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Spectral-Luminescent Properties of Terbium-Containing Zirconomolybdates

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Abstract

To date, double molybdates of mono- and tetravalent elements have been comprehensively studied, and systems with molybdates of mono- and trivalent elements have been studied quite thoroughly. Some materials based on double molybdates, for example, those containing lanthanides, are considered promising for laser technology and electronics. Meanwhile, there is limited information on the properties, especially optical ones, of the molybdates containing rare-earth elements and zirconium. The aim of this work was to study the luminescent properties of self-activated terbium-containing zirconomolybdates with the compositions $Tb_2Zr_3(MoO_4)_9$ (1:3) and $Tb_2Zr(MoO_4)_5$ (1:1), crystallising in two different structural types.

Powder samples of the studied molybdates were synthesised by ceramic technology. The absorption, excitation, and emission spectra were measured using a Perkin Elmer Lambda 950 spectrophotometer. Luminescence was excited by a 250 W DKSSh-250 xenon lamp through an MDR-2 monochromator and recorded using an SDL-1 double monochromator with a grating of 600 lines/mm. The optical properties of new zirconium molybdates containing Tb^{3+} ions were studied. They revealed bright luminescence in the green spectral region due to the transitions inside the 4f shell of the rare-earth Tb^{3+} ion, excited both in the bands associated with the 4f-4f transitions and in the band with a charge transfer. The observed spectral lines as well as luminescence and excitation bands were identified.

It was shown that the position of the wide excitation band associated with the “charge transfer” transitions from O^{2-} in MoO_4^{2-} groups via Mo–O bonds to luminescent centres (Tb^{3+}) does not depend on the matrix structure. The structure and intensity of the observed spectral lines, indicating a low symmetry of the Tb^{3+} crystalline environment, correlate with the structural analysis data. The results obtained in this work can be used when creating promising phosphors in the green spectral region under ultraviolet excitation.

Keywords: solid-phase synthesis, luminescence, terbium-containing zirconomolybdate.

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1. Introduction

Since lanthanoids luminesce in the UV and in visible and near-infrared regions, they can be used in various fields: laser and fibre optics technology, medical diagnostics, and the creation of scintillators and luminophores.

The electrons in lanthanoids, located on the 4f shell, are screened by the outer 5s² and 5p⁶ shells. As a result, the position of the energy levels is weakly dependent on the environment. In this case, the energetic states of the sublevels are completely determined by the immediate

environment of rare-earth ions due to the Stark splitting effect.

The studies aimed at the search for new materials for matrices activated by rare-earth ions are considered relevant. There are works of Russian and foreign scientists [1–6] dedicated to the study of luminescent properties of double zirconium molybdates and lanthanoids, although the luminescent properties of zirconomolybdates with Tb³⁺ of the Tb₂Zr(MoO₄)₅ composition were not studied.

Our study of the Tb₂(MoO₄)₃-Zr(MoO₄)₂ system allowed establishing for the first time the formation of three new molybdates with the following compositions: Tb₂Zr₃(MoO₄)₉ (1:3), Tb₂Zr₂(MoO₄)₇ (1:2), and Tb₂Zr(MoO₄)₅ (1:1) (Fig. 1) [7].

The structures of the first two molybdates, 1:3 (space group R $\bar{3}c$, Z = 6) and 1:2 (space group C2/c, Z = 4), were determined for monocrystals (Fig. 2a, b) [8–10].

The structure of the 1:1 molybdate was determined through the use of isostructural Er₂Zr(MoO₄)₅, the Rietveld refinement method, and principles of derivative difference minimisation (Fig. 3) [11].

The aim of this work was to study the luminescent properties of self-activated terbium-containing zirconomolybdates with the 1:3 and 1:1 compositions, crystallising in two different structural types.

