

Synthesis and physico-chemical study of systems of co-precipitated Eu/Me hydroxides

Olga Bugaets^{1}, Elena Kaygorodova¹, Ivan Bugaets², Tatiana Bokovikova², Natalia Bugaets², Elena Butina², Evgeny Gerasimenko², and Ekaterina Bugaets³*

¹Kuban State Agrarian University named after I.T. Trubilin, street named after Kalinin, 13, Krasnodar, 350044, Russia

²Kuban State Technological University, Moskovskaya street, 2, Krasnodar, 350072, Russia

³Municipal Autonomous Educational Institution Lyceum No. 12 named after A. S. Makarenko, 8 Zheleznodorozhnaya Street, Krasnodar, 350033, Russia

Abstract. The level of scientific and technical progress is determined in many respects by inorganic materials – phosphors, sorbents, catalysts, aluminates, chromates, ferrite. The luminescing materials are widely used in medicine, criminalistics, agriculture, in various industries. It creates prerequisites for improvement of methods of receiving phosphors and further research of influence of features of structure of firm phases of materials on their spectral properties. Initial substances for synthesis, the leading role belongs to oxides, hydroxides and systems on their basis. Red phosphors which part compounds of europium are of particular interest. The systems of in the common besieged hydroxides (CBH) received continuous sedimentation of water solutions of nitrates of Eu (III) and Al(III), Fe(III), Cr(III) alkali. The SOG systems were studied by methods of the physical and chemical analysis: differential and thermal, IR-spectroscopic, X-ray phase, X-ray fluorescent, power dispersive. Registration, the emitted luminescent radiation of Eu³⁺ in a system, in the field of 741.4-746.9 nanometers were carried out at a stage of crystallization of amorphous products. The dependence of intensity of a luminescence of systems on synthesis conditions was established.

1 Introduction

The main methods for obtaining aluminates, chromates, ferrites are: crystallization from a solution in a melt, from a pure melt, from a gas phase, chemical vapor deposition, hydrothermal method, floating zone method (crucibleless melting), coprecipitation, three-phase (ceramic) synthesis.

Also, synthesis is carried out by reprecipitation of the RZE complexes from solution to water solution of polyelectrolyte, with their further stabilization [1]. Synthesize hybrid nanomaterials under the influence of laser radiation on the heterogeneous system of a complex of family polynuclear the fosfin-alkinilnykh of heterometal cluster connections [2].

* Corresponding author: obugaec@yandex.ru

By method of hydrothermal autoclave synthesis receive rather perfect crystals thanks to lack of big thermal tension in the course of growth that is inevitable at cultivation by other methods [3].

Synthesis of aluminium magnesium spinel nanopowders doped with europium ions ($3+$) by the method of co-precipitation of hydroxocarbonates requires an additional stage - ultrasonic treatment [4].

The ceramic way of synthesis of polycrystalline connections can be divided into methods: a) agglomeration of mechanical mix of RZE oxides and carbonates alkaline metals and sulfurs; b) thermal decomposition of solid mix of the salts received by evaporation from water solutions with the subsequent agglomeration; d) agglomeration of in common besieged hydroxides, carbonates or oxalates; e) agglomeration of separate oxides of metals; e) isothermal roasting of the inverted opal; g) thermal roasting of the crystal sample $\text{Eu}_2(\text{MeO}_4)_3$ received by method of solid-phase amorphicity with use of comprehensive pressure [5]. Studying kinetics of course of reaction in a firm phase, ceramic synthesis, encounters some difficulties that is connected with high temperatures of process ($900\text{ }^\circ\text{C}$ - $1500\text{ }^\circ\text{C}$), complexity of phase structure of products of reaction, also strong dependence of structure of the final products of reaction on background of a model methods of receiving initial reagents and extent of their dissociation [6].

Each of these methods has the merits and demerits: from fusion with solvent crystals of various sizes turn out, reaction proceeds slowly, besides, there is a need of thorough selection of the corresponding solvent, many stages are required therefore, many questions concerning receiving aluminates, chromates, ferrite of europium of a certain structure and properties, especially at a stage of crystallization of amorphous products remain open.

2 Materials and methods

2.1 Description of the method of continuous co-deposition of Eu(III) and Al(III), Fe(III), Cr(III) hydroxides

Application of a continuous way of joint sedimentation of hydroxides the okristalizovannykh and fine products allows to receive connections with necessary structure (possibly to regulate synthesis conditions), in a look well; to provide the optimum maintenance and uniform distribution of Eu^{3+} (activator), to reduce temperature of synthesis of a powder phosphor [7].

