
**SYNTHESIS AND PROPERTIES
OF INORGANIC COMPOUNDS**

Extraction-Pyrolytic Synthesis and Luminescent Properties of Europium and Terbium Polyantalates

N. I. Steblevskaya^{a,*}, M. V. Belobeletskaya^a, M. A. Medkov^a, and V. S. Rudnev^b

^a*Institute of Chemistry, Far Eastern Branch, Russian Academy of Sciences, Vladivostok, 690022 Russia*

^b*Far Eastern Federal University, Vladivostok, 690950 Russia*

*e-mail: stblevskaya@ich.dvo.ru

Received December 30, 2015

Abstract—The promise of synthesis of europium and terbium polyantalates MTa_xO_y , where $M = \text{Eu, Tb}$; $x = 7, y = 19$; $x = 5, y = 14$; $x = 3, y = 9$ by low-temperature extraction-pyrolytic method has been shown. Luminescent properties of the prepared polyantalates have been assessed from excitation and luminescence spectra at 300 K. The dependence of luminescent characteristics of the studied rare earth metal polyantalates on the temperature and time of precursor pyrolysis has been established.

DOI: 10.1134/S0036023617030160

The continuing interest in rare earth elements and their compounds is caused by the variety of their properties and the expansion of scope of their practical application in chemical and optical industry, medicine, atomic, semiconductor, laser, magnetic, and luminophore technics. In particular, rare earth metal polyantalates and solid solutions on their basis are widely used as X-ray contrast dyes, luminophores, coatings for X-ray screens, optical materials, materials for electronics [1–6].

Particle size and other physical properties of functional materials vary in a wide range depending on preparation conditions [1, 4, 5]. The choice of methods for the synthesis of oxide composites as both bulk ceramic samples and thin films is one of the main tasks in designing materials with definite set of electrophysical, magnetic, optical, mechanical, and other useful properties. It is the used method for material preparation that considerably affects the composition, properties, structure, particle size, and manufacturability of its production. The development and improvement of particular procedures of preparation, energy-efficient including, is still one of the most important directions of contemporary studies in the field of synthesis of oxide materials.

The methods of synthesis of rare earth metal polyantalates widely used for manufacture of particular materials [1, 6] refer to solid-phase synthesis and consist in the careful mixing of initial tantalum and rare earth metal oxides in stoichiometric ratio and calcination at 1200–1400°C for 7–100 h. The method of solid-state synthesis is modified to obtain materials that satisfy requirements (for example, phase homogeneity). This approach includes different techniques:

intermediate homogenization of charge, hot-pressing of precursors or their mixing with flux, mechanochemical activation of initial oxide mixture, etc. [6–8]. The drawback of solid-phase synthesis is high temperatures and long duration of precursor calcination. A method of preparation of europium heptatantalate by coprecipitation of tantalum pentachloride and europium nitrate with ammonia from alcoholic solutions followed by filtration of resultant precipitate. However, the coprecipitated product next again subjected to long-term thermal treatment (350–400 h) at elevated temperatures (1000–1100°C). The preparation of europium metatantalate (EuTa_3O_9) and heptatantalate ($\text{EuTa}_7\text{O}_{19}$) by sol–gel method is briefly reported in the work [9].

This work deals with the study of possibility to obtain europium and terbium polyantalates by the low-temperature pyrolysis of organic extracts based on extraction systems with different polyfunctional ligands and the study of their luminescent properties. The preparation of functional materials containing or modified by rare earth elements corresponds to the Program of the Ministry of Industry and Trade accepted in 2013 for the restoration of rare earth elements industry, composite materials including.

EXPERIMENTAL

Experimental studies to determine the optimal concentrations of extractants in initial organic phase and composition of aqueous phases showed [10–12] that metal extraction with neutral, anion-exchange, and chelating extractants from aqueous solutions can be used to obtain saturated solutions with the aim of

their further use for the synthesis of functional materials based on mixed oxides of rare earth elements and transition metals by pyrolysis method. In this work, terbium and europium were extracted with mixed 1.95 mol/L acetylacetone and 0.0167 mol/L 1,10-phenanthroline solutions in benzene to obtain organic precursors. The concentration of Eu^{3+} and Tb^{3+} in aqueous phase was 8.0×10^{-3} mol/L. The pH value of aqueous phase equal to 7.5 necessary to obtain organic phases saturated with rare earth elements was made by addition of aqueous ammonia solution. The value of aqueous phase pH was controlled with the use of a Radelkis OP-211/1 pH meter.

