

Synthesis of red phosphors based on double molybdates of rare-earth elements and monovalent metals

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Formation and properties of isomorphously substituted red phosphors, $\text{Na}_{1-x}\text{Ag}_x\text{Y}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$, $x = 0.05-0.40$ (1) with structure of scheelite, and $\text{K}_{1-x}\text{Tl}_x\text{Y}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$, $x = 0.10-0.40$ (11) with structure of orthorhombic potassium-yttrium molybdate have been obtained. The wavelength of the principal luminescence line of the phosphors (1) is 617 nm, the time of luminescence quenching is $0.4 \cdot 10^{-3}$ s; for the phosphors (11), such characteristics are 615 nm and $(4.5 \pm 1.5) \cdot 10^{-3}$ s. The physical and chemical criteria for the choice of conditions for the synthesis of functional materials have been discussed.

Keywords: silver, DTA, europium, potassium, yttrium, sodium, double molybdate, thallium, XRF, red phosphor.

Изучены образование и свойства изоморфно замещенных красных фосфоров, $\text{Na}_{1-x}\text{Ag}_x\text{Y}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$, $x = 0.05-0.40$ (1), со структурой шеелита и $\text{K}_{1-x}\text{Tl}_x\text{Y}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$, $x = 0.10-0.40$ (11), со структурой орторомбического калий-иттриевого молибдата. Длина основной линии люминесцентных фосфоров (1) 617 нм, время гашения люминесценции составляет $0,4 \cdot 10^{-3}$ с; для фосфоров (11) такие характеристики составляют 615 нм и $(4,5 \pm 1,5) \cdot 10^{-3}$ с. Обсуждены физико-химические критерии выбора условий для синтеза функциональных материалов такого назначения.

Синтез червоних люмінофорів на основі подвійних молібдатів рідкоземельних елементів та одновалентних металів. *О.П.Перпелиця, С.Г.Неділько, В.І.Максін, Т.І.Ущанівська.*

Твердофазним методом із оксидних сполук натрію, аргентуму, калію, талію, ітрію, європію та молібдену одержано ізоморфнозаміщені червоні люмінофори $\text{Na}_{1-x}\text{Ag}_x\text{Y}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$, $x = 0.05-0.40$ зі структурою тетрагонального шееліту та $\text{K}_{1-x}\text{Tl}_x\text{Y}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$, $x = 0.10-0.40$ зі структурою ромбічного калий-ітрієвого молібдату, вивначено їх спектральні характеристики. Обговорено фізико-хімічні критерії вибору умов для синтезу функціональних матеріалів такого призначення.

1. Introduction

Red luminophores belong to the group of functionally important materials of advanced electronics. Among hundreds of in-

dividual inorganic and organic substances exhibiting luminescent properties in the red region, only a few meet technical requirements put to this group of substances. This requirements include, in particular, compli-

ance with respective standardized spectral characteristics: color purity, luminescent emission intensity, mechanical, thermal and chemical durability, useful life, adhesion of phosphor to the substrate surface, retention of phosphors' technical characteristics following its application to the surface of the product or device components, given nanosize of phosphor particles, price/quality ratio, potential for novel phosphors' application using old and utilized technologies, possibility to regenerate exhausted phosphors and etc. [1]. The best properties of all inorganic red phosphors have the materials that contain yttrium and europium oxides: $Y_2O_3 \cdot Eu^{3+}$, $Y_2O_2S \cdot Eu^{3+}$ and $YVO_4 \cdot Eu^{3+}$. Materials with other compositions, which comprise yttrium oxides and other rare-earth elements, are also considered as prospective. These materials include, amongst others, solid solutions of $M_5Y(EO_4)_4 \cdot R^{3+}$ and $MY(EO_4)_2 \cdot R^{3+}$ type; M — alkali metal, R — rare-earth element (activator), E — Mo, W [2–4]. Authors of [5] were the first to report the sensitizing effect of Tl^+ ions on Eu^{3+} luminescence in $TlEu(EO_4)_2$ compounds. This effect has not been observed with similar Ag^+ compounds [6]. Testing of individual $MEu(EO_4)_2$ substances, M—Ag, and Tl as red phosphors demonstrated a variety of disadvantages. These include the formation of large-size (> 60 nm) particles with sintering, poor adhesion to glass surfaces coated with emulsions of these compounds in polyvinyl alcohol, decreased fluorescent brilliance following exposition and heating of glass screen for fixing of luminescent coating.

