometry of the composition, structure, and characteristic properties. The obtained primary information is the basis for detecting, identifying, and controlling the phase state of processing objects in preparatory stages. It is important at the stages of forming transformational technological schemes, selecting criteria for the compatibility of constituent ingredients, and clarifying the stages and conditions for their implementation. The range of innovative applications includes the formation of monolayer and layered nanostructured oxide compositions of lanthanides and transition elements with catalytic and photocatalytic activity, as well as self-cleaning coatings with hydrophilic properties. The proposed methods include various combined activation of the processes under study and controlled changes in the properties of the resulting target products. The established technological-functional dependencies were assessed. To enhance the photocatalytic activity of coatings based on highly dispersed anatase TiO₂, a technique has been proposed for the chemical modification of oxidation centers in their surface layer, which involves heat treatment in contact with the melt of alkaline coordination lanthanide nitrates. An effective photocatalytic decomposition of organic substrate vapors is shown using ethanol as an example.

Keywords: alkaline coordination nitrates of lanthanides, formation conditions, crystal structure of compounds, characteristic properties, transformations with physical activation

Формування багатофункціональних перовскітоподібних шаруватих оксидних матеріалів з використанням прекурсорів на основі координованих нітратів лужних і рідкісноземельних металів. О.Г. Дрючко, В.В. Соловійов, Н.В. Бунякіна, Б.Р. Боряк, О.Е. Ілляш

Наведені в статті результати досліджень дають змогу узагальнити важливі для практичного використання відомості про лужні координаційні нітрати рідкісноземельних елементів церієвої підгрупи. Вони використовуються як прекурсор перспективних сучасних багатофункціональних матеріалів. З застосуванням комплексу фізико-хімічних методів з'ясовані дані щодо умов їх утворення й існування, природи хімічного зв'язку, складу, будови, форми координаційних поліедрів Ln, типу координації ліганд. Виявлено існування їх ізотипних рядів по стехіометрії складу, структурі та проявляємим характерних властивостей. Одержані відомості (як первинна інформація) є основою для виявлення, ідентифікації,

контролю фазового стану об'єктів перероблення у підготовчих стадіях. Особливу цінність вона представляє на етапах формування технологічних схем перетворень, при виборі критеріїв сумісності складових компонентів, з'ясуванні стадійності й умов їх проведення. Низка інноваційних застосувань включає формування одношарових і шаруватих наноструктурованих оксидних композиційних систем лантанодів і перехідних елементів широкого призначення з каталітичною і фотокаталітичною активністю, покриттів здатних самоочищатися з гідрофільними властивостями. Запропоновано способи розроблення різних комбінованих методів активації таких досліджуваних процесів та керованого модифікування властивостей одержуваних цільових продуктів. Проведено оцінювання встановлених технологічно-функціональних залежностей. Для підвищення фотокаталітичної активності зразків покриттів на основі високодисперсного TiO_2 анатазної модифікації запропонована методологія хімічного модифікування центрів окиснення у їхньому поверхневому шарі з термообробленням у контакті з продуктами термолізу розплавів лужних координаційних нітратів лантанодів. Виявлена ефективна тестова фотокаталітична деструкція парів органічних субстратів на прикладі етанолу.

1. Introduction

Currently, methods and complex technologies are being searched to create new and improve existing modes for obtaining perfect multifunctional oxide materials of transition and rare earth elements with the structure of defective perovskite and garnet with reproducible properties using low-temperature methods of “soft chemistry”, as well as precursors [1–4]. These are scientifically and technologically complex objects that are being intensively studied [5–9], including with the participation of the authors [10, 11]. Therefore, modern materials science based on them requires solutions that are simple in configuration, low-step, energy efficient, with the ability to reproduce products with a given homogeneity, stability, and a set of specified characteristics. The methods for the synthesis of these oxide multicomponent materials [2–13] are based on different physical and chemical principles. The main ones are the following:

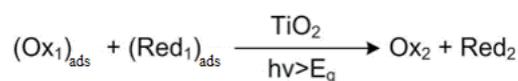
- high-temperature solid-phase chemical reactions;
- liquid-phase condensation for obtaining nanosized oxide materials, including:
 - various options for mixing the starting components (chemical precipitation (co-precipitation); sol-gel; hydrothermal; homogenization of complexonate; solvent replacement; synthesis under the influence of microwave radiation);
 - rapid thermal decomposition of solution precursors (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 a specific preparation method depends on the chemical nature of the compounds obtained, the size and morphological

characteristics of the synthesis product particles, the conditions and method of their formation; the material and surface state, the shape of the samples onto which the coating is applied; available technical capabilities, etc. These methods are used both independently and in combination.

Recently, titanium dioxide has attracted special attention due to new unique prospects for its use as nanostructured materials and nanocomposites with controlled morphological, physicochemical and optical properties. TiO_2 has high chemical and thermal stability and impurity levels in its electronic structure due to a certain type of doping, which makes it promising for the creation of new effective functional materials used in photocatalysis and photovoltaics, sensory, catalysis, for liquid chromatography and other areas.

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



In this case, part of electrons and holes can undergo recombination in the bulk or on the surface of TiO_2 . For the effective 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 substance and also a number of inorganic substances, such as CO , H_2S , HCN , NH_3 , NO_x , etc.; 2) room tem-

perature and atmospheric pressure; 3) the possibility of oxidizing even small concentrations of pollutants, the purification of which by other methods is not economically viable; 4) for the implementation of the photocatalytic purification method, no additional reagents are needed because oxygen from the air serves as the oxidizing agent.

However, the photocatalytic method of air purification has a number of disadvantages, such as: 1) a relatively low purification rate; 2) the need to use ultraviolet light sources when TiO_2 serves as a photocatalyst; 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 treating materials based on titanium dioxide, it is necessary to take into account the possibility of surface and volumetric defects in the TiO_2 crystal lattice (due to the phase heterogeneity in the range of $\text{O}/\text{Ti} < 2$ ratios on the Ti - O phase diagram [14]), which significantly affect the photochemical properties and photoinduced hydrophilic ability of the synthesis products [15].

The continuation of our study was initiated by available information on the state and possible technology improvements of such materials, their stability and reproducibility of properties [1–15], high activity of low-crystallized particles formed during thermolysis of structural components [16], reactivity and transformation of layered perovskite-like oxides, stabilization of photocatalytic and sensory-active crystalline modification of anatase due to NO_3^- ions [17], and doping TiO_2 with Ln_2O_3 [18, 19] when obtaining it from solutions [20]. Currently, ways to control the technical parameters of target products by selecting the composition, synthesis conditions and processing methods are being explored.

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 $(\text{Me}, \text{Ln})_{n+1} \text{Ti}_n \text{O}_{3n+1}$, where Ln are lanthanoids from La to Nd, Me are met-

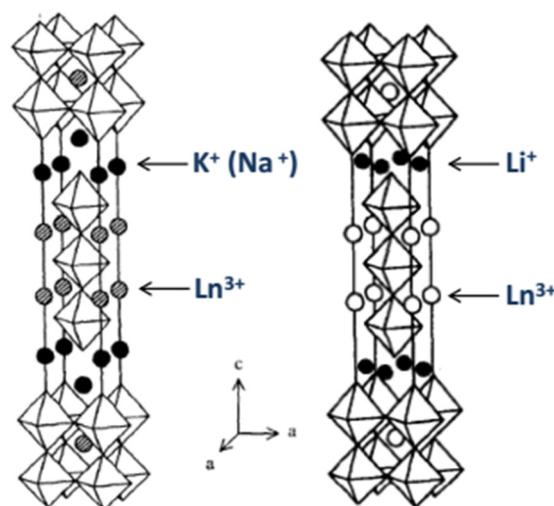


Fig. 1. Extended elementary cells of Ruddlesden-Popper phases

als from Li to Cs, n is the number of perovskite nanolayers (Ruddlesden-Popper phases) with a layer thickness of approximately 0.5 nm). Accordingly, MeLnTiO_4 contains one nanolayer of perovskite in its structure, $\text{Me}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ – three. Perovskite-like nanolayered titanates were obtained and studied in [21–24]. Figure 1 shows an extended unit cell for $\text{Me}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ (Ln - La, Nd; Me - Li, K) [23] and $\text{Na}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ [24].