Initial 0.0027 mol/L tantalum aqueous solution was prepared by the fusion of 0.2 g of Ta_2O_5 with 10 g of $\text{K}_2\text{S}_2\text{O}_7$ in a quartz crucible with gradual temperature elevation up to 700°C . The melt was leached with 50 g/L ammonium oxalate solution [13]. The pH value of initial aqueous tantalum solution at this method of preparation was 3–4. Tantalum concentration in aqueous solution was determined on a TXRF-8030C X-ray fluorescence spectrometer (FEI Company, Germany) with total external reflection. To obtain extract saturated toward tantalum, a benzene solution of trialkylbenzylammonium sulfate was used as an extractant. Organic and aqueous phases in 1 : 1 ratio were vigorously stirred at ambient temperature for 30 min on a SK-30 mechanical shaker (Korea). Saturated tantalum solutions of 0.0098 mol/L were obtained after double extraction of tantalum from fresh aqueous phases with the same extractant volume.

The composition of aqueous and organic phases was monitored by atomic absorption and X-ray fluorescence methods. Saturated europium and terbium extracts in benzene were mixed in required ratios with tantalum extract to produce homogeneous solution. The resultant mixed organic phase with definite metals ratio was evaporated at $60\text{--}80^\circ\text{C}$ and subjected to pyrolysis at different temperatures in a muffle furnace. Pyrolysis time varied from 1 to 4 h. X-ray powder diffraction patterns of the samples after pyrolysis were registered on a DRON-2.0 diffractometer in $\text{CuK}\alpha$ radiation. The obtained powders were studied using a Hitachi S 5500 high-resolution scanning electron microscope and an NT-MDT atomic force microscope manufactured by NT-MDT Corp. (Zelenograd, Russia). Luminescence excitation and luminescence spectra at 300 K were registered on a Shimadzu RF-5500 spectrofluorimeter.

RESULTS AND DISCUSSION

Previously [11, 12], we showed the promise of preparation of functional materials based on europium and terbium by low-temperature extraction-pyrolytic method. This method was also used for the introduction of modifying additives into composite material [14]. A paste obtained from the saturated extracts after

solvent removal, which contains the corresponding stoichiometric amounts of the main metals, was used as a precursor. The final products prepared by the low-temperature pyrolysis of such precursors are more homogeneous and their preparation requires less energy expense due to shorter duration and lower temperature of the process as compared with the known methods, for example, solid-phase synthesis.

Acetylacetone and 1,10-phenanthroline were used as previously [12–14] to prepare organic phases saturated with europium and terbium. Organic phases saturated with tantalum can be prepared from fluoride solutions [15], however, the pyrolysis of precursors obtained from phosphorus- or fluorine-containing phases results in metal phosphates and fluorides rather than oxides [11]. Tantalum completely passes into organic phase when oxalate aqueous solutions and benzene solution of trialkylbenzylammonium sulfate were used. Organic phase of this composition containing rare earth elements and tantalum are well mixed to form homogeneous precursors and, as shown below, allow preparation of rare earth metal polytantalates at relatively low pyrolysis temperature. Polyntantalates of different composition— EuTa_3O_9 , $\text{EuTa}_5\text{O}_{14}$, and $\text{EuTa}_7\text{O}_{19}$ —were prepared from the precursors according to X-ray powder diffraction analysis, Eu : Ta ratios in them were 1 : 3, 1 : 5, and 1 : 7, respectively. Figure 1 exhibits a micrograph of $\text{EuTa}_7\text{O}_{19}$ polyntantalate sample. Particle size in polyntantalate samples after dispersing in ethyl alcohol (Fig. 1a) was 80–100 nm according to atomic force microscopy (AFM).