The purpose of this work was to obtain improved red phosphors using individual double molybdates, $MEu(EO_4)_2$, M—Ag, and Tl as activators in the composition of solid solutions.

2. Experimental

Sodium or potassium carbonate, yttrium or europium oxide and molybdenum trioxide used in this study were of ASC-grade, and argentum nitrate — of AR-grade. Thallium nitrate, originally qualified as C.P.-grade, was recrystallized twice in bidistilled water. The mentioned starting materials have been used to prepare mixtures for solid solutions with specified compositions, namely, $Na_{1-x}Ag_xY_{1-x}Eu_x(MoO_4)_2$ ($x = 0.05-0.40$), or $K_{1-x}Tl_xY_{1-x}Eu_x(MoO_4)_2$ ($x = 0.10-0.40$). The mixture was homogenized in an agate mortar, transferred to agate crucibles prelimi-

nary kept in boiling nitric acid for 8 h, sintered using temperatures at which individual substances $MR(MoO_4)_2$ (M — Na, Ag, K, Tl) and R (Y, and Eu) did not undergo polymorphic transformations and were presented as stable modifications. For sodium- and argentum-containing modifications, this was the structure of scheelite, $MR(MoO_4)_2$ — a sole structure within the broad range of temperatures from 20°C to the melting point [7, 8]. For potassium- and thallium-containing molybdates of similar composition, the structure suitable for red phosphor synthesis was the α -modification of laminated $KY(MoO_4)_2$. In $TlEu(MoO_4)_2$, this type of structure was preserved up to 700°C with subsequent reverse conversion to the γ -modification [9], and in $TlY(MoO_4)_2$ this very type of structure demonstrated stability at temperatures from 20°C up to 800°C [9]. Thus, the choice of $NaY(MoO_4)_2$ and $KY(MoO_4)_2$ structures as crystalline matrices for $AgEu(MoO_4)_2$ and $TlEu(MoO_4)_2$, respectively, is sufficiently justified.

The reaction mixtures of starting materials have been pressed in alundum crucibles with an organic glass rod and placed into a muffle furnace. First, sintering at 500–600°C has been performed for 5 h. Then the crucibles have been transferred to desiccator, cooled down with subsequent homogenization of the mixture and transfer to the same crucibles, pressing in and sintering repeatedly at 600–650°C for 4 h. Then, the mentioned above procedures with the mixture have been repeated. The process ended up with repeated heating at 650–700°C for 3 hours for the substances with $AgEu(MoO_4)_2$, and at 600°C for 6 h for the substances with $TlEu(MoO_4)_2$. Elevation of the temperature to more than 700°C should be avoided (in the case of solid solutions with silver compound, this causes partial restoration of silver to a free metal by a light ray; in solid solutions containing $TlEu(MoO_4)_2$ this compound is subject to the phase reverse conversion at 700–720°C).

X-ray fluorescence analysis (XRF) has been carried out to confirm the single phase nature of the resulting phosphors; a DRON UM-1 diffractometer with copper radiation was used. The error in the measurements of 2 θ reflection angles was $\pm 0.04^\circ$. The thermographic analysis of thallium and yttrium or europium double molybdates has been performed with Paulik-Paulic-Erdey system derivatograph (sample weight is $(0.190-0.650) \cdot 10^{-3}$ kg, platinum crucibles, heating

rate is 0.33°C/s, DTA = 50). Luminescent spectra have been measured with a DFS-12 spectrometer (a laser spectrum complex based on ECM) using ultraviolet light as a source of excitation with $\lambda_{exc} = 337.1$ nm of a LGI-21 laser.