The systems of in common besieged hydroxides received in the continuous way of sedimentation of water solutions of nitrates of Eu (III) and Al(III), Fe(III), Cr(III) alkali in the fivefold volume of water. When receiving SOG concentration of the reacting components changed in the ratio Eu/Me equal 1:1 and 3:5. As the precipitator used sodium hydroxide. Speed of draining of reagents of 2-4 ml/min. Sedimentation was conducted at the room temperature, pH (10.5-11.40) - for solutions with a ratio of components 1:1 and pH (8.45 - 9.8) - for solutions 3:5.

2.2 A comprehensive study of the received precipitation

The received precipitation filtered, washed with the distilled water, wrung out under a press, dried up at the room temperature, and then carried out the complex thermal analysis on a derivatograph of the Hungarian firm "MOM", the speed of heating 5-100 C/mines, a hinge plate of 100-200 mg, temperature register Pt - Pt/Rh the thermocouple.

For identification of the received connections and products of their termoliz made the X-ray phase analysis (RFA). RFA is carried out on the DRONE 3M diffractometer ($\text{Cu}\alpha$ - radiation).

The IR-spectroscopic research was conducted on a spectrometer InfraLYuM FT-02 in the range of $4500\text{-}350\text{ cm}^{-1}$, with KBr.

Ranges of luminescent radiation registered on spectrophotometer Federation Council-4, with record on PPP-0.9 potentiometer. As a source of excitement, the xenon lamp of DRSh-1000 with the UFS-2 filter was applied to allocation of the line of mercury with the wavelength equal of 366 nanometers.

On the derivatogrammakh three endothermic effects and three exothermic effects are observed at temperatures: for SOG of EU/Al – 150, 300, 500 wasps and 400, 630, 1005°C; for SOG of EU/Cr-160, 295, 500°C and 420, 610, 870°C; for SOG of Eu/Fe-160, 297, 540°C and 420, 600, 980°C. On the derivatogrammakh of SOG, at a ratio 3:5, the shift of peaks on 5-7°C, towards increase is noted.

During the X-ray phase analysis of the Eu/Me COG systems, it was found that the freshly deposited sediments have an amorphous structure. Radiographs of samples calcined at temperatures of the second endoeffect show peaks characteristic of europium hydroxide and metal hydroxide. When calcining samples at the temperature of the first exoeffect, peaks characteristic of oxohydroxides are noted. X-ray images of samples calcined at 500-540°C show diffraction peaks corresponding to individual oxides. At the temperatures of the third exoeffect, peaks appear corresponding to compounds with the structure of distorted perovskite EuAlO_3 , EuGrO_3 , EuFeO_3 .

Because the systems of in common besieged hydroxides, have amorphous structure, for clarification of a question of whether there is an interaction between hydroxides in the course of sedimentation or it takes place only at a termoliza, the IR-spectroscopic research is conducted. For this purpose, removed IR spectrums of the freshly cooked samples and samples subjected to heat treatment at temperatures corresponding endo- and ekzoeffekt.

IR-ranges of SOG which are dried up at 25 °C and 90 °C, practically don't differ among themselves. At all ranges there is a wide strip of absorption at area $3610\text{ - }3330\text{ cm}^{-1}$ and a strip at $2360\text{ - }2320\text{ cm}^{-1}$. The front-page answers slabovozmushchenny hydrogen communication of the mastic ON-GROUP coordinate to metal atoms, the second strip corresponds to fluctuations of ON-GROUP of water which are most strongly connected with hydroxide [8]. In IR spectrums of all precipitation there is a strip in area $880\text{ - }420\text{ cm}^{-1}$, caused by communication fluctuations metal – oxygen, and, the shift of peaks of strips of absorption to the low-frequency area has such dependence: EU/GR → EU/Fe → EU/Al [9]. Visible changes of a firm phase happen at temperatures of calcinating of 260-280°C: sharply the intensity of strips of $1660\text{ - }1620\text{ cm}^{-1}$ decreases; amplify intensity of strips of communication metal – oxygen. Establishment of strips of deformation fluctuations of hydroxyl groups at all samples SOG, irrespective of a way and conditions of their receiving, allows to claim that at coprecipitation hydroxides don't interact, and are besieged in solution in the form of true hydroxides [10].