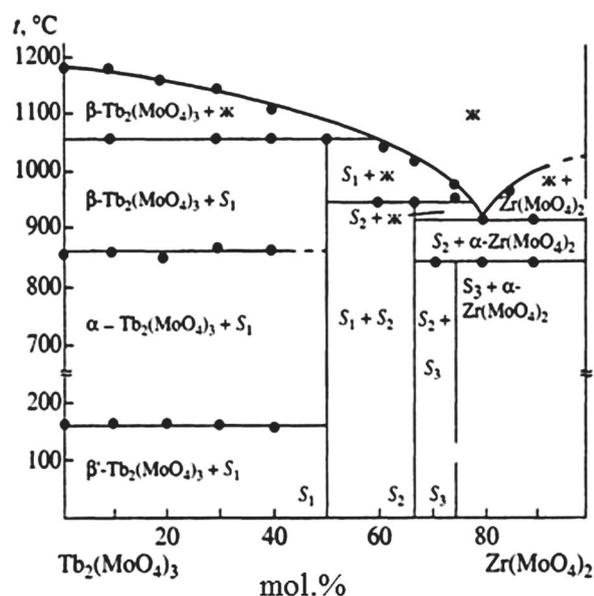


Fig. 1. Phase diagram of the system Tb₂(MoO₄)₃ – Zr(MoO₄)₂

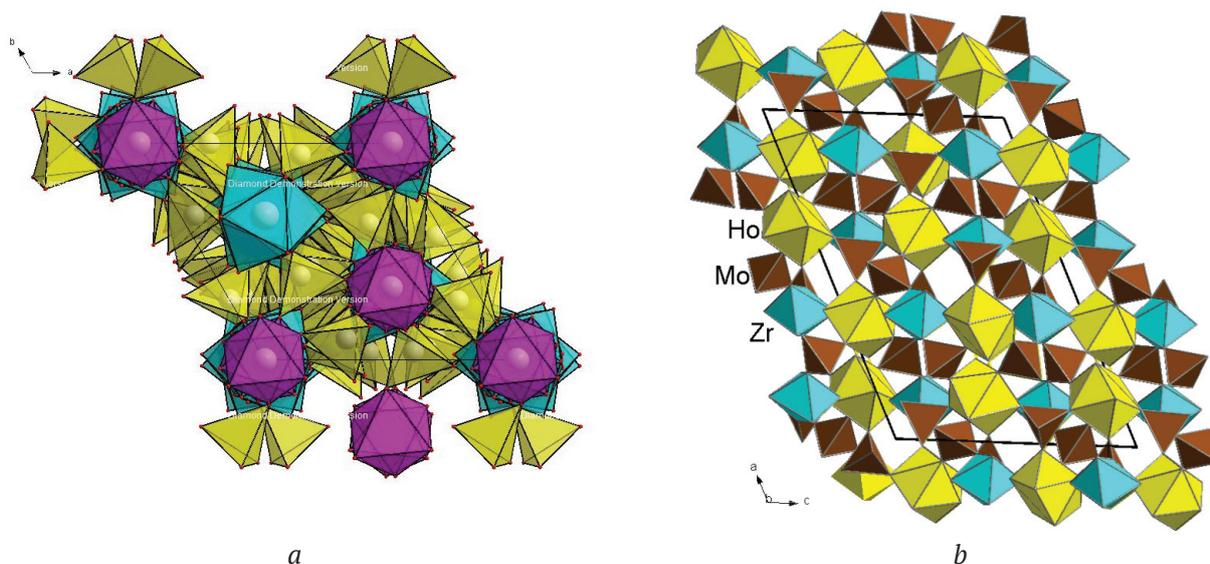


Fig. 2. Part of the structure Ln₂Zr₃(MoO₄)₉ (space group R $\bar{3}c$, Z = 6) (Ln = Nd) (a); Part of the structure Ln₂Zr₂(MoO₄)₇ (space group C2/c, Z = 4) (b)

