

# Low-Temperature Extraction-Pyrolytic Synthesis of Functional Composites

N.I. Steblevskaya, M.V. Belobeletskaya, M.A. Medkov, V. S. Rudnev

**Abstract**—Perspective of use of the extraction-pyrolytic method for obtaining mixed-oxide composites, including nano-scale ones, based on the rare-earth elements, iron, manganese, bismuth, zirconium, tantalum, niobium, platinum, and other elements displaying important practical properties: magnetic, optic, catalytic – was shown. The composition, morphology, and properties of the functional materials prepared were studied.

**Index Terms**— nanocomposites, pyrolysis, rare-earth oxides, functional materials.

## I. INTRODUCTION

The choice of a method for synthesis of various functional materials, in which a rare-earth element is the main bearer of useful properties or an agent modifying these properties, as thin films on various supports or voluminous ceramic samples influences on the composition, structure, and size of the particles and determines the technological process of their obtaining.

There exists a lot of methods for obtaining functional materials including nano-scale ones. Numerous monographs and papers are devoted to description of these methods, summarizing among them [1]-[5].

High-disperse powder materials were prepared by means of solid-phase and gas-phase chemical reactions, sol-gel, kryochemical and vacuum-sublimation technologies, precipitation and co-precipitation from solution, thermal dissociation or by pyrolysis of salts of low-molecular organic acids. In some cases, for synthesis of rare-earth oxides and other inorganic compounds, decomposition of complex compounds with O-, S- and N- containing ligands was used [6]-[9]. Nanocomposites were prepared by chemical modification of layer and porous structures using the same physico-chemical methods for applying coatings on various substrates or by intercalation of particles into matrix pores. Each of these methods has its preferences and deficiencies in case of obtaining certain functional materials for either purpose.

As compared to the high-temperature solid-phase synthesis,

**N.I. Steblevskaya**, Professor, Laboratory of mineral raw material processing, Institute of Chemistry, FEB RAS, Vladivostok, Russia.

**M.V. Belobeletskaya**, Doctor, Laboratory of mineral raw material processing, Institute of Chemistry, FEB RAS, Vladivostok, Russia.

**M.A. Medkov**, Professor, Laboratory of mineral raw material processing, Institute of Chemistry, FEB RAS, Vladivostok, Russia.

**V. S. Rudnev**, Professor, Laboratory of plasma-electrolytic processes, Institute of Chemistry, FEB RAS, Far Eastern Federal University, Vladivostok, Russia.

the so-called methods of “soft chemistry” or solution methods: sol-gel and extraction-pyrolytic are perspective [1]-[3]. In the latter case one can obtain different forms of simple and complex oxides based on the rare-earth elements including nano-scale as both powders and thin-film coatings on various substrates by low-temperature pyrolysis of organic extracts. The extraction-pyrolytic method is used for obtaining homogeneous high-temperature superconductors of various compositions, e.g.  $\text{YBa}_2\text{Cu}_3\text{O}_x$  and  $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_x$ , [1], active materials for lithium current sources and solid electrolytes [10], various luminophors [11]-[14], and magnetic materials with ultra-disperse structure [15]-[17].

Dependence of the composition, properties, morphology, and size of the products of pyrolysis and conditions of its carrying out on the chemical nature of the extractant and the composition of the extraction systems remains insufficiently studied. Working out of specific methods for synthesis of several practically important composites including nano-scale powders, coatings, and thin films is also interesting. The present report describes suggested and realized methods and some regularities of the extraction-pyrolytic synthesis of some compounds and composites based on rare-earth, transition, and non-transition metals.

## II. EXPERIMENTAL

### A. Chemical preparation

As a result of analysis of the literature and our own experimental data on extraction of rare-earth elements with anion-exchange, neutral, and chelating extractants we chose extraction systems efficient for formation of powders and thin films of functional materials based on rare-earth oxides by extracts pyrolysis. Moreover, it is clear that for preparation of materials based on rare-earth elements, only extraction systems having considerable distribution coefficients for metals may be used [14], [18]-[20].

For synthesis of the composites based on metal oxides the saturated rare-earth extracts were prepared by mixing acetylacetone (AA) solution in benzene and aqueous rare-earth chloride or nitrate solution in the presence of 1,10-phenanthroline (Phen) or 2-2'-dipyridil (Dip). The necessary value of  $\text{pH}=7-7.5$  of the aqueous phase was achieved by addition of ammonia aqueous solution. To obtain composites based on metal oxides, the saturated rare-earth extracts prepared by extraction with tributylphosphate (TBP) were used. Bismuth (III) extraction was carried out with benzene solutions of methylhexylketone (MHK), trialkylbenzylammonium thiocyanate (TABAT) or chloride (TABAC) and AA. Iron (III), manganese (II), and platinum

(II, IV) were extracted with benzene solution of trioctylamine (TOA) from aqueous chloride solutions, and zirconium (IV) – from oxalate-chloride ones. Gold (III) and silver (I) saturated extracts were prepared by extraction from chloride and thiocyanate aqueous solutions, respectively, with TOA or diphenylthiourea (DPTU) solutions. To obtain niobium (V) and tantalum (V) saturated extracts TABAC solution in benzene was used. The initial aqueous solutions were kept for contact for half an hour with the same volume of the organic phase. For obtaining bulk composite powders, the organic phase saturated by the metal was separated and the solvent was distilled at 30-60°C. The precursor prepared was exposed to pyrolysis in a muffle furnace at 500-900°C for 1-3 hours. For synthesis of composites based on mixed rare-earth and other metal oxides, before the solvent distillation, one of the above-mentioned rare-earth saturated extract was mixed with the saturated extract of the respective metal in the required amount.