Table 1. Quantitative characteristics of AgEu(MoO₄)₂ luminescent spectrum

λ , nm	I/I_0
552.4	12
567.0	11
588.5	14
595.4	18
603.1	15
612.5	20
614.2	65
618.1	100
621.4	28
633.9	17
698.7	27
705.1	48

3. Results and discussion

Red phosphors compositions Na_{1-x}Ag_xY_{1-x}Eu_x(MoO₄)₂ ($x = 0.05-0.40$) and K_{1-x}Tl_xY_{1-x}Eu_x(MoO₄)₂ ($x = 0.10-0.40$) have been prepared and investigated in this work. Table 1 shows quantitative characteristics of the luminescent spectrum of individual AgEu(MoO₄)₂, crystallized in the structure of tetragonal scheelite. Red color luminescence attributable to the lines within the range of $\lambda = 614.2-705.1$ nm is caused by the following transitions: $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$.

As previously noted, the AgEu(MoO₄)₂ substance may not be used in practice as phosphor, therefore, solid solutions have been obtained with the following composition: Na_{1-x}Ag_xY_{1-x}Eu_x(MoO₄)₂ ($x = 0.05-0.40$). The compositions of the starting materials, XRF results and luminescent emission intensities are shown in Table 2. The luminescence spectra of Na_{1-x}Ag_xY_{1-x}Eu_x(MoO₄)₂ solid solutions demonstrate two narrow, intense and closely-spaced lines, namely $\lambda_1 = 613$ nm ($I/I_0 = 65$ %) and $\lambda_2 = 617$ nm ($I/I_0 = 100$ %). The phosphors have hardly visible light yellow color, while in AgEu(MoO₄)₂ it is clear cut. Activator's concentration in-

Table 2. Compositions of initial mixtures for the synthesis of Na_{1-x}Ag_xY_{1-x}Eu_x(MoO₄)₂ red phosphors; XRF and luminescence intensity data

Sample No.	Composition of initial mixtures, g	AgEu(MoO ₄) ₂ content, mol.%	Parameters of tetragonal unit cell lattice, nm		I of luminescence, % (for lines with $\lambda = 617$ nm)
			$a = b$	c	
1	Na ₂ CO ₃ — 1.007 Y ₂ O ₃ — 2.145 Eu ₂ O ₃ — 0.175 MoO ₃ — 5.758 AgNO ₃ — 0.162	5 ($x = 0.05$)	5.200	11.342	29
2	Na ₂ CO ₃ — 0.954 Y ₂ O ₃ — 2.03 Eu ₂ O ₃ — 0.352 MoO ₃ — 5.758 AgNO ₃ — 0.339	10 ($x = 0.10$)	5.203	11.368	72
3	Na ₂ CO ₃ — 0.795 Y ₂ O ₃ — 1.690 Eu ₂ O ₃ — 0.880 MoO ₃ — 5.758 AgNO ₃ — 0.849	25 ($x = 0.25$)	5.220	11.409	100
4	Na ₂ CO ₃ — 1.007 Y ₂ O ₃ — 1.355 Eu ₂ O ₃ — 0.407 MoO ₃ — 5.758 AgNO ₃ — 0.358	40 ($x = 0.40$)	5.224	11.442	70

Table 3. Quantitative characteristics of luminescent spectra of α - and β -modifications of $\text{TlEu}(\text{MoO}_4)_2$, (I — relative intensity of luminescence)

λ , nm	I relative		
	β -modification (800°C)	α -modification (500°C)	α -modification (100°C)
589.0	10	9	8
592.6	10	9	8
593.0	7	—	—
593.7	—	8	—
594.0	—	—	8
602.5	7	1	2
607.0	40	8	8
609.0	60	10	15
612.6	100*	80	70
618.0	—	5	3
624.5	5	—	—
644.0	2	1	1
648.0	3	1	—
651.0	9	3	6
653.0	—	9	8
654.5	—	2	1
691.0	30	30	40
692.5	20	9	8
700.5	—	9	—
701.0	50	40	10
707.0	20	40	40
712.0	20	10	—

Note: * The intensity of this luminescence line (β - $\text{TlEu}(\text{MoO}_4)_2$, 800°C) has been taken as 100 relative units.

crease by over 25 mole led to concentration quenching in the composition of this phosphor. The time of the luminescence quenching of the phosphor (determined by graphic processing of experimental data) was $0.4 \cdot 10^{-3}$ s. Obtained $\text{Na}_{1-x}\text{Ag}_x\text{Y}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ $x = 0.10$ – 0.25) phosphors demonstrated higher luminescence intensity than an individual $\text{AgEu}(\text{MoO}_4)_2$ compound.