For example, $\text{K}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ oxides crystallize in a tetragonal structure; the spatial group is $I4/mmm$. Layered oxides of this type are characterized by three titanium-oxygen octahedra [$\text{Nd}_2\text{Ti}_3\text{O}_{10}$], alternating with each other and separated by alkali metal cations, in this case, potassium cations, between the layers. The lattice parameter c ($\approx 30\text{\AA}$) indicates the displacement of adjacent perovskite layers by $\frac{1}{2}$. 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 preserved when stored in humid air, that is confirmed by scanning electron microscopy [26]. The stability of the systems makes them promising photocatalysts under their operating conditions and important for other innovative applications. An analysis of recent publications shows that titanium dioxide is mainly used in the form of thin films to make the most of its properties needed for photocatalysis, solar energy, sensors, self-cleaning coatings and much more.

The practical implementation of the composite photocatalyst variant proposed by modern technologies [27], consisting of granules structured in three layers: an adsorbent, silicon dioxide, and a photocatalyst (anatase titanium dioxide), will allow you to simultaneously solve several problems: 1) effective adsorption of both polar and non-polar molecular substances (for instance, pollutants); 2) eliminating the influence of the conductive properties of the sorbent on the recombination of photogenerated electron-hole pairs; 3) ensuring complete absorption of incident light by the photocatalyst particles rather than the adsorbent; 4) exhibiting photocatalytic activity under visible light.

Thanks to technological advancements in 'soft chemistry' reactions, it has become possible to create substances with diverse structural characteristics and obtain metastable compounds through a sequence of low-temperature topochemical syntheses. These reactions, which change the structure and morphology of particles, occur at low temperatures while maintaining the fundamental structural features of perovskite-like layered oxide compounds. Depending on the nature and stoichiometry of the cations present, these compounds can exhibit various physical and chemical properties: superconductivity, giant magnetoresistance, ferroelectricity, catalytic and photocatalytic activity, ion exchange capability in solutions and melts, hydration ability in interlayer spaces, etc. Therefore, studying the features of the transformation of alkali-coordination nitrates of rare earth elements as intermediate precursors and their reactivity during the synthesis of layered perovskite-like oxide phases directly affects the potential areas of their further application.

For layered perovskite-like compounds, the following processes are considered: ion exchange [25], intercalation and deintercalation [28], various substitution and condensation processes [29], fission processes [30], and mutual transformations from one structure to another [31] as part of their investigative scope (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 of "soft" chemistry are ion exchange reactions, during which the replacement of weakly bound cations in the interlayer space occurs, while the perovskite layers are quite stable mainly due to covalent metal-oxygen bonds and play the

role of a framework in the layered structure. This makes it possible to replace some interlayer cations with 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.

To effectively control the properties of the resulting products, a deep understanding of the physical and chemical processes and phenomena that occur during their formation is necessary. Complex studies using modern physicochemical methods make it possible to expand knowledge about the features of fast processes, stages of evolution of the structure and microstructure of technological objects.

The goal of this research is to study the mutual behavior of structural components in systems of nitrate precursors of rare earth elements (REE) and elements from IA Group of the Periodic Table (Li, Na, K). The features of cooperative processes will be studied under conditions similar to those for creating multifunctional oxide materials using photocatalytically active TiO_2 .

To achieve this goal, the following tasks are solved:

1) studying the mechanisms of transformations in the coordination nitrate precursors of REE and alkali metals during the formation of photocatalytically active layered oxide materials;

2) production of samples of photocatalysts based on anatase-modified TiO_2 and compositions with a three-layer titanate structure $\text{K}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ by two-stage deposition on structured metal substrates;

3) studying the kinetic of photocatalytic oxidation reactions of organic vapors (for example, ethanol) in a static reactor;

4) establishment of technological and functional dependencies for controlled changes in the properties of the resulting product.