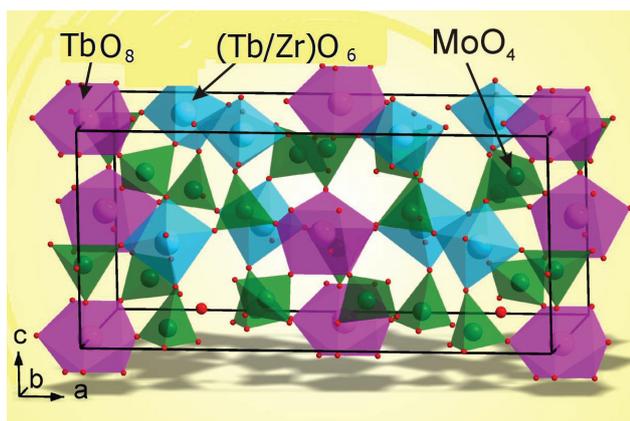


Fig. 3. Part of the structure $\text{Ln}_2\text{Zr}(\text{MoO}_4)_5$ (space group Cmc2_1 , $Z = 2$)

2. Experimental

The absorption, excitation, and emission spectra of Tb^{3+} were measured in two terbium-containing matrices $\text{Tb}_2\text{Zr}(\text{MoO}_4)_5$ (space group Cmc2_1 , $Z = 4$) and $\text{Tb}_2\text{Zr}_5(\text{MoO}_4)_9$ (space group $\text{R}\bar{3}\text{c}$, $Z = 6$). The molybdates were obtained by ceramic technology [7].

In order to study the optical properties of the investigated samples, the absorption, emission, and excitation spectra were recorded in the integrating sphere at various temperatures.

The absorption spectra were recorded using a Perkin Elmer Lambda 950 spectrophotometer with an integrating sphere. When recording the absorption spectra, the studied sample

was poured into a KU-1 quartz-glass ampoule and placed inside the integrating sphere. The absorption of the test glass was subtracted from the absorption spectra.

Luminescence was excited in the spectral interval of 200–500 nm by a 250 W DKSSh-250 xenon lamp through an MDR-2 monochromator with a ruled grating of 1200 lines/mm. The emissions were recorded using an SDL-1 double monochromator with a grating of 600 lines/mm. The spectral dimension of the monochromator slits varied from 1.2 nm to 0.3 nm. The measurements at temperature 77 K were conducted in the evacuated cryostat. The excitation spectra were corrected by the lumogen excitation spectra.

3. Results and discussion

Two types of bands were observed in the excitation spectra of the studied samples: narrow bands, corresponding to the transitions inside the 4*f* shell of the rare-earth ion, and wide bands, associated with the bands of charge transfer in the MoO_4^{2-} complexes to the rare-earth element.

Intensive luminescence was observed in the green spectral region in $\text{Tb}_2\text{Zr}(\text{MoO}_4)_5$ upon the excitation in the UV region (Fig. 4).

The emission spectrum upon the excitation in the band with the energy 26500 cm^{-1} ($\lambda = 377 \text{ nm}$), measured at a temperature of 77 K, is presented in Fig. 4 (curve 1). The bands observed in the