The coatings were applied on various substrates: amorphous silicon dioxide, quartz glass, aluminium or titanium oxide, silicon carbide (Hi-Nicalon fibre). The substrate was impregnated with the above-mentioned saturated extracts of respective metals or their mixture. The coatings were obtained by applying saturated extracts on respective substrates, repeatedly alternating moistening with following drying at 50-70°C. The precursors obtained by this way were exposed to pyrolysis at 600-700°C.

### B. Investigation techniques

The metal concentrations and the aqueous phase compositions in each case were controlled using the atomic-absorption, X-ray fluorescent and X-ray radiometric analysis as well as the luminescent and IR spectroscopy methods. The atomic-absorption analysis of the aqueous and organic phases was carried out at a Solaar 6M (Thermo Electron Corporation) spectrometer with ionization in flame. For determination of the metal concentrations by the X-ray fluorescent method with the total external reflection (TXRF) a TXRF 8030 C device (FEI Company, Germany) was used. The sample 10µL was applied on a support of polished quartz glass. The determination time equaled 500 sec; MoK<sub>α</sub> and WBr<sub>35</sub> served as excitation sources. Itrium solution with the concentration 50 µg/mL was used as an internal standard. The limit of detection for various elements varied from 10<sup>-7</sup> to 10<sup>-10</sup> %. To determine zirconium content in the extracts, excitation of Zr characteristic radiation was carried out using Am-241 radionuclide source with activity to 1 GBk and registration by Si(Li) semiconductor detector with 25 mm<sup>2</sup> sensitive surface and 200 eV energetic resolution on MnK<sub>α</sub> line. The intensities of ZrK<sub>α</sub> analytical lines were used as the analytical parameter.

The IR spectra of extracts and crystal samples were registered at a Spectrum - 1000 (Perkin-Elmer) spectrophotometer in the range 400 – 4000 cm<sup>-1</sup> and at a Specord 75-IR spectrophotometer. The crystal samples were prepared as suspension in vaseline oil and tablets in KBr. The accuracy of determination of the vibrational frequencies equaled ± 1.0 cm<sup>-1</sup>.

The luminescence spectra of the extracts were recorded at a

SDL-1 spectrophotometer. A DRSh mercury lamp served as an excitation source. The measurements were carried out at 300 and 77 K (in the second case the test tubes with the samples were put into a Dewar vessel with liquid nitrogen). The luminescence and luminescence excitation spectra of the luminophore samples were recorded at a Shimadzu RF-5301PC spectrofluorimeter at 300K.

The X-ray diffraction patterns of the samples after pyrolysis were registered at a DRON-2,0 diffractometer in CuK<sub>α</sub>-radiation. To carry out the X-ray analysis the program “Eva” with the “PDF-2” database was used.

Morphology of the nanocomposite samples was investigated by means of a Hitachi S 5500 high-resolution electron scanning microscope and a NT-MDT atomic-power microscope. The microsound analysis of distribution of zirconium oxide film was carried out at a (WDS/EDS) JXA – 8100microanalyzer (Japan, EDS – UK) with accelerating voltage equaled 20kV, current 1·10<sup>-8</sup>A, and the beam diameter – 1 µm. The Hi-Nicalon fibres were placed into epoxide resin. In result of polishing rectangular microscopic sections were obtained in the longitudinal direction of the fibre while in the transverse direction – ellipsoidal sections with zirconium oxide distribution along the cross-section perimeter. For improvement of charge pouring down from the samples the polished surface was covered with a thin layer of carbon film.

The magnetic parameters of the samples were measured at a SQUID MPMS 7 magnetometer in the temperature range 2 – 300K.

### III. RESULTS AND DISCUSSION

The choice of the extractants for every metal considerably influences not only on efficiency of obtaining its saturated extracts for following pyrolysis but also on the composition of resulting products and the temperature of the process as well as morphology and the size of the particles obtained in result of this process [1], [3]. The Table 1 presents the conditions of preparation and the compositions of some pyrolysis products for illustration of the discussing possibilities of the extraction-pyrolytic method (EPM) for synthesis of functional materials.

Specifically, pyrolysis of europium and terbium extracts with TBP lets to obtain both nano-scale powders and thin films of the phosphates - EuPO<sub>4</sub> or TbPO<sub>4</sub> (not rare-earth oxides). Substitution of triphenylphosphin oxide (TPPO) for TBP in extractant solution may result in obtaining these nano-scale phosphates at a lower temperature for the same time of the process as it takes place in obtaining rare-earth oxides when AA, Phen or DP substitutes for TABAC. EuPO<sub>4</sub> was prepared by pyrolysis of the saturated extracts after europium extraction with TBP from thiocyanate solutions while the systems with hexafluoroacetylacetone (HFAA) produces EuF<sub>3</sub>.