2. Experiment

Water-salt systems of $\text{MeNO}_3 - \text{Ln}(\text{NO}_3)_3 - \text{H}_2\text{O}$, (Me – Li, Na, K; Ln – La-Sm) were studied as model systems within the temperature range of 25-100°C. The choice of the composition of the objects and temperature ranges are determined by a number of factors.

Among REE, Pr and Nd exhibit the most significant changes in the composition, structure, and properties of their compounds. The selected components determine the technical characteristics of the target product or serve as modifiers

of its properties. Temperature ranges are determined by the existence regions of crystalline hydrate forms of the initial components.

According to [32], three-layer potassium titanates $K_2Ln_2Ti_3O_{10}$ ($Ln - La, Nd$), obtained using ceramic technology, exhibit the highest known photocatalytic activity among various layered phases when suspended in aqueous-alcohol solutions and exposed to UV radiation, leading to decomposition H_2O and hydrogen evolution. This is due to the peculiarities of the morphology of their particles and their ability to reversibly intercalate water molecules into the interlayer spaces. This phenomenon can lead to an increase in the effective specific surface area of the photocatalyst and contribute to the spatial distribution of oxidation-reduction centers.

To determine the nature of the chemical interaction and phase equilibria in water-salt systems of the studied nitrates (precursors of multicomponent oxide multifunctional materials) at full concentration ratios in the solubility temperature range, the additive method described in [33, 34] is used. This method is based on studying solubility as most sensitive to detecting phase transformations in systems. This method allows us to identify the limits of self-development toward which an isolated system of a specific composition tends under certain conditions in an equilibrium state.

The phase equilibrium was achieved within 2-3 days. Hydrated and anhydrous nitrates of the specified elements, marked as 'pure for analysis', were used as initial salts.

Chemical analysis of the "residues" of the liquid and solid phases was carried out for the content of Ln^{3+} and nitrogen. The content of Ln^{3+} was determined trilonometrically in the presence of xylenol orange as an indicator (acetate buffer solution, $pH=5-6$) [35]; nitrogen – by the distillation method [36]; the content of Me^+ ions was calculated based on the difference based on the total content of nitrates and partially on the dry residue. The obtained data for individual ions were converted to salt content and displayed on solubility diagrams according to the principle of correspondence. Graphic representation of the composition of solid phases formed was carried out according to the Skreinemakers method [33, 34]. For characterization, chemical, crystal optical, X-ray phase, X-ray structural, IR-spectroscopic, thermographic and other methods were used.

The crystal-optical study was carried out by the immersion method using a MIN-8 microscope. Phase analysis was performed by the "powder" method on a DRON-3M diffractometer (Cu-K α radiation, Ni filter). Diffraction patterns were interpreted using the JCPDS PDF file. The symmetry, unit cell parameters, and intensity of diffraction reflections from single crystals were determined using an automatic X-ray single-crystal diffractometer CAD - 4F "Enraf - Nonius" (Mo K α - radiation, graphite monochromator; $\omega / 2\theta$ - 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. Thermogravimetric analysis was carried out in the range of 293 K to 1273 K in air at a heating rate of 10 degrees/min on a Q - 1500 D derivatograph and the developed device for DTA.

To study the photocatalytic oxidation of organic vapors to form samples of composite photocatalysts, titanium oxide micropowder (TiO_2 , anatase, 1500 nm, 99.9%, US Research Nanomaterials, Inc.) was used.

Photocatalytic oxidation of organic compounds (using ethanol as an example) was carried out statically in order to study the effect of the resulting photocatalyst samples on the kinetics of the formation of a gas-phase intermediate. The studies were carried out in a specially designed sealed container chamber equipped with adjustable hanging sample holders, an internal evaporative doser, and an external reactor for small and batch substrate injections. The installation also included a fan for mixing the internal gas environment, an additional internal heater, a sensor for measuring CO_2 concentration, hanging "passive" adsorber plates and a lighting system.