Spectral luminescence characteristics of α - and β -modifications of $\text{TlEu}(\text{MoO}_4)_2$ kept at various temperatures (Table 3) showed increased luminous intensity with elevated temperatures. β - $\text{TlEu}(\text{MoO}_4)_2$ that has been kept at 800°C demonstrated the highest intensity (however, without stable spectral characteristics), as this modification gradually changed to the low-temperature α -modification. For this reason, the $\text{K}_{1-x}\text{Tl}_x\text{Y}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ red phosphor may be produced on the base of α - $\text{TlEu}(\text{MoO}_4)_2$ only, available at 20–700°C. Table 3 shows that red luminescence color of α - $\text{TlEu}(\text{MoO}_4)_2$ is attributable to spectral lines with $\lambda = 612.6$ – 707.0 nm (quantum transitions $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ from the upper metastable levels to the lower

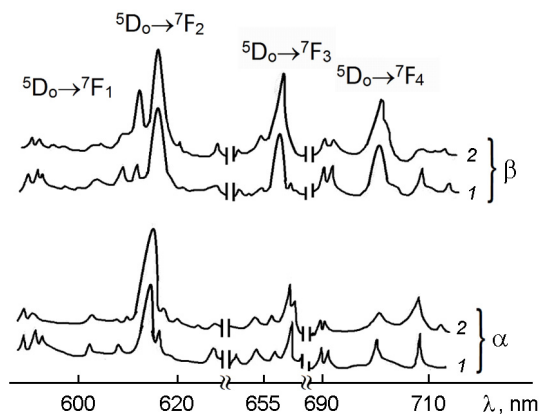


Fig. 1. Luminescent spectra of α - and β -modifications of $\text{TlEu}(\text{MoO}_4)_2$ recorded at 77 (1) and 300 K (2).

levels of the primary multiplet). Fig. 1 demonstrates spectra of α - and β -modifications of $\text{TlEu}(\text{MoO}_4)_2$ registered at 77 and 300 K. At lower temperatures, the spectral lines were more distinct and their intensity increased. Fig. 2 shows excitation spectra of commercial $\text{Y}_2\text{O}_3 \cdot \text{Eu}^{3+}$ and α - $\text{TlEu}(\text{MoO}_4)_2$

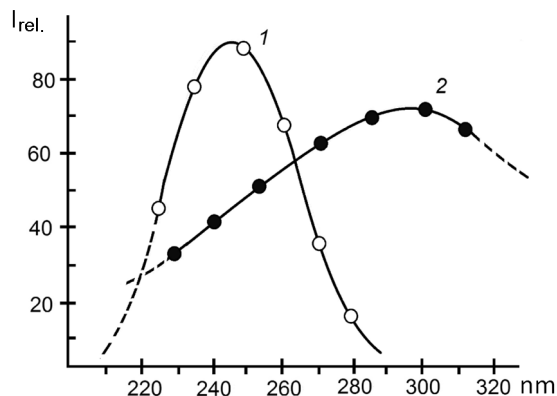


Fig. 2. Luminescence excitation spectra of commercial red phosphors $Y_2O_3 \cdot Eu^{3+}$ (1) and $\beta-TiEu(MoO_4)_2$ (2).

red phosphors which have $\lambda_{max\ exc} \approx 245$ nm and ≈ 300 nm, respectively. Their excitation spectra also differ in the width: the first phosphor has narrow spectrum and the second — wide.