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Table 1: Composition of extract pyrolysis products

Extraction systems	T, °C	Phase composition
BiCl <sub>3</sub> + MHK	800	Bi <sub>x</sub> O <sub>y</sub>
BiCl <sub>3</sub> + TABAC + AA	800	Bi <sub>2</sub> O <sub>3</sub> (sillenite) + γ-Bi <sub>2</sub> O <sub>3</sub>
BiCl <sub>3</sub> + TABAC + AA	600	Bi <sub>2</sub> O <sub>2,33</sub>
BiCl <sub>3</sub> + TABAT	700	β-Bi <sub>2</sub> O <sub>3</sub> + Bi <sub>x</sub> O <sub>y</sub>
BiCl <sub>3</sub> + TABAT + MHK	800	β-Bi <sub>2</sub> O <sub>3</sub> + Bi <sub>2</sub> O <sub>3</sub> (sillenite)
EuCl <sub>3</sub> or TbCl <sub>3</sub> +AA + TBP	700	EuPO <sub>4</sub> + TbPO <sub>4</sub>
EuCl <sub>3</sub> or TbCl <sub>3</sub> + AA + TPPO	600	EuPO <sub>4</sub> + TbPO <sub>4</sub>
EuCl <sub>3</sub> or TbCl <sub>3</sub> +HFAA+TABAC	700	EuF <sub>3</sub> or TbF <sub>3</sub>
EuCl <sub>3</sub> + AA +TABAC	700	Eu <sub>2</sub> O <sub>3</sub>
EuCl <sub>3</sub> + AA+Dimethylsulphoxide	400	Eu <sub>2</sub> O <sub>2</sub> S
EuCl <sub>3</sub> + AA + DP or Phen	350	Eu <sub>2</sub> O <sub>3</sub>
(BiCl <sub>3</sub> +MHK +AA)+( EuCl <sub>3</sub> + or TbCl <sub>3</sub> + MHK+ AA)	700	BiEuO <sub>3</sub> or BiTbO <sub>3</sub>
(BiCl <sub>3</sub> + TABAX + AA)+ (EuCl <sub>3</sub> + benzoic acid + tris-hydroxymethylaminometane)	700	Bi <sub>0,775</sub> Eu <sub>0,225</sub> O <sub>1,5</sub>
PtCl <sub>4</sub> + TOA	700	Pt 1 hr
PtCl <sub>4</sub> + TBP + DPTU	700	Pt 1 hr
PtCl <sub>4</sub> + TOA	400	Pt 4 hr
AgSCN(SO <sub>4</sub> ) + TOA	600	Ag
AgSCN(SO <sub>4</sub> ) + TOA	400	Ag and Ag <sub>2</sub> SO <sub>4</sub>
AgNO <sub>3</sub> + TBP	800	Ag <sub>3</sub> P <sub>3</sub> O <sub>9</sub> +AgPO <sub>3</sub> +Ag <sub>4</sub> P <sub>2</sub> O <sub>7</sub>

EuPO<sub>4</sub> was prepared by pyrolysis of the saturated extracts after europium extraction with TBP from thiocyanate solutions while the systems with hexafluoroacetylacetone (HFAA) produces EuF<sub>3</sub>.

Fine-disperse metal Pt, Au, and Ag, including those as thin films on quartz and amorphous dioxide, were prepared by pyrolysis of the extracts of any composition besides the extracts with TBP (DPTU, TOA) obtained from sulphate-thiocyanate solutions at various duration of the process.

The samples of nano-scale rare-earth oxides after pyrolysis were agglomerates with the size 100-200 nm (Fig. 1,a).

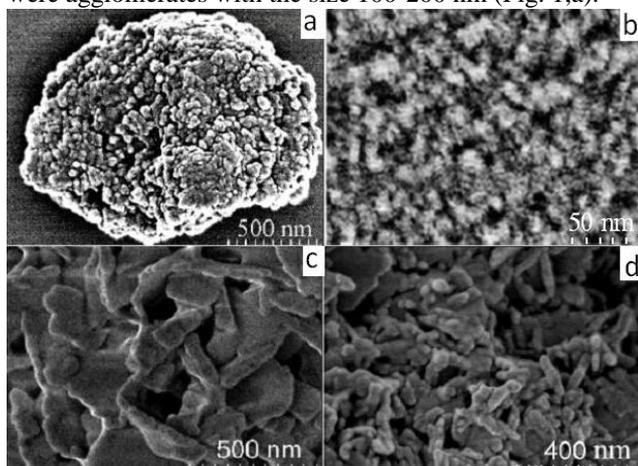


Fig. 1: Micro-image of Eu<sub>2</sub>O<sub>3</sub> sample prepared by pyrolysis of Eu+TABAC+AA extract at 700°C: a – before, b – after

dispersion in ethanol; Eu+AA+CH<sub>3</sub>COOH (c) and Eu+AA+DP (d)

Decomposition of the agglomerates by dispersion in solvent resulted in the change of the particles size to 5-10nm (according to the AFM data) (Fig. 1,b). However, in the samples prepared by pyrolysis of the extracts of different compositions at the same temperature and time, one could observe some differences in morphology of the nano-particles (Fig. 1,c,d).

The influence of the extracts composition was the most clearly demonstrated in displaying polymorphism of nano-scale bismuth oxide compounds prepared from various extracts under the same conditions of pyrolysis that may have essential significance for obtaining bismuth-containing oxide materials, e.g. high-temperature superconductors.

It was shown [18] that bismuth was extracted with trialkylbenzylammonium thiocyanate (TABAT) from mixed chloride-thiocyanate solutions as (TABA)<sub>2</sub>BiCl<sub>5</sub> and, consequently, its saturated extract contained the mixture of bismuth complex chloride and TABAT. It is known [21] that according to various data the boiling point of BiCl<sub>3</sub> is in the range 439-447°C whereas thermal dissociation of bismuth thiocyanate complex at 480°C proceeds with obtaining bismuth sulphide Bi<sub>2</sub>S<sub>3</sub> and metal bismuth [22]. However, pyrolysis of the above-mentioned extracts does not result in BiCl<sub>3</sub> sublimation and Bi<sub>2</sub>O<sub>3</sub> formation. In this case the two phases formed. One of these phase was identified as β-Bi<sub>2</sub>O<sub>3</sub> and another was an unknown phase isostructural to Bi<sub>12</sub>PbO<sub>20</sub>.