For measuring the CO_2 concentration in the chamber, a portable multifunctional electronic gas analyzer AZ 7755 (AZ Instrument Corp., Taiwan) was used. This device allows you to simultaneously measure temperature and relative humidity, and also has the ability to connect to an external interface. In the study, illumination was provided by an 8W low-pressure fluorescent lamp and a germicidal lamp of the same power with a wavelength of 254 nm.

3. Results and their discussion

3.1 Transformation mechanisms in systems of coordination nitrate precursors of REE and alkali metals during formation of polyfunctional photocatalytically active shaly oxide materials

The authors systematized the relevant information on alkali-coordination nitrates of rare earth elements of the cerium subgroup, which are precursors of promising multifunctional materials. Details about the conditions of their formation and existence, the nature of the chemical bond, composition, structure, type of coordination of ligands, the existence of isotopic series based on the stoichiometry of the composition, as well as the observed properties are described in [10, 11] and are more clearly presented in Tables 1–3.

The revealed regularities in 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 applica-

tion of the latter predecessors in the area under study. The reasons for this are the features of the electronic structure, low chemical activity and complex-forming ability of Ln^{3+} in comparison with the cerium subgroup elements. To clarify the behavior of such technological precursors, the authors studied the systems of natural series Y, La - Lu, Li - Cs [10, 11, 38, 39].

In triple REE-containing systems of nitrate precursors, which are integral components of more complex multicomponent systems, exchange transformations begin from the moment of dissolving the components in water. It has been established that under conditions under study, Ln^{3+} ions of the cerium subgroup act as active complexing agents, forming anionic coordination compounds with Me^+ of all alkali metals. Their stability and the complex of their inherent properties significantly influence the nature of transformations in systems both at intermediate stages and on the overall results of the process.

The information obtained makes it possible to simulate the behavior of structural components at the preparatory stages of the formation of photocatalytically active materials ac-

Table 1. Isothermal concentration limits of crystallization of alkali-coordinated neodymium nitrates from solutions of water-salt systems $\text{MeNO}_3 - \text{Nd}(\text{NO}_3)_3 - \text{H}_2\text{O}$ (Me - Li, Na, K)

Compound composition	t, °C	Compositions of saturated solutions corresponding to transition and eutonic points, mas. %		Solubility nature
		MeNO_3	$\text{Nd}(\text{NO}_3)_3$	
$\text{Li}_3[\text{Nd}_2(\text{NO}_3)_9] \cdot 3\text{H}_2\text{O}$	65	19.32	59.61	incongruent
		13.95	65.63	
	100	24.03	54.68	congruent
$\text{Na}_2[\text{Nd}(\text{NO}_3)_5] \cdot \text{H}_2\text{O}$	50	9.68	72.51	incongruent
		16.55	51.62	
	65	8.60	62.58	incongruent
		20.44	50.40	
100	3.03	70.17	incongruent	
	25.27	47.28		
$\text{K}_2[\text{Nd}(\text{NO}_3)_5 (\text{H}_2\text{O})_2]$	50	4.15	76.96	incongruent
		27.26	51.62	
$\text{K}_3[\text{Nd}_2(\text{NO}_3)_9] \cdot \text{H}_2\text{O}$	50	21.34	54.91	incongruent
		11.49	63.31	
	65	32.57	47.88	congruent
		8.67	70.44	
	100	40.15	45.02	congruent
		3.39	76.44	

according to innovative technological regulations using nitrate-containing REE precursors.

The identified trends in phase formation in the studied model systems represent thermodynamically the most probable limits of transformations in technological objects during the formation of target products. However, potential deviations in such systems are associated with the heterogeneity of the composition of the reaction medium, the content of reacting components, limited conversion rates, diffusion features, heat capacity, viscosity, the nature of transformations at the boundaries of the resulting phases, activation methods, etc. The identified processes of complex formation in aqueous solutions of nitrates contribute to the homogenization of systems of structural components at the molecular level during complex or combined processing.