The luminescent characteristics of europium and terbium polyntantalates were assessed from excitation and luminescence spectra at 300 K. The luminescence excitation spectra (Fig. 2) of europium polyntantalates of different composition display narrow bands corresponding to intra-configurational $f\text{--}f$ transitions of Eu^{3+} ion [16]. Polyntantalate luminophores based on europium show strong red luminescence in the region 550–700 nm with $\lambda_{\text{max}} \approx 620$ nm (Figs. 3–5).

To select the optimal temperature and time of synthesis for each rare earth metal polyntantalate with efficient functional properties, we studied the effect of these parameters of sample synthesis on luminescence intensity as one of the main characteristics. Luminescence spectra of samples were recorded under identical conditions. Luminescence excitation wavelength was selected from the most intense line after recording luminescence excitation spectra of luminophores. It was 402 nm for all prepared europium polyntantalates. The luminescence intensity of luminophores was compared using the band in luminescence spectrum with maximum at ≈ 620 nm corresponding to the ${}^5D_0\text{--}{}^7F_2$ transition of Eu^{3+} ion.

Figure 3 displays luminescence spectra of $\text{EuTa}_7\text{O}_{19}$ sample obtained by pyrolysis of precursors for different time. Figure 3 shows that increase in pyrolysis time from

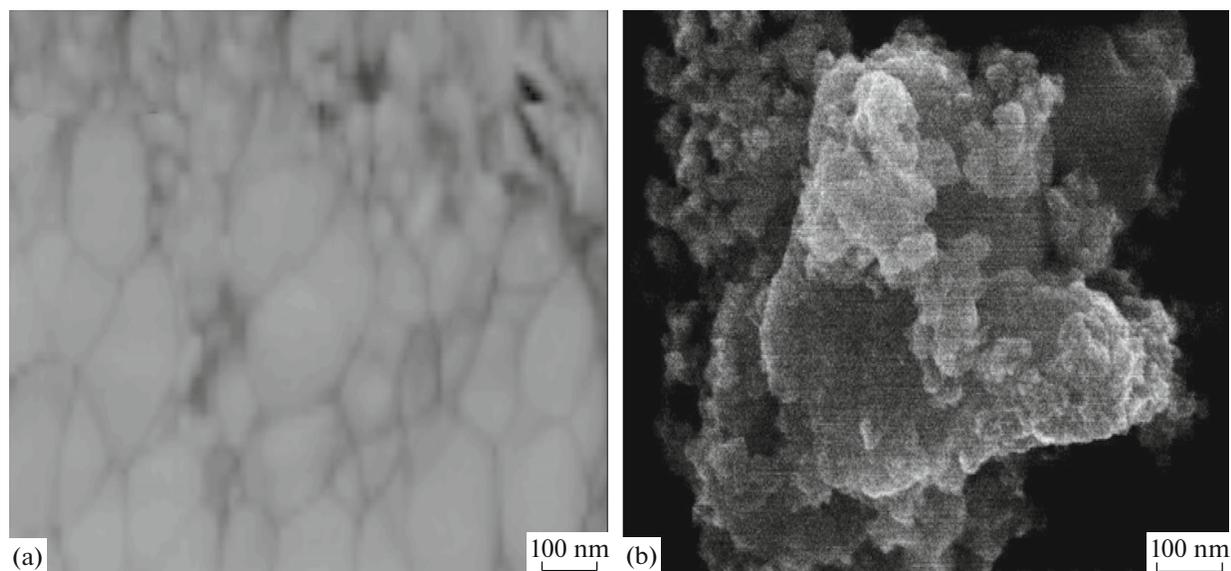


Fig. 1. Micrograph of $\text{EuTa}_7\text{O}_{19}$ sample.

2 to 4 h leads to growth of luminescence intensity of europium polytantalate almost by a factor of three and then luminescence intensity remains constant. No samples of europium and terbium polytantalates with intense luminescence were obtained at pyrolysis time < 2 h.