One of the purposes of this work consisted in study of possibility of nano-composites synthesis by pyrolysis of extracts based on rare-earth mixed oxides with other metal oxides. Specifically, possibility to obtain the individual bismuth compounds with rare-earth BiEuO<sub>3</sub>, BiTbO<sub>3</sub>, BiFeO<sub>3</sub>, Bi<sub>0,775</sub>Eu<sub>0,225</sub>O<sub>1,5</sub>, nano-scale europium ferrites EuFeO<sub>3</sub> and Eu<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>, terbium manganites TbMnO<sub>3</sub> and TbMn<sub>2</sub>O<sub>5</sub> and lanthanum manganate LaMnO<sub>3</sub> by the extraction-pyrolytic method was studied and proved. This method may be also successfully applied to inclusion of any amount of modifying additions into a composition material. Since these additions are included as extracts on the stage of mixing, precursors obtained and finished products will be characterized by the great degree of homogeneity. Low-temperature pyrolysis of mixed extracts at respective ratios of doping ions resulted in obtaining terbium and lanthanum manganites containing silver and potassium ions as modifying additions: Tb<sub>0,8</sub>Ag<sub>0,2</sub>MnO<sub>3</sub> and La<sub>1-x</sub>K<sub>x</sub>MnO<sub>3</sub>, where x= 0.1, 0.15 and 0.185.

Dependence of the composition of the products obtained on the ratio of the rare-earth ions and bismuth, manganese, and iron content in the organic phase was also studied. One can examine influence of the ratio of the metal contents in the organic phase on example of the synthesis of various rare-earth ferrites and manganites. According to the X-ray data, terbium extraction with solution of AA+TABAC in benzene and that of manganese with TOA in benzene at any ratio of terbium and manganese in the saturated mixed solutions resulted in obtaining the products which pyrolysis

produced manganites  $TbMnO_3$  and  $TbMn_2O_5$ . However, in case of double excess of Mn concentration over Tb, the pyrolysis products contain the only manganite  $TbMnO_3$  in a trace amount. Moreover, manganese oxides  $Mn_2O_3$  and  $Mn_3O_4$  also formed though they were absent in all other pyrolysis products of the mixed extracts as well as non-stoichiometric terbium oxide  $TbO_{1.81}$ . The only terbium oxide  $Tb_4O_7$  was found in the pyrolysis products at the ratio Tb:Mn=1:1 in the organic phase. Increase of terbium concentration in the mixed organic phase to the ratio Tb:Mn=3:1 resulted in formation of manganites  $TbMnO_3$  and  $TbMn_2O_5$  and terbium oxide  $TbO_{1.81}$  after pyrolysis. Pyrolysis of the saturated mixture of the same manganese extract with that of terbium prepared with use of another extract – solution of AA+DP in benzene at the ratio Tb:Mn=1:1 and Tb:Mn=2:1 produced individual manganites  $TbMnO_3$  and  $TbMn_2O_5$ , respectively, which particles in the nano-scale powders had the sizes 20-40 nm according to the AFM data. As for europium ferrites, the X-ray analysis showed that the two compounds  $EuFeO_3$  and  $Eu_3Fe_5O_{12}$  with the particles 5-20nm in size were obtained by pyrolysis of the mixture of the saturated europium extracts of a certain concentration with saturated iron extracts at the molar ratios Eu:Fe= 1:1 or Eu:Fe= 3:5 respectively.

The temperature and field dependences of the specific magnetization values of the magnetic samples prepared by the extraction-pyrolytic method were also studied. One can observe [24], [25] wide variation of the physical properties of the magnetic materials depending on the method and conditions of their synthesis.

It was shown by investigation of the magnetic parameters of  $TbMnO_3$  that at 300K this compound is paramagnetic. The temperature dependence of its magnetization in the field 3000Oe indicated to its transition into another magnetic state in the range 45-35K (Fig. 2). This state is characterized by a higher magnetization as well as the coercive force equaled 320Oe. According to [25], [26] such display of the magnetic properties is typical for multiferroics with magnetic and ferroelectric transitions in the range 30-40K. The data of the magnetic study proved the compound  $Bi_{0.775}Eu_{0.225}O_{1.5}$  to be paramagnetic. The nano-scale multiferroic  $BiFeO_3$  belongs to the materials with a high value of magnetic and electric ordering [16].

Magnetization M, emu/g

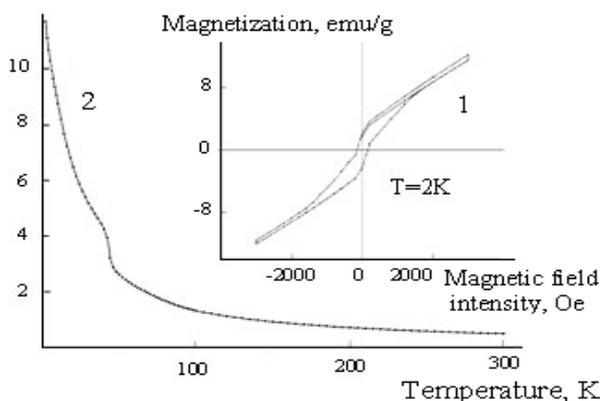


Fig.2: Dependence of magnetization of  $TbMnO_3$  on magnetic field intensity at 2K (1) and on temperature in field 3000Oe (2)

The dependences of the total and remanent magnetization of the nano-scale  $Eu_3Fe_5O_{12}$  and  $EuFeO_3$  prepared by the extraction-pyrolytic method shows display of the magnetic properties depending on their composition. As for the former, one can observe almost the linear dependence of the total magnetization on the value of the constant magnetic field while behavior of the remanence is typical for display of ferromagnetic properties [19]. Such behavior of the total and remanent magnetization is a property of the nano-crystal ferromagnetic structures and amorphous magnetic materials.