Analysis of the data obtained indicates competing processes of substitution of water molecules with nitrate ions in the systems in the immediate vicinity of Ln^{3+} complexing agents. The degree of substitution completeness depends on the nature of Ln^{3+} , present Me^+ ions, properties of electron-donating oxygen atoms, spatial structure of ligands, concentration of anions, and the amount of solvent. A significant influence of temperature on these processes was revealed. There are differences in the complexing ability of elements of cerium and yttrium subgroups, Y, as well as among REEs in the middle of the first subgroup. The obtained results indicate a staged nature of complex formation processes. The presence of specific temperatures at which the complex compound begins to enter the solid phase also indicates the existence of an energy barrier and the need for a certain activation energy for 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 complexes, 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 crystal chemical analysis of alkaline rare earth nitrate compounds is based on the results of our own research [39, 11] and on literature data [40]. Particular attention is paid to the structure of coordination polyhedra Ln, which largely determines the basic properties of the corresponding compounds. Analyzing the shape, symmetry and other properties of the polyhedra, we get the opportunity to approach the understanding of the individual features of REE.

All established coordination compounds were synthesized in a single-crystalline form and characterized using a complex of physicochemical methods. Table 2 presents the X-ray diffraction characteristic parameters of the newly formed phases for their identification and detection during processing.

The data obtained on the average Ln – O distances in rare-earth nitrates of alkaline cations are in good agreement with the expected trend of decreasing the Ln – O distances in accordance with the lanthanide contraction and increasing these distances with an increase in the coordination number for a fixed REE ion. The Ln – O (H_2O) distances, as a rule, are among the shortest contacts in polyhedra. This fact can be explained on the basis of competing interactions bonds of the Ln – O (NO_3^-) type. 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, the coordination numbers of representatives of lanthanides of the cerium subgroup was 12.

The analysis of the structural data showed a remarkably limited variety of coordination polyhedra for such high coordination numbers of rare-earth elements. In cases where water is not included in the coordination sphere of the Ln atom, the polyhedra have exactly the same structure. Their equivalence is that the shortened O – O edges (common to NO_3^- – ligands) occupy the same positions. An exception is one of 2 independent Ln polyhedra in two isostructural compounds $\text{Li}_3[\text{Ln}_2(\text{NO}_3)_9] \cdot 3\text{H}_2\text{O}$ (Ln - La, Nd). 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 edges in this case is different.

Analysis of the considered Ln polyhedra shows the tendency of rare earth elements to organize a symmetrical coordination environ-

Table 2. X-ray diffraction data for neodymium lithium, sodium, potassium coordination nitrates

$\text{Li}_3[\text{Nd}_2(\text{NO}_3)_9] \cdot 3\text{H}_2\text{O}$				$\text{Na}_2[\text{Nd}(\text{NO}_3)_5] \cdot \text{H}_2\text{O}$		$\text{K}_2[\text{Nd}(\text{NO}_3)_5 (\text{H}_2\text{O})_2]$				$\text{K}_3[\text{Nd}_2(\text{NO}_3)_9] \cdot \text{H}_2\text{O}$			
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	–	–
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/I₀, % - the relative intensities of reflections.

ment in this class of compounds. In some cases, despite the fact that Ln³⁺ ions are located in conventional positions, their coordination polyhedra have at least one noncrystallographic symmetry axis 2.

The thermographic data on lithium, sodium, potassium coordination nitrates of rare earth elements of the cerium subgroup (Table 3) clarify the nature and patterns of thermal transformations of these compounds in the temperature range of 25-1000 °C. Their heat resistance, intervals, staged processes, phase formation depending on the composition, content, nature of the components, the way of packing coordination polyhedra in spatial construction, conditions and method of processing, etc. were established. These results make it possible to predict the behavior of the applied potential predecessors in real technological systems under similar conditions. For a comparison and analysis there is information about the low stability and heat resistance of potassium coordination nitrates Y, Gd - Lu composition $\text{K}[\text{Ln}(\text{NO}_3)_4(\text{H}_2\text{O})_2]$,

which leads to restrictions in the use of this type of precursors for technological modifying the properties of target products.