It should be noted that the composition of each europium polytantalate: EuTa_3O_9 , $\text{EuTa}_5\text{O}_{14}$, and $\text{EuTa}_7\text{O}_{19}$, remained constant within studied temperature range according to XRD data. Moreover, the character of luminescence spectra for all polytantalate samples obtained in pyrolysis temperature range 600–900°C is not changed markedly (Fig. 4). Figure 4

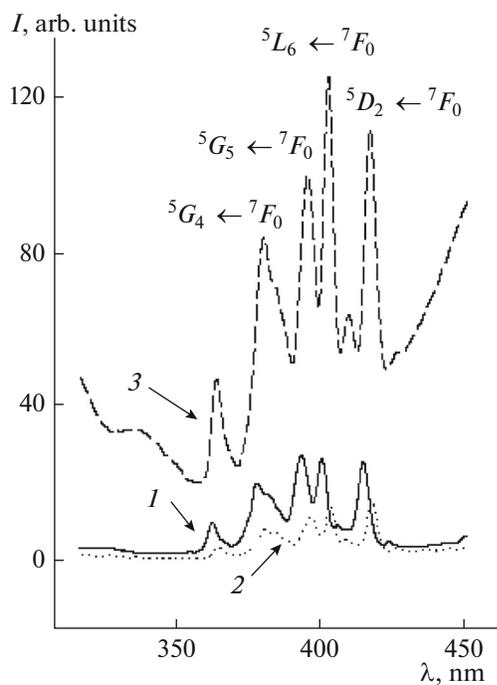


Fig. 2. Luminescence excitation spectra $\lambda_{\text{em}} = 615$ nm (300 K) of europium polytantalates EuTa_3O_9 (1), $\text{EuTa}_5\text{O}_{14}$ (2), and $\text{EuTa}_7\text{O}_{19}$ (3), prepared at pyrolysis temperature 900°C.

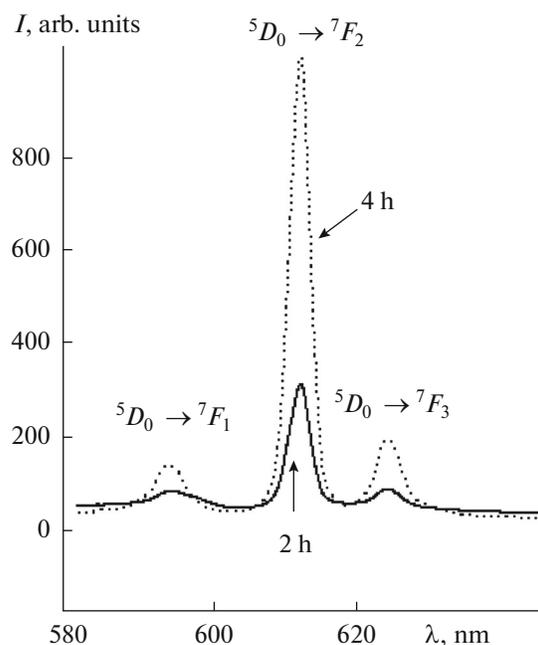


Fig. 3. Luminescence spectra for $\text{EuTa}_7\text{O}_{19}$ sample, $\lambda_{\text{ex}} = 402$ nm (300 K), prepared at pyrolysis temperature 900°C depending on pyrolysis time.