Just as  $TbMnO_3$ , the sample  $Tb_{0.8}Ag_{0.2}MnO_3$  is paramagnetic at the room temperature (Fig. 3-2, curve b). In the range 40-45K it transfers from paramagnetic state into ferromagnetic one. The coercive force value at 10K equals 715Oe. The further fall of the temperature to 4K results in the phase transition of  $Tb_{0.8}Ag_{0.2}MnO_3$  from ferromagnetic state into antiferromagnetic (Fig. 3-1).

Magnetization M, emu/g

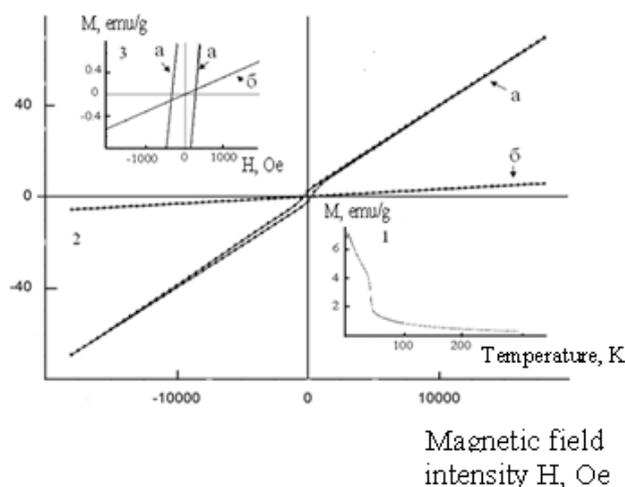


Fig.3: Dependence of magnetization of  $Tb_{1-x}Ag_xMnO_3$  on temperature in field 3000Oe (1) and on magnetic field intensity (2,3) at 10K (a) and 300K (b).

Shift of the hysteresis loop with the temperature change (Fig. 3-3, curves a and b) also indicates to the exchange interaction of the “ferromagnetic-antiferromagnetic” type and is related to complex magnetic structures. This suggestion is confirmed by the presence of the hysteresis loop for this compound at 10K (Fig. 3-2, curve a).

$LaMnO_3$  is the initial compound for manganite doped with potassium ions. The temperature dependences of magnetization for  $LaMnO_3$  cooled in the ZFC and FC regimes have the shape typical for superparamagnetic materials [32], [33] consisted of the superparamagnetic and ferromagnetic phases with the former as predominant. In this case, the temperature of transition of the superparamagnetic phase into a metastable state ( $T_b$ ) is 20K. Moreover, such behavior of the magnetization curves in the ZFC and FC regimes lets to conclude that  $LaMnO_3$  sample prepared by the low-temperature extraction-pyrolytic method consists of nano-particles or their ensembles. It was stated [23] that substitution of potassium ions for some  $La^{3+}$  ions in  $LaMnO_3$  resulted in change of its magnetic properties. This change was explained by variation of the crystal lattice parameters, appearance of interjunction defects and exchange interactions

with formation of the mixed-valent  $Mn^{3+}/Mn^{4+}$  ions in the composition of the compound. According to the temperature dependences of magnetization in the range 2-300K, all the compounds  $La_{1-x}K_xMnO_3$  are ferromagnetics with Curie temperature over 300K. The samples  $La_{1-x}K_xMnO_3$  with potassium contents 0.1 and 0.15 have approximately the same temperature dependences of magnetization. Under the same

conditions,  $La_{0.815}K_{0.185}MnO_3$  has larger magnetization values. The field dependences of magnetization obtained at 2 and 300K shows (Fig. 4, a) that at 300K the samples  $La_{1-x}K_xMnO_3$  have similar magnetic parameters while in the fields over 10000Oe (Fig. 4, b) magnetization of the sample with  $x=0.185$  exceeds that of the samples with  $x=0.1$  and 0.15.