It has been established that coordination number 12 of the Ln³⁺ cerium subgroup, found in low-temperature associated forms, remains unchanged until the formation of stable high-temperature multicomponent oxide phases MeLnO_2 , $\text{Me}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$. This indicates the feasibility of using alkaline coordination nitrate REE-containing precursors in such technological innovative solutions.

3.2 Influence of formed photocatalyst samples (with the structure of three-layer titanate $\text{Me}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ (Me - K; Ln - Nd) on kinetics of oxidation of organic vapors (on an example of ethanol)

A complex of empirical knowledge about the compatible behavior and properties of the constituent components in the systems under study resulted in develop one of the possible methods for applying and forming composite photocatalytically active coatings on structured

Table 3. Temperatures of detected effects during the heat treatment of representatives of established groups of alkaline coordinated REE nitrates

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
$\text{Li}_3[\text{Ln}_2(\text{NO}_3)_9] \cdot 3\text{H}_2\text{O}$ cubic.; P2_13	La – Sm	65-100	congr.	65 183 216	183	–	274	LiLnO_2
$\text{Na}_2[\text{Ln}(\text{NO}_3)_5] \cdot \text{H}_2\text{O}$ monocl.; $\text{P2}_1/a$	La – Sm	50-100	congr.	81 148 236	–	271	328	NaLnO_2
$\text{K}_2[\text{Ln}(\text{NO}_3)_5 (\text{H}_2\text{O})_2]$ rhomb.; $\text{Fdd}2$	La – Nd	50-100	incongr.	95,111	95	219	314	KLnO_2 , Ln_2O_3
$\text{K}_3[\text{Ln}_2(\text{NO}_3)_9] \cdot \text{H}_2\text{O}$ cubic.; P4_332	La – Sm	50	congr.	126	–	–	347	Ln_2O_3
$\text{K}[\text{Ln}(\text{NO}_3)_4 (\text{H}_2\text{O})_2]$ prim. rhomb.; P2_1cn	Y, Gd - Lu	50-100	congr.	138, 172	138	–	–	Ln_2O_3

metal substrates. The choice of this type of substrate is determined by the need to increase the photoinduced contribution and minimize the contribution of the adsorption component to the overall effect of the complex transformation. Varying the photocatalytic properties of the coating material was achieved by applying dispersed submicron particles of the anatase TiO_2 phase with modified properties of the surface layer. Then, comparative tests of their activity in the processes of photodestruction of vapors of organic compounds (using ethanol as an example) in ambient air under the influence of UV radiation were carried out. The activity of oxidative centers was modified by step-by-step heat treatment of samples at the following separate stages: 1) application and fixation of coating materials onto a substrate using water-suspension systems of TiO_2 and soluble nitrate precursors of lanthanides taken in specified ratios; 2) formation of diffusion flows at the interfacial boundaries of the components of heterogeneous composite systems; and 3) adjustment of the composition and processing conditions of nitrate precursor melts

(aimed at creating favorable conditions for the association of titanates with a layered structure of $\text{Me}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$). Such composite systems are structures of crystallization-condensation curing. (Requirements for such structured functionally active coatings, their preparation procedures and characteristics are discussed in several review articles [41, 42]).

During the preparatory heat treatment of initial water-suspension systems containing a composition of soluble nitrate precursors in a ratio corresponding to the formation of a three-layered perovskite-like titanate $\text{Me}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ ($\text{Me}_2\text{O Nd}_2\text{O}_3 \cdot 3\text{TiO}_2$, Me – Li, Na, K; Ln – La-Nd), the removal of the solvent from the saturated dispersed medium occurs. According to the polythermal solubility diagram [11] (transformation in the region of concentration congruency), gradual nucleation of crystals of Ln alkaline coordination nitrates takes place. Further heating of these intermediate newly formed phases leads to their melting and subsequent decomposition with the release of oxygen and nitrogen oxides. The transition of submicron titanium dioxide powder from anatase to ru-