IR - the spectroscopic analysis of the grown old samples showed that intensity of strips of valent fluctuations of ON-GROUP and deformation fluctuations of water decrease; strips of absorption of deformation fluctuations of a hydroxyl and Me-ON are shown more accurately; the intensity of fluctuations increased in low-frequency area (for the systems of EU/Al structure 3:5 strips in this area are a little intensive).

At roentgenograms of all samples there are diffraction lines answering to crystal hydroxides. Showed researches of precipitation which grew old within a year that forms of crystals become more accurate, and the sizes increased by $0.002\text{ - }0.003\text{ \AA}$ (at a ratio of components 1:1) and on $0.001\text{ - }0.0018\text{ \AA}$ (at a ratio of components 3:5). The X-ray phase analysis showed that precipitation consists from poorly okristalizovannykh of particles of oxohydroxides.

2.3 Luminescent properties of co-precipitated hydroxides

Luminescent properties of complex inorganic systems are caused, both properties of substance of a basis, and availability of impurity-aktivatorov which form in the main substance the centers of a luminescence, a soaktivator and a sensitizer. Observed ranges of a luminescence of trivalent europium, are usually interpreted as transitions in blank 4f – covers which are screened from external crystal field 5s25p6 electrons. Due to the shielding of the 4f shell, various crystals with the same activator (Eu^{3+}) have very similar spectra that are shifted relative to each other by 10 -10.6nm. Luminescence of Eu^{3+} occurs mainly during transitions from excited state $5D^0$ to state $F7j$ ($j = 0.1,2,3,4$). These transitions cause the color of phosphors containing Eu^{3+} . The nature of the luminescence spectra depends on the relative position of the excited terms 4fk and 4fk-1 5d. Change of crystal base leads to displacement of term, which indicates stronger influence of crystal field on optical electron of 4f-shell [11].

Visually, the color of compounds containing Eu^{3+} is perceived as red with different shades, moreover, for Eu/Me SOG systems at a ratio of 1:1, the color is perceived as saturated pink, and at a ratio of 3:5 - red. For the Eu/Cr LPG system, the luminescence color is the brightest; a significant increase in color intensity is noted for aged samples. The luminescence spectra in Figure 1 and Figure 2, of europium hydroxide (calcined at the temperature of the second endo-effect - 280 ° C) consist of three bands: at $\gamma = 560.3$ nm (intensity $I = 0.0735$ otn. units or 7.35%); $\gamma = 596.4$ nm ($I = 0.0678$ otn. units or 6.78%); $\gamma = 748.58$ nm ($I = 0.0251$ otn. units or 2.51%). Crystals of three-, four- and polygonal shapes have size 0.005-0.009 nm. On radiographs of europium hydroxide, clearly marked peaks are noted: 5,52; 3,18; 3,03; 2,757; 1,828. Crystalline chemical characteristics of hydroxide: hexagonal modification; pr. gr. P63/m; $a=b=6,39$, $c=3,6582$. $\alpha=\beta=90^\circ$, $\gamma=120^\circ$; $Z=2$; $V_e = 127.88 \cdot 10^{-24} \text{ cm}^3$.

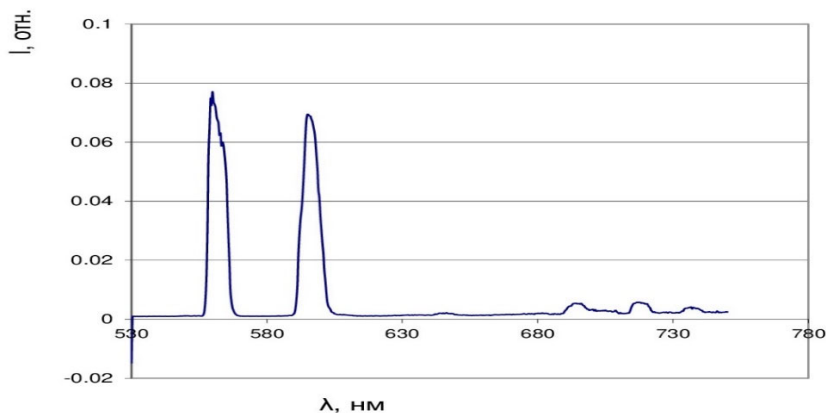


Fig. 1. Luminescence spectra of europium hydroxide.

