

## Luminescence of Ln–Zr Molybdates

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**Abstract**—The crystallographic characteristics and optical and thermal properties of Ln–Zr molybdates synthesized using ceramic technology are described.

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### INTRODUCTION

Double molybdates containing rare earth elements (REEs) are promising materials for use in laser physics and radio engineering. A number of studies have been devoted to investigating the optical properties of double molybdates of alkaline elements with REEs or activated REEs [1–6]. Studying their optical and luminescent properties enables us to expand the number of compounds that can be used for optical purposes.

We obtained a wide set of Ln–Zr containing molybdates (Ln = La – Tb) in [7]. This work presents results from studying the structural, luminescent and thermal characteristics of Ln<sub>2</sub>Zr<sub>3</sub>(MoO<sub>4</sub>)<sub>9</sub> (Ln = Ce, Pr, Eu).

### X-RAY PHASE ANALYSIS AND CONFIRMATION OF STRUCTURE

Double molybdates were synthesized on the basis of initial agents Eu<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub>, high grade MoO<sub>3</sub>, reagent grade Ce(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O, and ZrO<sub>2</sub> obtained by sintering pure ZrOCl<sub>2</sub> · 8H<sub>2</sub>O. Stoichiometric amounts of the corresponding agents were annealed stepwise over 150 h with homogenization of the mixtures after each 50°C. Sintering began at 400°C in order to avoid MoO<sub>3</sub> losses due to sublimation. The final synthesis

temperature of Ln<sub>2</sub>Zr<sub>3</sub>(MoO<sub>4</sub>)<sub>9</sub> molybdates (Ln = Ce, Pr, Eu) was 700°C.

Phase content and completeness of synthesis was verified via X-ray phase analysis on a Bruker Advance D8 diffractometer using CuK<sub>α</sub> radiation (geometry, Bragg–Brentano) and a Vantec linear detector. Structure was confirmed using arrays of experimental data obtained in the 2θ 8°–100° range of angles at a temperature of 300 K. Peak positions were determined using the EVA program in the Bruker DIFFRAC-PLUS PC software package.

The crystallographic characteristics of the synthesized compounds were confirmed using the Rietveld approach with the FullProff program and WinPLOTR software package [8] based on monocrystalline data for the isostructural compound Nd<sub>2</sub>Zr<sub>3</sub>(MoO<sub>4</sub>)<sub>9</sub> [9]. The correspondence between the measured and computed X-ray patterns was analyzed. The quality of our verification and the correctness of selected model were assessed using the numerical values of the *R*-factors.

X-ray phase analysis of double molybdates Ln<sub>2</sub>Zr<sub>3</sub>(MoO<sub>4</sub>)<sub>9</sub> (Ln = Ce, Pr, Eu) showed that single-phase ceramic samples forming an isostructural set of compounds were obtained. The structure of double molybdates with trigonal singony (a prototype of Nd<sub>2</sub>Zr<sub>3</sub>(MoO<sub>4</sub>)<sub>9</sub>; spatial group *R* $\bar{3}c$ , *Z* = 6, *a* = 9.804(1) Å, *c* = 58.467(12) Å (Table 1)) was con-

Crystallographic characteristics of double molybdates Ln<sub>2</sub>Zr<sub>3</sub>(MoO<sub>4</sub>)<sub>9</sub> (Ln = Ce, Pr, Eu)

Compound	Elementary cell parameters		<i>V</i> , Å <sup>3</sup>	<i>R</i>
	<i>a</i> , Å	<i>c</i> , Å		
Ce <sub>2</sub> Zr <sub>3</sub> (MoO <sub>4</sub> ) <sub>9</sub>	9.8453(1)	58.8887(7)	4943.3(1)	<i>R</i> <sub><i>p</i></sub> – 0.088 <i>R</i> <sub>Bragg</sub> – 0.058 <i>R</i> <sub><i>f</i></sub> – 0.045
Pr <sub>2</sub> Zr <sub>3</sub> (MoO <sub>4</sub> ) <sub>9</sub>	9.8342(1)	58.7671(3)	4922.0(1)	<i>R</i> <sub><i>p</i></sub> – 0.081 <i>R</i> <sub>Bragg</sub> – 0.037 <i>R</i> <sub><i>f</i></sub> – 0.037
Eu <sub>2</sub> Zr <sub>3</sub> (MoO <sub>4</sub> ) <sub>9</sub>	9.7867(1)	58.0907(1)	4818.5(1)	<i>R</i> <sub><i>p</i></sub> – 0.045 <i>R</i> <sub>Bragg</sub> – 0.066 <i>R</i> <sub><i>f</i></sub> – 0.046