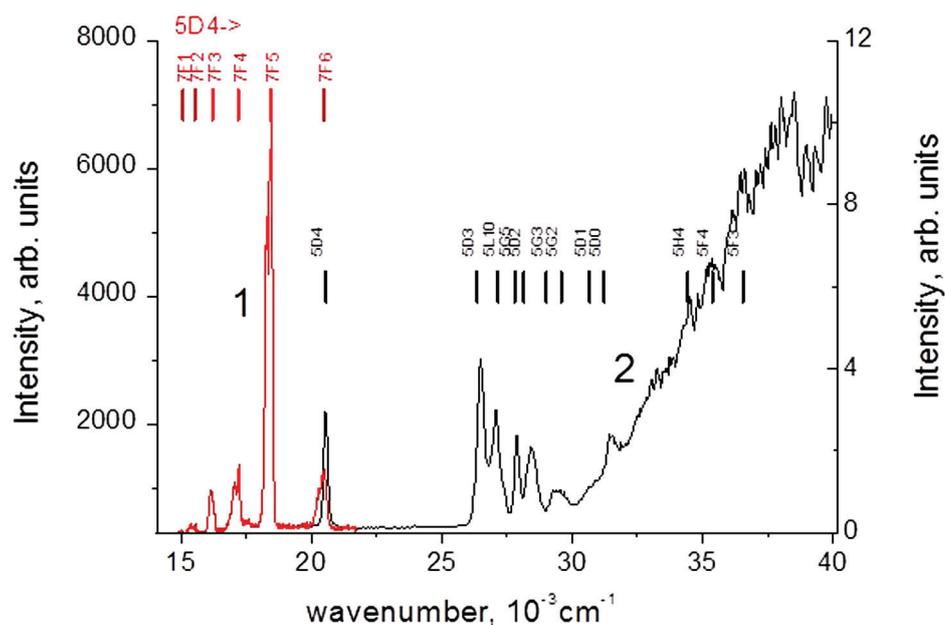


Fig. 4. Emission (curve 1) and excitation (curve 2) spectra of the $\text{Tb}_2\text{Zr}(\text{MoO}_4)_5$ sample measured at temperature 77 K

spectrum are related to the electronic transitions inside the $4f$ shell from the 5D_4 term to the 7F_J ($J = 1-6$) terms. The greatest intensity in the emission spectrum was found in the band with the maximum in the 18500 cm^{-1} region ($\lambda = 540\text{ nm}$). The band is related to the magnetic dipole transition of ${}^5D_4-{}^7F_5$. The intensity of this transition changes only slightly depending on the value of the crystalline field. The observed band is split into three lines with the energies of 18280 , 18405 , and 18460 cm^{-1} .

The luminescence band with the 20500 cm^{-1} maximum ($\lambda = 488\text{ nm}$) is associated with the electronic dipole transition of ${}^5D_4-{}^7F_6$ in the Tb^{3+} ion, which is environment-sensitive (but not hypersensitive) and depends on the symmetry of the crystalline field. Transitions of ${}^5D_4-{}^7F_1$ in the emission of the Tb^{3+} ion have low intensity. Band intensities related to the $f-f$ transitions diminish with a decreasing value of J in the following way: ${}^5D_4 \rightarrow {}^7F_6 > {}^7F_4 > {}^7F_5 > {}^7F_2$. The presence of the thin structure in the emission spectra of the ${}^5D_4-{}^7F_J$ transitions in terbium ions is associated with their sensitivity to the ligand environment.

The ${}^5D_4-{}^7F_6$ band is more intense as compared to the intensities of other bands (except for ${}^5D_4-{}^7F_5$) and is split into three peaks, which can be indicative of spacial distortion of the nine-peak TbO_9 with symmetry decreased to C_{2v} [12], which correlates with the data of the structure. The presence of intensive lines of magnetic dipole and

electronic dipole transitions in the spectrum is also indicative of the presence of several various types of ligands [13].

The emission was excited in the band with energy of 26500 cm^{-1} ($\lambda = 377\text{ nm}$), corresponding to the ${}^4F_0-{}^5D_3$ transition, and the excitation spectrum was measured for the band with energy of 18500 cm^{-1} ($\lambda = 540\text{ nm}$), corresponding to the ${}^5D_4-{}^4F_5$ transition. Vertical lines show the energies of the term of the Tb^{3+} free ion. A row of thin bands was observed in the excitation spectrum (Fig. 4, curve 2) that are related to the transitions from the ground state 7F_0 to the states split by spin-orbital interaction of the $4f^8$ term. The band in the 37000 cm^{-1} region ($\lambda = 270\text{ nm}$) is associated with the charge transfer transition in the $(\text{MoO}_4)^{2-}$ complexes. The emission spectrum excited in this band is almost the same as the spectrum excited in the region of $4f-4f$ transitions.