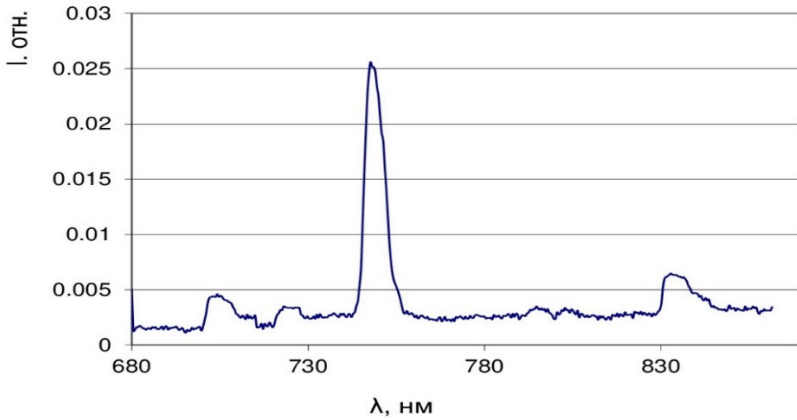


Fig. 2. Luminescence spectra of europium hydroxide.

IR spectra of europium hydroxide have the following absorption bands: 3450, 1620, 1150, 1050, 960, 840, 754, 480 cm^{-1} . When the sample is heated at 280 °C, a significant decrease in the band of valence fluctuations of hydroxyl and deformation vibrations of water is observed on the spectra; strips at 1150, 1050, 960, 840, 754 cm^{-1} become more intense.

The luminescence spectra of the Eu/Me LPG systems consist of narrow lines located in the wavelength region $\gamma = 742\text{-}747.5$ nm in Figure 3, Figure 4, Figure 5.

On the luminescence spectra of the Eu/Al LPG systems calcined at the temperatures of the second endoeffects, a band is observed at $\gamma = 746.9$ nm ($I = 0.0114$ otn. units or 1.14%) for LPG 1:1 and band at $\gamma = 741.4$ nm ($I = 0.0197$ otn. units or 1.97%) for COG 3:5.

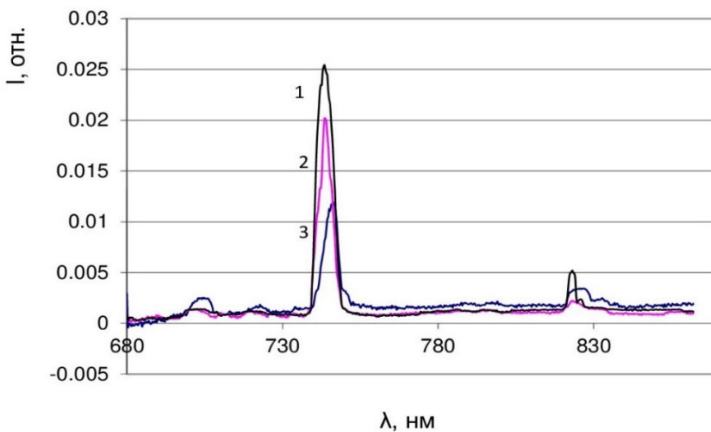


Fig. 3. Luminescence spectra of Eu/Al LPG systems at the ratio of components: 1- (1:1); 3- (3:5); 2- after a year of aging (1:1).

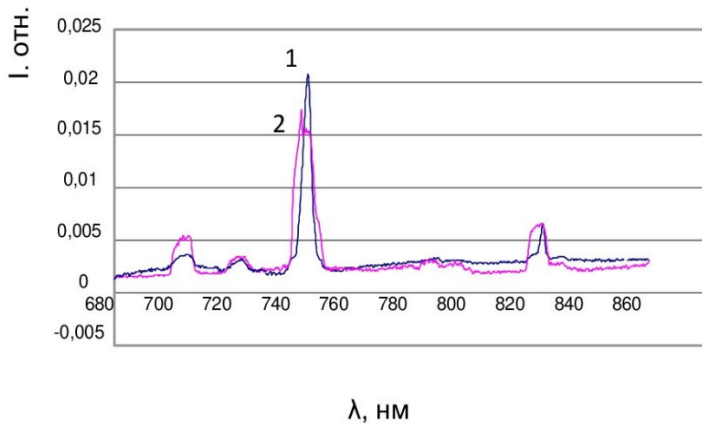


Fig. 4. Luminescence spectra of LPG Eu/Cr systems, with the ratio of components: 1- (1:1); 2- (3:5).

The Eu/Al system (1:1) after the year of aging has a band at $\gamma = 743.8$ nm ($I = 0.0250$ otn. units or 2.50%) in Figure 3. According to microscopic analysis, the COG precipitates are polygonal, as well as distorted elongated rectangular crystals, measuring 0.0037-0.0060 Å.