Red phosphors have been produced on the basis of $KY(MoO_4)_2$ and $\alpha-TiEu(MoO_4)_2$ solid solutions using the starting materials

in the quantities necessary to make the solid solutions $K_{1-x}Tl_xY_{1-x}Eu_x(MoO_4)_2$, $x = 0.10; 0.20; 0.30$ and 0.40 (Table 4). The principal line of luminescence of the phosphors with the mentioned above composition has $\lambda = 615$ nm; the line becomes narrower with increased x value. The time of luminescence quenching of this phosphor is $(4.5 \pm 1.5) \cdot 10^{-3}$ s.

According to its nature, the phosphor containing $\alpha-TiEu(MoO_4)_2$ is a solid solution with a crystalline matrix represented by laminated orthorhombic potassium-yttrium molybdate. The potential for exchange reaction in the solid phase with formation of $TiEu(MoO_4)_2$ has been taken into account when producing the solid solution. Therefore, before the synthesis of the phosphor, the structure of similar yttrium and europium compounds with thallium and temperature ranges of modifications stability should be considered. Fig. 3 shows thermograms of $TiEu(MoO_4)_2 \cdot xH_2O$ and $TiEu(MoO_4)_2 \cdot xH_2O$. The DTA curve of the yttrium compound demonstrates endoeffect

Table 4. Compositions of initial mixtures for the synthesis of $K_{1-x}Tl_xY_{1-x}Eu_x(MoO_4)_2$ red phosphors, XRF and luminescence intensity data

Sample No.	Composition of initial mixtures, g	$TiEu(MoO_4)_2$ content, mol. %	Parameters of orthorhombic unit cell lattice, nm			I of luminescence, % (for the line with $\lambda = 612.6$ nm)
			a	b	c	
1	K_2CO_3 — 0.652 Y_2O_3 — 1.061 Eu_2O_3 — 0.158 MoO_3 — 2.879 $TiNO_3$ — 0.260	10	18.313	7.951	5.071	16
2	K_2CO_3 — 0.559 Y_2O_3 — 0.903 Eu_2O_3 — 0.352 MoO_3 — 2.879 $TiNO_3$ — 0.533	20	18.322	7.967	5.088	25
3	K_2CO_3 — 0.484 Y_2O_3 — 0.790 Eu_2O_3 — 0.528 MoO_3 — 2.879 $TiNO_3$ — 0.849	30	18.358	7.987	5.088	41
4	K_2CO_3 — 0.207 Y_2O_3 — 0.339 Eu_2O_3 — 0.352 MoO_3 — 1.439 $TiNO_3$ — 0.533	40	18.304	8.017	5.098	100

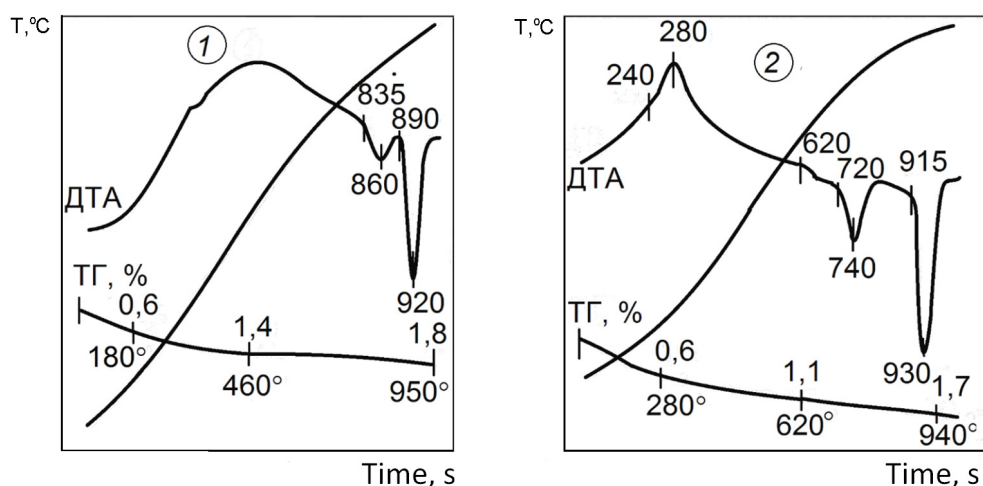


Fig. 3. Thermograms of $\text{TlY}(\text{MoO}_4)_2 \cdot x\text{H}_2\text{O}$ (1) and $\text{TlEu}(\text{MoO}_4)_2 \cdot x\text{H}_2\text{O}$ (2).