The absorption spectrum of $\text{Tb}_2\text{Zr}_3(\text{MoO}_4)_9$ is presented in Fig. 5 [2]; it consists of a wide absorption band in the ultraviolet region and one narrow low-intensity peak, related to the $4f-4f$ transition from the ground state of terbium ions 7F_6 to the lower excited state 5D_4 . The Tb^{3+} transitions are characterised by the low force of the oscillator. As a result, most of the bands of intracentre transitions in the absorption spectrum are not visible as compared to other absorption bands.

Fig. 6 [2] shows the excitation and luminescence spectra $\text{Tb}_2\text{Zr}_3(\text{MoO}_4)_9$. Intensive narrow emission

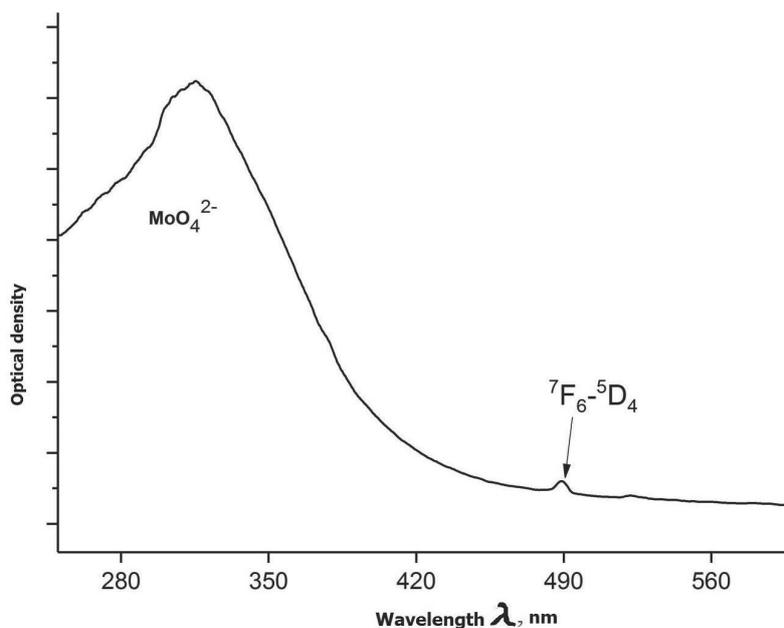


Fig. 5. Absorption spectrum of $\text{Tb}_2\text{Zr}_3(\text{MoO}_4)_9$

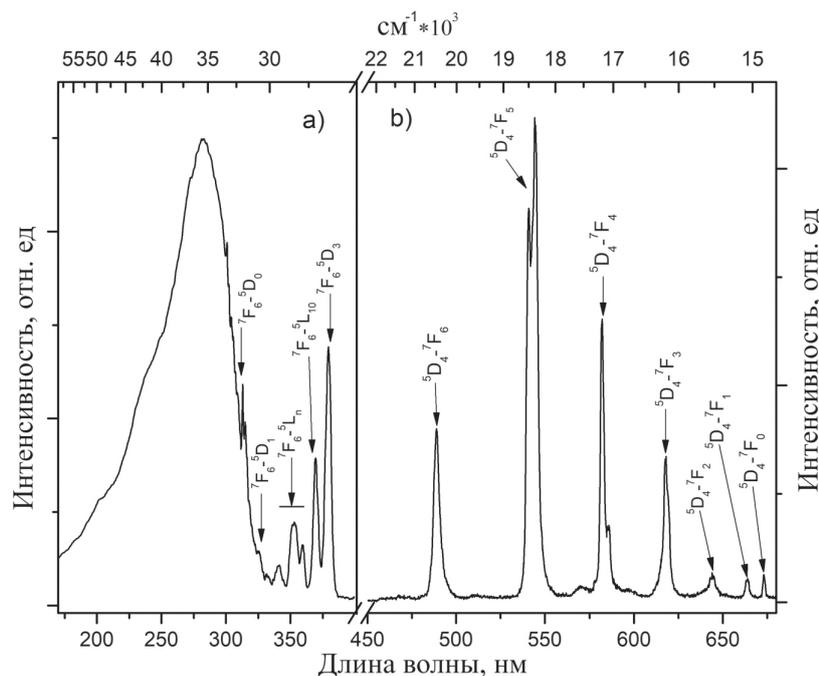


Fig. 6. Excitation (a) and emission spectra (b) of $\text{Tb}_2\text{Zr}_3(\text{MoO}_4)_9$ at liquid nitrogen temperature