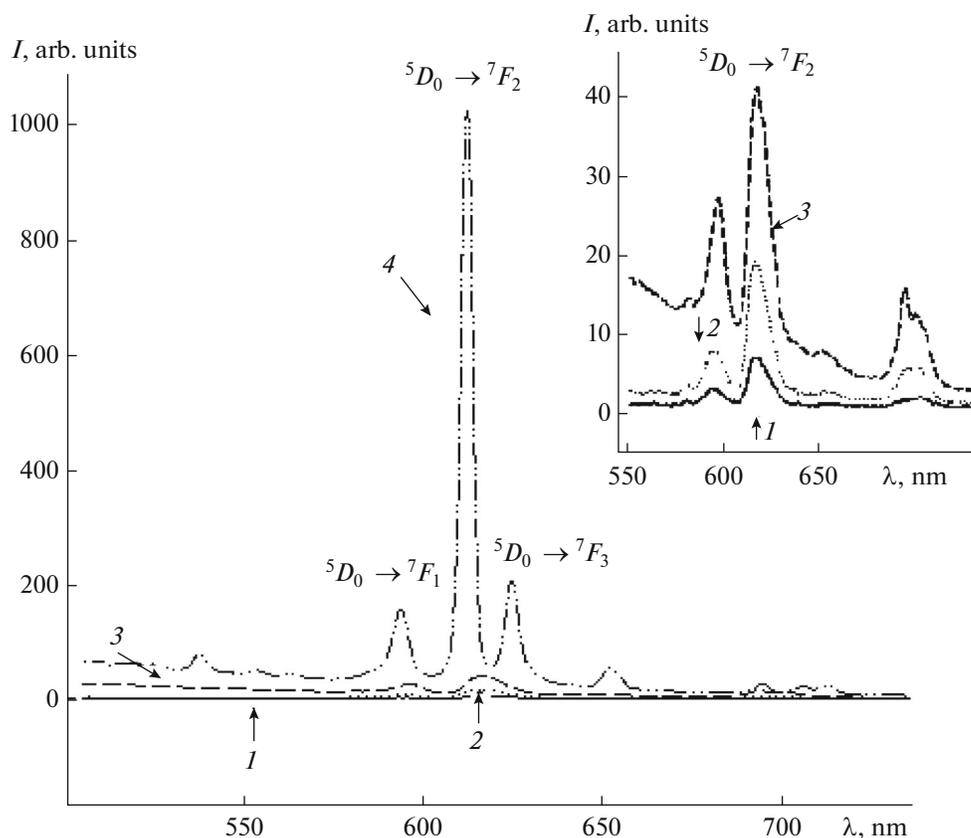


Fig. 4. Luminescence spectra for $\text{EuTa}_7\text{O}_{19}$ sample, $\lambda_{\text{ex}} = 402$ nm (300 K), prepared at pyrolysis temperature: (1) 600, (2) 700, (3) 800, and (4) 900°C.

exemplifies the luminescence spectra of europium polytantalate $\text{EuTa}_7\text{O}_{19}$ samples obtained at different pyrolysis temperatures. The luminescence spectra of

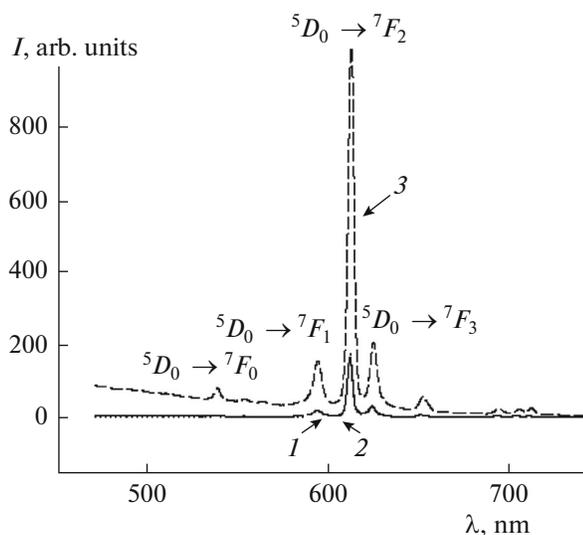


Fig. 5. Luminescence spectra for EuTa_3O_9 (1), $\text{EuTa}_5\text{O}_{14}$ (2), and $\text{EuTa}_7\text{O}_{19}$ (3) samples, $\lambda_{\text{ex}} = 402$ nm (300 K), prepared at pyrolysis temperature 900°C.

$\text{EuTa}_7\text{O}_{19}$ luminophore samples obtained at 600, 700, 800, and 900°C are identical in terms of position of bands for $^5D_0-^7F_j$ transitions (Fig. 4), where $j=0, 1, 2, 3$. Consequently, individual $\text{EuTa}_7\text{O}_{19}$ forms even at 600°C. Gradual increase in pyrolysis temperature (inset in Fig. 4) leads to the growth of luminescence intensity for europium polytantalate samples. Luminescence intensity for $\text{EuTa}_7\text{O}_{19}$ polytantalate sample obtained at 900°C is much higher (Fig. 4, curve 4) than for samples obtained at lower temperatures. Thus, the intensity of the band with maximum at ≈ 620 nm corresponding to the $^5D_0-^7F_2$ transition of Eu^{3+} ion increases by more than 20 times. Literature data and previous studies allow one to explain decrease in luminescence intensity for samples obtained at lower temperatures by the formation of nanocompounds with nanoparticles of minimal size [10, 17].