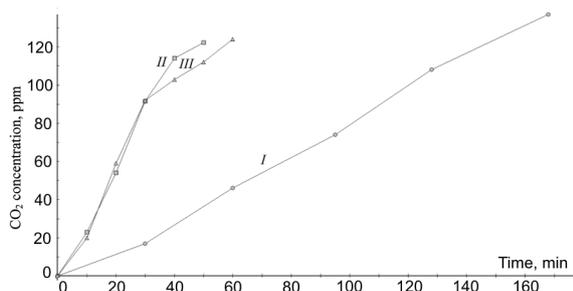


Fig. 2. Kinetics of ethanol vapor oxidation processes under UV irradiation of titanium dioxide (anatase) (I) photocatalysts and compositions (II, III) modified with the structure of layered perovskite-like oxides $K_2Nd_2Ti_3O_{10}$

tile occurs at 750 -850 °C and powder particles serve as primary structural elements in such dispersed objects [43].

In the studied multicomponent heterogeneous system, TiO_2 (anatase) behaves chemically indifferent with respect to the constituent structural components until the nucleation of nitrate coordination precursors of weakly crystallized chemically active particles of double oxides $MeLnO_2$ ($Me_2O \cdot Ln_2O_3$) in the thermolysis products of the melt [16]. When the activation energy of the system and, accordingly, the energy of thermal motion of the structural elements increases ($t > 520$ °C), the possibility arises for their approach at shorter distances; the coordination chemical bonds are strengthened between cations of the corresponding metals and the atoms of oxygen anions with the formation of perovskite cation-ordered (to one degree or another) three-layer oxide structures $Me_2Ln_2Ti_3O_{10}$, which have a complex of inherent properties.

The transition of submicron titanium dioxide powder from anatase to rutile occurs at 750 -850 °C and powder particles serve as primary structural elements in such dispersed objects [43].

The photocatalytic activity of the synthesized materials was studied on the example of the test reaction of ethanol vapor oxidation in a static reactor. The process occurs with the formation of an intermediate product – acetaldehyde in the gas phase, which is eventually completely oxidized to CO_2 . For the formed composite photocatalysts, an increase in the oxidation rate of the substance was observed in comparison with pure TiO_2 (see Fig. 2, Table 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.

Table 4. 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. 2, 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 cm ²
t = 18.8°C	t = 19.0°C
$\tau_{\gamma} = 40$ min.	$\tau_{\gamma} = 128$ 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.

The rate of substrate oxidation depended on the coating application method, the nature of the modifiers, the sequence of treatment stages and conditions, the compatibility of the coating and base material, the composition and content of impregnating systems, as well as on the method for introducing treated substrates into the reactor. To ensure comparability of the developed photocatalyst activities, equal amounts of TiO_2 were used both in the initial water-suspension fillings of samples with pure titanium dioxide and in samples with applied modified compositions.

Cation-ordered three-layered composite materials like $K_2Nd_2Ti_3O_{10}$ under specific conditions, can serve as alternatives to TiO_2 anatase modification, exhibiting a conditional specific activity index 6.2 times higher compared to such a characteristic of titanium dioxide.

The information obtained makes it possible to optimize the conditions for the formation of cationically ordered layered titanates, find out the conditions and determine the temperature range of use of this class of compounds. The obtained physicochemical, thermochemical and structural data, as well as their interpretation are a stage in the development of experimental and theoretical scientific databases on layered compounds and processes with their participation.

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. These properties can be used in innovative fields of science, technology, energy, electronics and ecology.

4. Conclusions

The study shows the processes for producing oxide REE-containing materials using nitrates of elements with different electronic structure by chemical mixing of the starting components with the simultaneous extraction of products from the liquid phase by sequential or coprecipitation followed by heat treatment occur stepwise, accompanied by the formation of a series of intermediate phases. Data on their composition, content and behavior in each case require prior systemic empirical knowledge in complete concentration ratios within the specified temperature interval.

Discrepancies in the behavior of structural components in the lanthanide systems of the cerium and yttrium subgroups were revealed. These differences are manifested in the nature of the interaction, stages, specificity and regularities of the course.

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 obtaining of the target product
- creation of modern perfect low-cost technologies of formation of functional materials of various functions with reproducible properties.

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