On the spectra of the Eu/Cr LPG systems, calcined at the temperatures of the second endoeffect in Figure 4, a band is noted at $\gamma = 747.5$ nm ($I = 0.020$ otn. units or 2%) for COG 1:1; spectrum of the system 3:5 has an intense band at $\gamma = 745.7$ ($I = 0.0180$ otn. units or 1.80%). On the spectrum of the sample, which became old during the year, a band is observed at $\gamma = 742$ nm ($I = 0.0150$ otn. units or 1.50%).

According to microscopic analysis, the sediments of SOG europium and chromium are three-, four- and polygonal crystals of gray-blue and white, measuring 0.005-0.0075 Å.

The luminescence spectra of the Eu/Fe LPG systems calcined at the temperatures of the second endoeffect have a band at $\gamma = 743.8$ nm ($I = 0.005$ otn. units or 0.5%) for LPG 1:1; on the LPG spectrum 3:5, a band is noted at a value of $\gamma = 746.3$ nm ($I = 0.0023$ otn. units or 0.23%).

The spectrum of the Eu/Fe system (1:1) after the year of aging has a band at $\gamma = 740$ nm ($I = 0.025$ otn. units or 2.5%) in Figure 5. Sediments of the LNG system europium and iron crystallize into hexagons, measuring 0.005-0.006 Å light brown and white.

Diffraction lines corresponding to crystalline hydroxides are present on the radiographs of all samples.

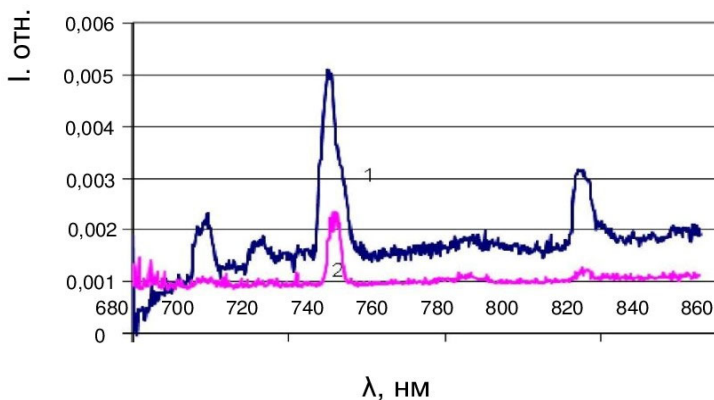


Fig. 5. Luminescence spectra of Eu/Fe LPG systems at the ratio of components: 1 - (1:1); 2 – (3:5).

3 Results and discussion

Analysis of the luminescence spectra of Eu/Me COG systems obtained by continuous deposition of metal hydroxides at the crystallization stage of amorphous products showed that:

- relative to the luminescence spectrum of europium hydroxide ($\gamma = 748.58$ nm, $I = 0.0251$ otn. units or 2.51%) shows a gypsochromic shift for COG at a ratio of 1:1: Eu/Cr at 1.01 nm, for Eu/Al at 1.68 nm, for Eu/Fe at 4.78 nm;
- for COG systems, at a ratio Eu/Me of 3:5, there is a hypsochromic shift of 2-5 nm relative to the COG spectra at 1:1, which is associated with concentration quenching of luminescence;
- stability of light recoil of LNG systems also depends on temperature: the relative intensity of luminescence decreases by 4-6% with an increase in calcination temperature for every 20 ° C. Calcination temperature above 700 ° C leads to a decrease in luminescence intensity of LPG systems;
- for aged samples (6 months), compared with freshly precipitated, there is a hypsochromic shift of 3-5 nm (with a COG ratio of 1:1); Note here that radiation intensity decreases by 0.0052 otn. units for Eu/Cr and increases by 0.02 otn. units, for Eu/Fe system and at 0.0136 otn. units for Eu/Al.

When studying Eu/Me LPG systems, it was found that the highest relative intensity of luminescence spectra is noted in Eu/AL LPG systems with a ratio of 1:1 components obtained from diluted solutions.

4 Conclusions

The use of the method of synthesis of COG made it possible to reduce the temperature of synthesis of perovskites by 300-600 ° C compared to the method of solid-phase synthesis. A study of the co-deposition process of Eu (III)/Me (III) hydroxides showed that compounds with a perovskite structure are formed by calcining systems of co-precipitated hydroxides at appropriate exo-effect temperatures. It was found that in the range of COG, the Eu/Al→Eu/Fe→Eu/Cr temperatures of the synthesis of perovskites decrease. When chromates (III) were formed as intermediates, chromates (VI) were interpreted.