Characteristic for Eu^{3+} ion luminescence in the region of $^5D_0-^7F_j$ ($j=0, 1, 2, 3$) transitions is observed for all europium polytantalates: EuTa_3O_9 , $\text{EuTa}_5\text{O}_{14}$, and $\text{EuTa}_7\text{O}_{19}$ (Fig. 5). A sole line corresponding to $^5D_0-^7F_0$ transition indicates the homogeneity of luminescence center, which evidences the formation of individual europium compounds. Radiation energy distribution over $^5D_0-^7F_{0,1,2,3}$ transitions in the lumi-

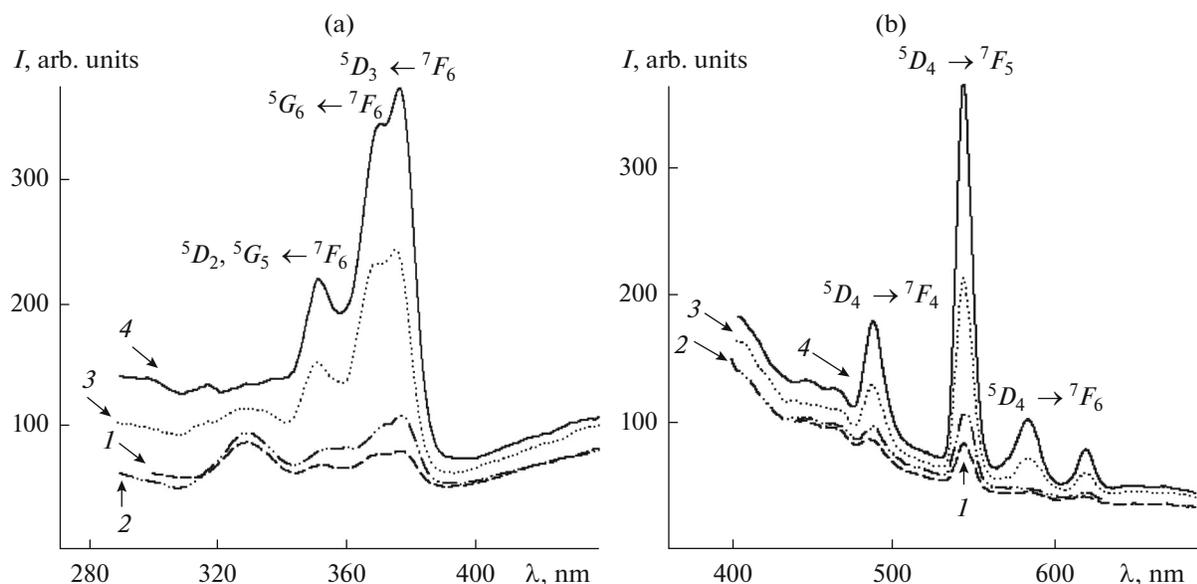


Fig. 6. Luminescence excitation spectra, $\lambda_{em} = 545$ nm (a) and luminescence spectra, $\lambda_{ex} = 378$ nm (b), for $TbTa_7O_{19}$ sample (300 K) prepared at pyrolysis temperature: (1) 600, (2) 700, (3) 800, and (4) 900°C.

nescence spectra of the studied polytantalates, in particular the presence of strong band of $^5D_0-^7F_2$ transition at ≈ 620 nm (Fig. 5), is also typical for Eu^{3+} ion in individual inorganic and organic compounds [16, 18].