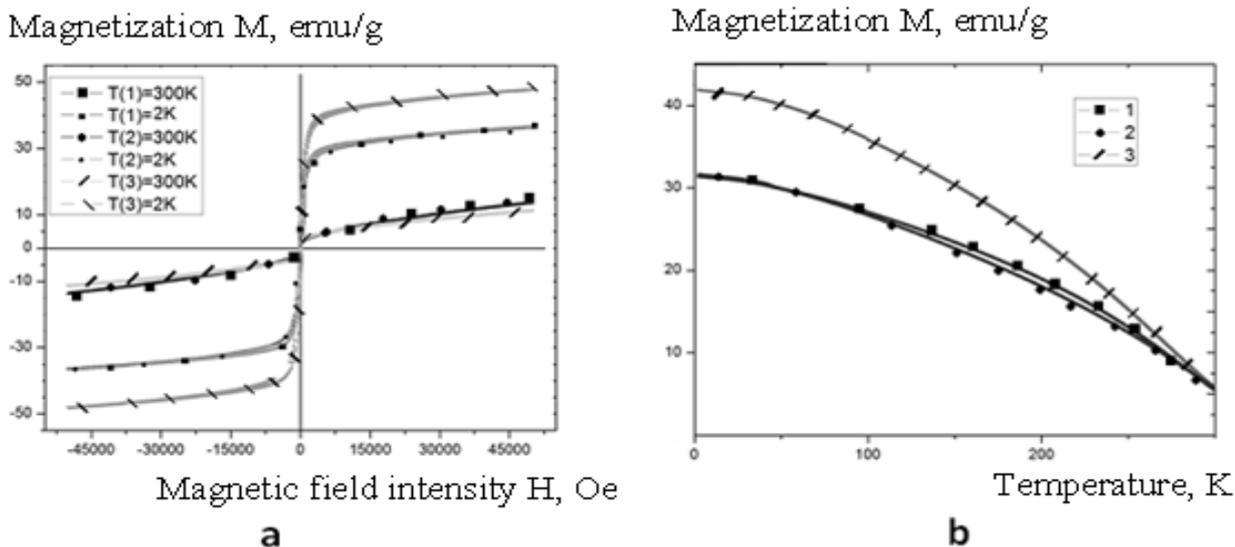


Fig.4: Field (at 2K and 300K) (a) and temperature (in field 10000Oe) (b) dependences of magnetization for  $La_{1-x}K_xMnO_3$  ( $x = 0.1$  (1), 0.15 (2), 0.185 (3)) prepared by the extraction-pyrolytic method.

Fall of the temperature results in increase of the coercive force and saturation magnetization with the sample  $x=0.185$  having the highest values.

The extraction-pyrolytic method lets to optimize preparation of luminophors based on rare-earths due to lowering of the synthesis duration and temperature. We worked out the technique of obtaining nano-disperse luminophors based on europium oxides, oxysulphides, polyniobates, and polytantalates as well as europium oxides, oxysulphides and phosphates with co-activators: yttrium, praseodymium, and terbium and luminophors based on terbium, gadolinium, and niobium by low-temperature pyrolysis of extracts. The luminophor samples are agglomerates, 100-200nm in size. According to the SEM data, decomposition of the agglomerates by dispersion in ethanol resulted in decrease of the particles size to 40-50nm.

The luminescent parameters of luminophors prepared were estimated by their luminescence and excitation spectra at 300K. The luminescence and luminescence excitation spectra of europium oxysulphide with the co-activators are presented as examples in Fig.5. In the short-wave region of the luminescence excitation spectra of the nano-scale europium oxide and oxysulphide samples without co-activators as well as europium oxide, oxysulphide (Fig. 5, a), and phosphate with co-activators – yttrium, praseodymium, and terbium an intensive narrow band ( $\lambda_{max} = 250$  nm) related to transfer of excitation energy to  $Eu^{3+}$  ion is observed. In the long-wave region of the luminescence excitation spectra of europium oxide and oxysulphide (Fig. 5, b) in the range 400-500  $cm^{-1}$  one can observe weak bands of intraconfigurational f-f transitions of  $Eu^{3+}$  ion. In the spectrum of europium

oxysulphide there are also the bands connected with the transitions related to the presence of sulphide sulphur in the composition of the samples.

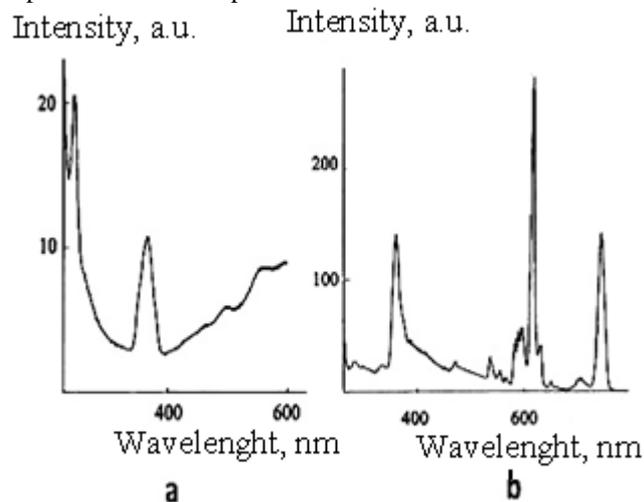


Fig.5: Excitation luminescence (a) and luminescence (b) spectra of yttrium, europium, terbium, and praseodymium oxysulphide luminophor; 300K.

Blue luminescence as a result of the presence of sulphide sulphur and red luminescence of  $Eu^{3+}$  ion are observed in the luminescence spectra of europium oxide and oxysulphide samples ( $\lambda_{excit}=250$ nm and 620nm, respectively). However, it should be noted that in absence of co-activator intensity of  $Eu^{3+}$  luminescence is insignificant. It increases several times with inclusion of co-activator into the composition of a sample. Thus, intensity of the band with the maximum at

615nm corresponding to  $^5D_0-^7F_2$  transition rises 5 times. The luminescence band at 545nm is registered in the spectrum of terbium phosphate. Inclusion of gadolinium and neodymium as co-activators shifts this band in the short-wave region and it displays at 535-538nm. Moreover, intensity of this band increases. Both these facts testify to increase of excitation energy transfer to  $Tb^{3+}$  ion in the presence of co-activators –  $Gd^{3+}$  and  $Nd^{3+}$  ions.

The luminescence spectra of europium oxide, oxysulphide and phosphate nanocomposites containing terbium and yttrium are similar to each other. Intensive luminescence of these nanocomposites is observed in the range 600-750nm (Fig. 5, b) and is related to the presence of both  $Eu^{3+}$  and  $Tb^{3+}$  ions in the luminophor composition. It should be noted that luminescence intensity and the character of the luminescence spectra of these luminophors prepared in the temperature range 550-700°C does not appreciably change. Luminophores obtained at the lower temperature 400°C are the only exception. The literature data and our earlier investigation let to explain this fact by formation of nanoparticles minimum in size.