bands were observed in the region of 480–680 nm (20800–14700 cm^{-1}), which is typical for the Tb^{3+} transitions from the D_4 level to the lower ${}^7\text{F}_J$ levels ($J = 0, 1, 2, 3, 4, 5$). Transitions from the ${}^7\text{F}_6$ ground state were observed in the excitation spectrum. Upon the excitation in the $4f-4f$ bands, the greatest intensity of luminescence was achieved with the excitation wavelength of 380 nm (${}^7\text{F}_6-{}^5\text{D}_3$ transition). In the region of 300 nm (33300 cm^{-1}) a wide intensive excitation band was observed. Seven narrow lines in the emission spectrum belong to the transitions $\text{Tb}^{3+}: {}^5\text{D}_4-{}^7\text{F}_J$ (electronic dipole transition, 488 nm (20500 cm^{-1})), ${}^5\text{D}_4-{}^7\text{F}_5$ (magnetic dipole transition, 540 nm (18500 cm^{-1})), ${}^5\text{D}_4-{}^7\text{F}_4$ (582 nm (17180 cm^{-1})), ${}^5\text{D}_4-{}^7\text{F}_3$ (618 nm (16180 cm^{-1})), ${}^5\text{D}_4-{}^7\text{F}_2$ (644 nm (15530 cm^{-1})), ${}^5\text{D}_4-{}^7\text{F}_1$ (663 nm (15080 cm^{-1})), and ${}^5\text{D}_4-{}^7\text{F}_0$ (673 nm (14860 cm^{-1})). The most intensive line reaching the peak at 540 nm (18500 cm^{-1}) is responsible for the green colour of $\text{Tb}_2\text{Zr}_3(\text{MoO}_4)_9$.

Decay times of luminescence, corresponding to different transitions inside the f shell with different lengths of the excitation waves, were measured at temperatures 297 K and 77 K (Table).

4. Conclusions

As a result of the conducted studies, we can draw the following conclusions:

Table. Decay times of principal transitions of Tb^{3+} at 297 and 77 K

$({}^5\text{D}_4-{}^7\text{F}_J)$	Wave length (nm)		Decay time (μs)	
	Emission	Excitation	297 K	77 K
6	488	270	420	400
		352	390	360
		370	430	400
		380	430	390
5	540	270	420	400
		352	460	410
		370	450	400
		380	450	420
4	582	290	420	400
		352	500	390
		370	420	370
		380	420	410

1. Spectral-luminescent properties of terbium-containing zirconium molybdates of two compositions (1:3 and 1:1) and structures ($R\bar{3}c$, $Z = 6$ and $\text{Cmc}2_1$, $Z = 4$) were studied. The observed spectral lines as well as luminescence and excitation bands were identified. Specific features of the matrix structure determine the spectral-luminescent properties of Tb^{3+} ions.

2. The comparison of the excitation spectra of terbium-containing molybdates with different

structures showed that the position of the wide excitation band associated with the “charge transfer” transitions from O^{2-} in MoO_4^{2-} groups via Mo–O bonds to luminescent centres (Tb^{3+}) does not depend on the matrix structure and the nature of REE.

3. The structure of the band associated with the electronic dipole transition ${}^5D_4 \rightarrow {}^7F_6$ in the Tb^{3+} ion is indicative of spacial distortion of TbO_9 with decreasing symmetry. The presence of intensive lines of magnetic dipole (${}^5D_4 \rightarrow {}^7F_5$) and electronic dipole (${}^5D_4 \rightarrow {}^7F_6$) transitions is also indicative of the presence of low symmetry. All this data correlates with the data of the structural analysis.

4. The results obtained in this work can be used when creating promising phosphors in the green spectral region under ultraviolet excitation.

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Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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