The luminescence excitation spectra of terbium polytantalates exhibit bands corresponding to the intra-configurational transitions of Tb^{3+} ion [16]. Figure 6 exemplifies the luminescence excitation and luminescence spectra of terbium polytantalate $TbTa_7O_{19}$. The choice of luminescence excitation wavelength for terbium polytantalates was made like for europium from the most intense line after recording luminescence excitation spectra. It was $\lambda_{max} = 378$ nm for the all prepared terbium polytantalates (Fig. 6a). Terbium polytantalates display intense green luminescence in the region 500–600 nm, whose maximum corresponds to $^5D_0-^7F_5$ transition with $\lambda_{max} \approx 550$ nm. For polytantalates $TbTa_7O_{19}$ (Fig. 6b) and $EuTa_7O_{19}$ (Fig. 4), increase in pyrolysis temperature from 600 to 900°C leads to considerable growth of luminescence intensity.

Our study of the dependence of luminescence parameters for europium and terbium polytantalates on the time and temperature of precursor pyrolysis allowed us to develop procedures for the low-temperature extraction-pyrolytic synthesis of polytantalate luminophores. Luminescent properties of the prepared rare earth metal polytantalates were assessed from excitation and luminescence spectra at 300 K.

ACKNOWLEDGMENTS

This work was supported by the Far Eastern Branch, Russian Academy of Sciences (grant no. 15-I-3-015).

REFERENCES

1. A. M. Sych and A. M. Golub, *Usp. Khim.* **56**, 417 (1977).
2. E. E. Nikishina, E. N. Lebedeva, and D. V. Drobot, *Inorg. Mater.* **48**, 1243 (2012).
3. M. C. Roco, *J. Nanopart. Res.* **5**, 181 (2003).
4. N. Abe, K. Taniguchi, and S. Ohtani, *Phys. Rev. Lett.* **99**, 1215 (2007).
5. P. A. Shcheglov, E. E. Nikishina, D. V. Drobot, and E. N. Lebedeva, *Nano- i Mikrosistemnaya Tekhnika*, No. 11, 15 (2006).
6. F. A. Rozhdestvenskii, M. G. Zuev, and A. A. Fotiev, in *Trivalent Metal Tantalates* (Nauka, Moscow, 1988) [in Russian].
7. E. N. Isupova, E. P. Savchenko, T. I. Panova, and E. K. Keler, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **16**, 555 (1980).
8. V. V. Molchanov, M. G. Zuev, and S. V. Bogdanov, *Khim. Interesakh Ustoich. Razvit.*, No. 10, 185 (2002).
9. K. A. Cmironova, E. E. Nikishina, and D. V. Drobot, in *Abstracts of papers, 17-th International Exhibition on Chemical Industry and Engineering* (Moscow, 2013), p. 38 [in Russian].
10. A. I. Khol'kin and T. N. Patrusheva, *Extraction-Pyrolytic Method: Preparation of Functional Oxide Materials* (KomKniga, Moscow, 2006) [in Russian].

11. N. I. Steblevskaya and M. A. Medkov, *Ros. Nanotekhnologii*, Nos. 1–2, 33 (2010).
12. N. I. Steblevskaya, M. A. Medkov, M. V. Belobeletskaya, and I. A. Tkachenko, *Russ. J. Inorg. Chem.* **60**, 1337 (2015).
13. A. I. Busev, V. G. Tiptsova, and V. M. Ivanov, *A Guide to Analytical Chemistry of Rare Elements*, 2nd ed. (Khimiya, Moscow, 1978) [in Russian].
14. N. I. Steblevskaya, M. A. Medkov, and M. V. Belobeletskaya, *Khim. Tekhnol.* **10**, 350 (2009).
15. S. I. Stepanov and A. M. Chekmarev, *Extraction of Rare Metals with Quaternary Ammonium Salts* (IzdAT, Moscow, 2004) [in Russian].
16. A. G. Mirochnik, N. V. Petrochenkova, and V. E. Karasev, *Vysokomol. Soedin., Ser. A*, **42**, 1763 (2000).
17. N. I. Steblevskaya, M. V. Belobeletskaya, and M. A. Medkov, *Khim. Tekhnol.* **16**, 101 (2015).
18. M. I. Gaiduk, V. F. Zolin, and L. S. Gaigerova, *Luminescence Spectra of Europium* (Nauka, Moscow, 1974) [in Russian].

Translated by I. Kudryavtsev