The typical for  $Eu^{3+}$  ion luminescence in the region of  $^5D_0-^7F_j$  ( $j=0,1,2,3$ ) transitions is registered for all polytantalates  $EuTa_xO_y$  ( $x=7, y=19$ ;  $x=5, y=14$ ;  $x=3, y=9$ ) and polyniobates  $EuNb_3O_9$  and  $EuNb_5O_{14}$  [7], [13]. The isolated line respective to transition of  $^5D_0-^7F_0$  level indicates to homogeneity of the luminescence centre that, in turn, proves formation of individual europium compounds. Distribution of radiation energy at  $^5D_0-^7F_{0,1,2,3}$  transitions in the luminescence spectra of polyniobates, especially the presence of the intensive band of  $^5D_0-^7F_2$  transition in the range ~620nm, is also typical for  $Eu^{3+}$  in individual organic and inorganic compounds [4,7,13,14].

As for the samples of europium polyniobates and polytantalates prepared by pyrolysis in the temperature range 600-900°C, the character of their luminescence spectra (positions of the bands of  $^5D_0-^7F_j$ , where  $j=0,1,2,3$ ) does not appreciably change as it can be seen from the spectra of  $EuTa_7O_{19}$  (Fig. 6).

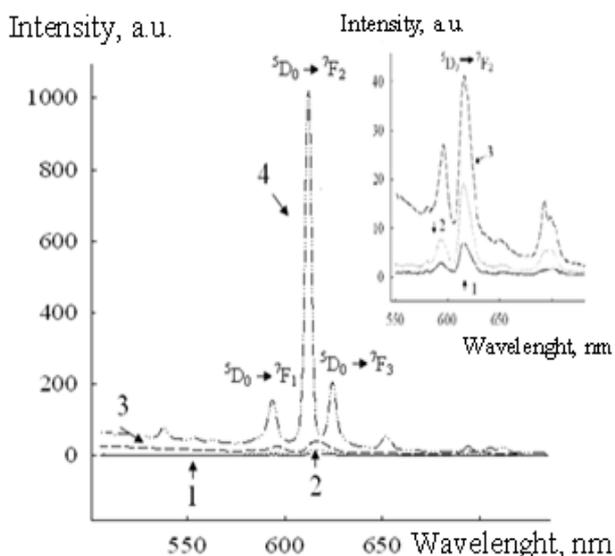


Fig.6: Luminescence spectrum of  $EuTa_7O_{19}$   $\lambda_{ex}=402$  nm (300 K) prepared by pyrolysis at: 1-600°C, 2-700°C, 3-800°C, 4-900°C.

Hence, at 600°C the individual  $EuTa_7O_{19}$  forms. Gradual increase of the pyrolysis temperature (inset in Fig. 6) results in growth of luminescence intensity of the samples. Luminescence intensity of  $EuTa_7O_{19}$  prepared at 900°C was much higher (Fig. 6, curve 4) than that of the samples obtained at lower temperatures. Thus, intensity of the band at ~620nm respective to  $^5D_0-^7F_2$  transition of  $Eu^{3+}$  ion increased more than 20 times.

Possibilities of the extraction-pyrolytic method are displayed the most completely in preparation of nano-scale films and coatings of materials for various purposes. Specifically, it was shown [29] that at 800°C one could obtain the coatings of high-temperature cubic zirconia on composition materials which main component was the ceramic arming fibre SiC (Hi-Nicolon fibre) [30], [31]. The thickness of the cubic  $ZrO_2$  film equaled 1  $\mu m$ . The coatings consisted of the two zirconia modifications – monoclinic and tetragonal – at the same silicon carbide fibre were obtained by the sol-gel method at 1000°C [32]. The extraction-pyrolytic method is easy in fulfilment that may do it more preferable than the most popular now method of gas-phase deposition. This is particularly important for the complicated and expensive process of applying of coatings on thin films.

We also prepared the coatings of  $Eu_2O_3$  and multiferroic  $EuFeO_3$  on amorphous silica as well as the light-protective coating based on europium and cerium oxides on quartz glass. The test data of the light-shielding properties for the nano-scale coating of europium and cerium oxide are presented in Fig.7. The coating is characterized by efficient absorption in the UV region. Transmittance in the UV radiation region ( $\lambda = 200-300$  nm) achieves 30-33%.

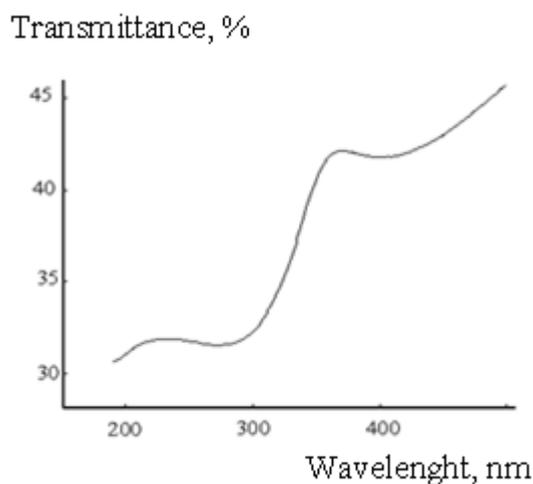


Fig.7. Dependence of transmittance for coating of europium and cerium oxides on quartz glass (T, %) on incident light wavelength.