An examination of the aging process of LOG systems showed that freshly precipitated samples are gel-like, X-ray amorphous precipitates. It was found that: Eu/Al COG form a mechanical mixture; the aging process proceeds along the path of ordering the structure with subsequent recrystallization, in parallel there is hydration of aluminum oxohydroxide.

The aging process of COG Eu/Cr proceeds by the mechanism of one-sided (limited) protection against crystallization, created by chromium hydroxide particles, and then, the aging process proceeds by the mechanism of collective recrystallization. Eu/Fe COG systems form a mechanical mixture, aging proceeds according to the scheme: structure ordering, collective recrystallization. SOG systems are referred to as rapidly aging hydroxides [12, 13].

Eu/Me LPG systems can be recommended as phosphors.

The research was carried out using the equipment of the Research Center for Food and Chemical Technologies of KubSTU (CKP_3111) which development is supported by the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 075-15-2021-679).

References

1. A. A. Vasilieva, I. E. Kolesnikov, A. A. Manshina, *Synthesis of associated hybrids based on luminescent nanocrystalline materials and noble metal nanoparticles*. In the collection: Science, education and innovation. Collection of articles of the International Scientific and Practical Conference (Ufa. Russia: Omega Sainz Limited Liability Company) **25** (2016)
2. E. V. Goleva, I. E. Kolesnikov, M. D. Mikhailov, I. A. Sokolov, A. A. Manygin, *Journal of General Chemistry* **86(12)**, 2096-2097 (2016)
3. A. M. Nikolaev, I. E. Kolesnikov, O. V. Frank-Kamenetskaya, M. A. Kuzmina, *Method for production of nano-sized high-luminescent apatite with admixture of europium (EU)*. 21.08.2017. Application No. 2016124206 dated 17.06.2016 *St. Petersburg. Russia: Federal state-funded educational institution of the higher education St. Petersburg State University (St. Petersburg State University)*. RU 2628610 C1. B 24 (2016)
4. V. A. Yukhno, A. V. Povolotsky, M. G. Krzhizhanovskaya, I. E. Kolesnikov, R. S. Bubnova, *Physics and chemistry of glass* **46(5)**, 497-508 (2020)
5. D. V. Mamonova, I. E. Kolesnikov, E. V. Goleva, M. D. Mikhailov, S. A. Pulkin, V. M. Smirnov, *Russian nanotechnologies* **10(9)**, 32-35 (2015)
6. Yu. G. Galyametdinov, O. A. Turanova, A. A. Knyazev, V. I. Haase, *Chemistry* **384(2)**, 206-209 (2002)
7. T. N. Bokovikova, O. N. Chemeris, J. V. Kapustyanskaya, *Depp. in VINITI RAS* **1384** (2003)
8. E. A. Kaigorodova, *News of higher educational institutions Series: Chemistry and chemical technology* **46(8)**, 3 (2003)
9. S. Z. Shmurak, V. V. Kedrov, A. P. Kiselev, T. N. Fursova, I. I. Zverkova, S. S. Khasanov, *Solid state physics* **61(11)**, 2142-2153 (2019)
10. T. N. Bokovikova, L. P. Afonina, O. N. Chemeris, N. M. Privalova, *Series: Natural Sciences* **53**, 59-62 (2005)
11. N. A. Shamsutdinova, «Luminescent and paramagnetic polyelectrolyte-stabilized colloids based on complexes Tb (III) and Gd (III) with 1,3-diketones on a calixarene platform for bioanalytic use» *Federal Research Center "Kazan Scientific Center of the Russian Academy of Sciences," Institute of Organic and Physical Chemistry named after A.E. Arbuzov Kazan Scientific Center of the Russian Academy of Sciences Autoreferat dissertation for the degree of candidate of chemical sciences (Kazan, Russia)* **11** (2017)
12. T. N. Bokovikova, O. N. Chemeris, J. V. Kapustyanskaya, *Aging process of coprecipitated hydroxides systems Eu/Al, Cr, Fe Deposited manuscript B2003 14.07. 2003* **1385** (2003)
13. O. N. Bugaets, E. A. Kaigorodova, I. A. Bugaets, T. N. Bokovikova, *Differential thermal, X-ray phase methods for investigating systems of jointly deposited hydroxides Eu/Me, where Me - Al, Cr, Fe*. *Science of the XXI century: challenges, formation, development: collection of articles of the IV International Scientific and Practical Conference (20 June 2022). Petrozavodsk ICNP "New Science"* **217** (2022)