at 835°C resulting from the reverse phase change, which was proven with high-temperature XRF by P.V.Klevtsov [10]; below this temperature, $\text{TlEu}(\text{MoO}_4)_2$ has a structure of potassium-yttrium molybdate. $\text{TlEu}(\text{MoO}_4)_2$ demonstrates a reversible transition from $\text{KY}(\text{MoO}_4)_2$ -type structure to the structure of rhomboid (pseudo-tetragonal), $\text{RbPr}(\text{MoO}_4)_2$, at 720°C; the fact was confirmed by the same method and the same author [9]. Consequently, both the crystalline base and the compounds formed therein have an identical structure existing over a wide range of temperatures from 20 to 720°C.

According to XRF findings (Tables 2 and 4), the obtained phosphors, $\text{Na}_{1-x}\text{Ag}_x\text{Y}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ and $\text{K}_{1-x}\text{Tl}_x\text{Y}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$, are isomorphously substituted solid solutions, where Na^+ is substituted by Ag^+ , K^+ with Tl^+ and Y^{3+} with Eu^{3+} . Following application of both the first and the second phosphors to the glass surface using a standard technique with ammonium dichromate as polymerization activator (a dried layer of the phosphor was illuminated with ultraviolet light), there has been observed a decrease in luminescence intensity resulting from the effect of the Cr_2O_3 micro impurity. This negative consequence may be avoided with the use of similar soluble molybdenum compounds [11] instead of ammonium dichromate, for example, methylammonium molybdates.

4. Conclusions

Using a solid-phase method, isomorphously substituted red phosphors of the

given compositions, $\text{Na}_{1-x}\text{Ag}_x\text{Y}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ ($x = 0,05-0,40$) and $\text{K}_{1-x}\text{Tl}_x\text{Y}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ ($x = 0,10-0,40$), with the structures of scheelite and potassium-yttrium molybdate, respectively, have been obtained from oxide compounds of sodium, silver, potassium, thallium, yttrium, europium and molybdenum. The physical and chemical criteria for the choice of optimum conditions for the synthesis of functional materials of that type have been discussed. Spectral characteristics of the obtained red phosphors with potential for application in modern electronic devices have been determined.

References

1. N.M.Kozhevnikova, *Inorg. Mater.*, **53**, 417 (2017).
2. V.A.Morozov, A.V.Arakcheeva, P.Pattion et al., *Chem.Mater.*, **27**, 5519 (2015).
3. V.A.Morozov, A.M.Abakumov, J.Haderman et al., *Acta Crystall. A: Found. Adv.*, **74**, 94 (2018).
4. V.A.Morozov, B.I.Lazoryak, S.Z.Shmurak et al., *Chem.Mater.* **26**, 3238 (2015).
5. M.U.Belyi, G.I.Yermolenko, L.V.Kulyk et al., *J.Appl.Spectr.*, **28**, 268 (1978).
6. A.P.Perepelytsia, V.N.Ischenko, I.Ya.Pyschai, *J.Inorg.Chem.*, **36**, 485 (1991).
7. L.Li, J.Zhang, W.Zi et al., *Solid State Sci.*, **59**, 58 (2014).
8. N.M.Kozhevnikova, *JInorg.Chem.*, **61**, 1579 (2016).
9. P.V.Klevtsov, A.P.Perepelytsia, A.M.Golub, *Crystallography*, **22**, 771 (1977).
10. P.V.Klevtsov, A.P.Perepelytsia, A.M.Golub, *Crystallography*, **23**, 309 (1978).
11. USSR's Invention Certificate No. 11570119, Discoveries. Inventions, No.19 (1985).