The preferences of the extraction-pyrolytic method in preparation of  $Eu_2O_3/SiO_2$  composite were demonstrated by the experiment: amorphous silica used consisted of micron particles composed from long blocks 100nm in width. We did not succeed in obtaining the coating of europium oxide when shaking amorphous silica with europium chloride aqueous solution, and evaporating and calcinating at 700°C. In this case  $Eu_2SiO_5$  phase was prepared. Impregnation of

amorphous silica with solution of complex europium stearate in turpentine oil and following calcination at the above-mentioned temperature and duration results in formation of the two phases:  $\text{Eu}_2(\text{CO}_3)_3$  and  $\text{Eu}_2\text{O}_3$ . The nano-scale  $\text{Eu}_2\text{O}_3$  phase forms after processing of  $\text{SiO}_2$  with saturated europium extrates and following calcination at  $700^\circ\text{C}$ . The nanocomposite  $\text{Eu}_2\text{O}_3/\text{SiO}_2$  consists of dense  $\text{Eu}_2\text{O}_3$  particles, close to oval in their shape, with the cross-size equaled 50-100nm and arranged on the sides of  $\text{SiO}_2$  particles. For determination of the true size of the particles in the samples prepared by the low-temperature solvate-thermal method we used the known technique – dispersion in ethanol. The composite consisted of the nanoparticles ~ 10nm in size and had the multilevel hierarchic structure where small particles were assembled into agglomerates on every level.

The same technique was used for preparation of the catalytic active coatings on various supports:  $\text{Pt}/\text{SiO}_2$  and  $\text{Pt}/\text{Eu}_2\text{O}_3/\text{SiO}_2$ ,  $\text{Pt}/\text{Eu}_2\text{O}_3/\text{Ce}_x\text{O}_y/\text{SiO}_2$ ,  $\text{Pt}/\text{TiO}_2/\text{Ti}$ ,  $\text{Pt}/\text{Eu}_2\text{O}_3/\text{Bi}_2\text{O}_3/\text{Ce}_x\text{O}_y/\text{SiO}_2$ ,  $\text{Pt}/\text{Eu}_2\text{O}_3 + \text{Ce}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$ . Such catalysts based on the noble metals are widely used for CO conversion [33]. The catalytic tests of the nanocomposites obtained by the extraction-pyrolytic method showed that for  $\text{Pt}/\text{Eu}_2\text{O}_3/\text{SiO}_2$  containing 1% Pt and 99%  $\text{Eu}_2\text{O}_3$  and comparable with  $\text{Eu}_2\text{O}_3$  by its specific surface the total CO conversion was achieved at a lower temperature which further falled with addition of cerium into the nanocomposite [20]. It is obvious that substitution of the expensive platinum in a catalyst lets to reduce its coast and to widen its use for burning of exhaust gases in internal-combustion engines.

## I. CONCLUSIONS

Conditions of obtaining nano-scale oxide materials by the low-temperature pyrolysis of extracts based on the extraction systems of the rare-earth elements with various polyfunctional ligands were investigated. Perspective of synthesis of nano-scaled composites containing iron, manganese, bismuth, zirconium, europium, terbium oxides, and metal platinum as both powders and thin coatings on dielectric substrates was proved. The composition, morphology, catalytic, luminescent, and magnetic properties of the materials prepared were studied.

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**Steblevskaya Nadezhda Ivanovna**, Professor of chemical science, Institute of Chemistry. Main scientific interests – chemistry and technology of rare and scattered elements, extraction of rare and scattered elements with nitrogen- and oxygen-containing extractants, use of liquid extraction for selective recovery of metals and obtaining various nanotubullar forms of potential functional materials by extracts pyrolysis; synthesis of functional materials by low-temperature solution methods. Achievements: investigation of mechanism of Bi, Zn, In, Fe and rare-earth metals extraction from aqueous solutions with neutral, anion-exchange and chelating extractants. Proposal-extraction obtaining pure organic and inorganic compounds of some metals.

**Belobeletskaya Margarita Vitalyevna**, Doctor of chemical science, Institute of Chemistry. Main scientific interests – chemistry and technology of noble, rare, and scattered elements; theory and practice of extraction processes. Achievements: working out of technological schemes for recovery and separation of Au, Hg and Ag from technogenic raw-material of Far-East region. Perspective of use of the extraction-pyrolytic method for obtaining mixed – oxide composites, including nano-scale ones, based on the rare – earth elements, iron, manganese, bismuth, zirconium, tantalum, niobium, platinum, and other elements displaying important practical properties: magnetic, optic, catalytic – was shown.

**Medkov Mikhail Azarievich**, Professor of chemical science, head of laboratory of mineral raw-materials processing, Institute of Chemistry. Main scientific interests – hydrometallurgical processing of polymetallic raw-material; chemistry and technology of noble, rare, and scattered elements; theory and practice of extraction processes. Co-author of over 300 papers and 50 inventions. Achievements: investigation of mechanism of Bi, In, Fe, Zn, Zr, Ag, Au and rare-earths extraction from acid solutions with neutral and anion-exchange extractants; working out of technological schemes for recovery of Bi, Au and Ag from mineral and technogenic raw-material of Far-East region.

**Rudnev Vladimir Sergeevich**, Professor of chemical sciences, head of laboratory, Institute of Chemistry. Professor of chair "Material science and Metals technology", Engineering school of Far-East federal university. Co-author of more than 400 papers including 2 monographs published in 1999 and 2014. Main-scientific direction – physics and chemistry of new functional coatings on metals and alloys. Scientific interests – surface, functional coatings and materials, aimed synthesis of oxide layers, plasma-electrolytic oxidation, heterogeneous catalysis, photocatalysis, magnetic coatings, biocompatible coatings.