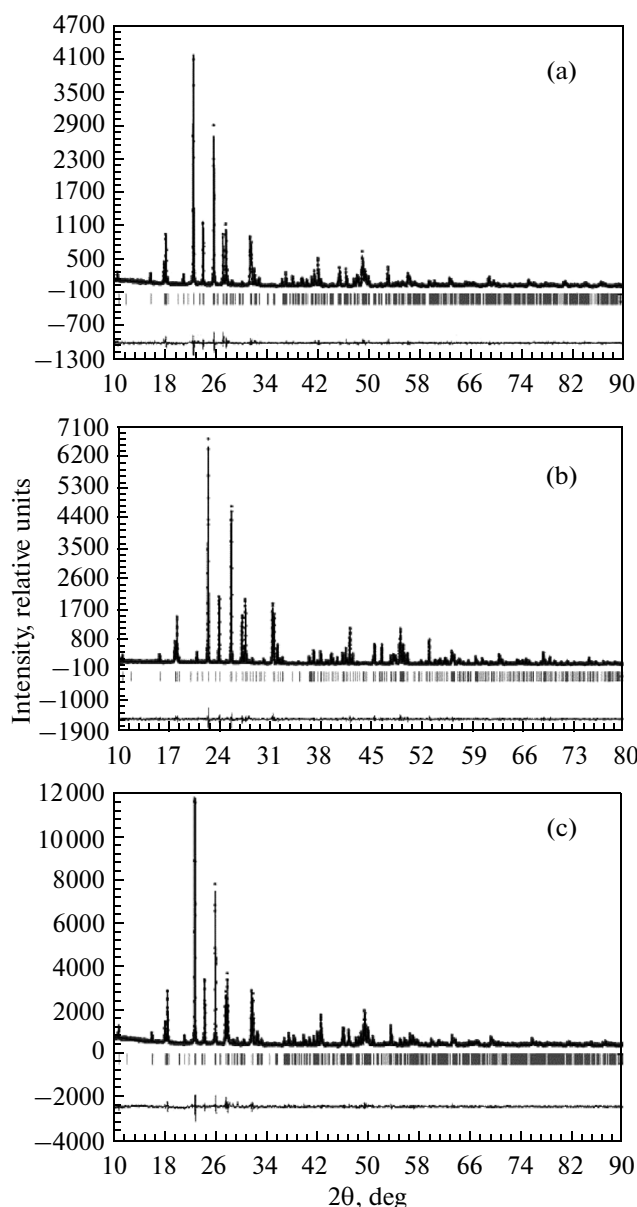


Fig. 1. Measured and calculated X-ray patterns: (a)  $\text{Ce}_2\text{Zr}_3(\text{MoO}_4)_9$ , (b)  $\text{Pr}_2\text{Zr}_3(\text{MoO}_4)_9$ , (c)  $\text{Eu}_2\text{Zr}_3(\text{MoO}_4)_9$ .

firmed. The measured and computed X-ray patterns are presented in Figs. 1a–c. The crystallographic structure is a three-dimensional framework in which  $\text{LnO}_6$  polyhedrons and  $\text{ZrO}_6$  octahedrons, connected by the common oxygen vertices of two types of bridged Mo tetrahedrons, are arranged in rhombohedral order (Fig. 2).

### THERMAL ANALYSIS

Differential scanning calorimetry (DSC) was performed on a NETZSCH STA 449 C (Jupiter) thermal analyzer. Sample size was 15–10 mg; the temperature

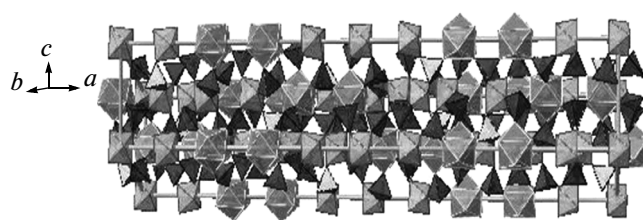


Fig. 2. Projection of  $\text{Ln}_2\text{Zr}_3(\text{MoO}_4)_9$  crystalline structure onto plane 111.

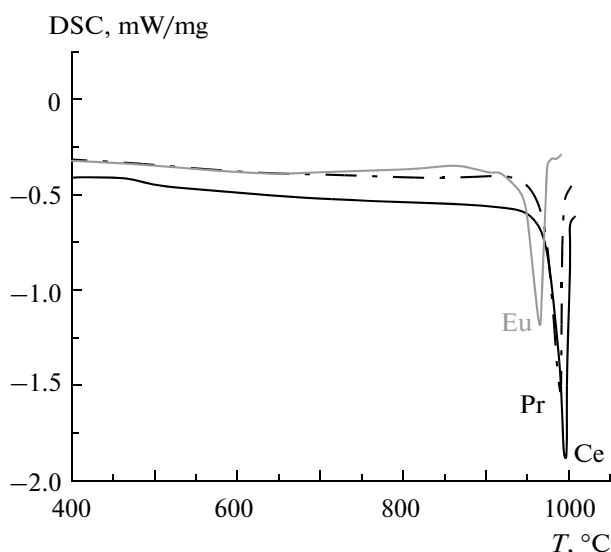


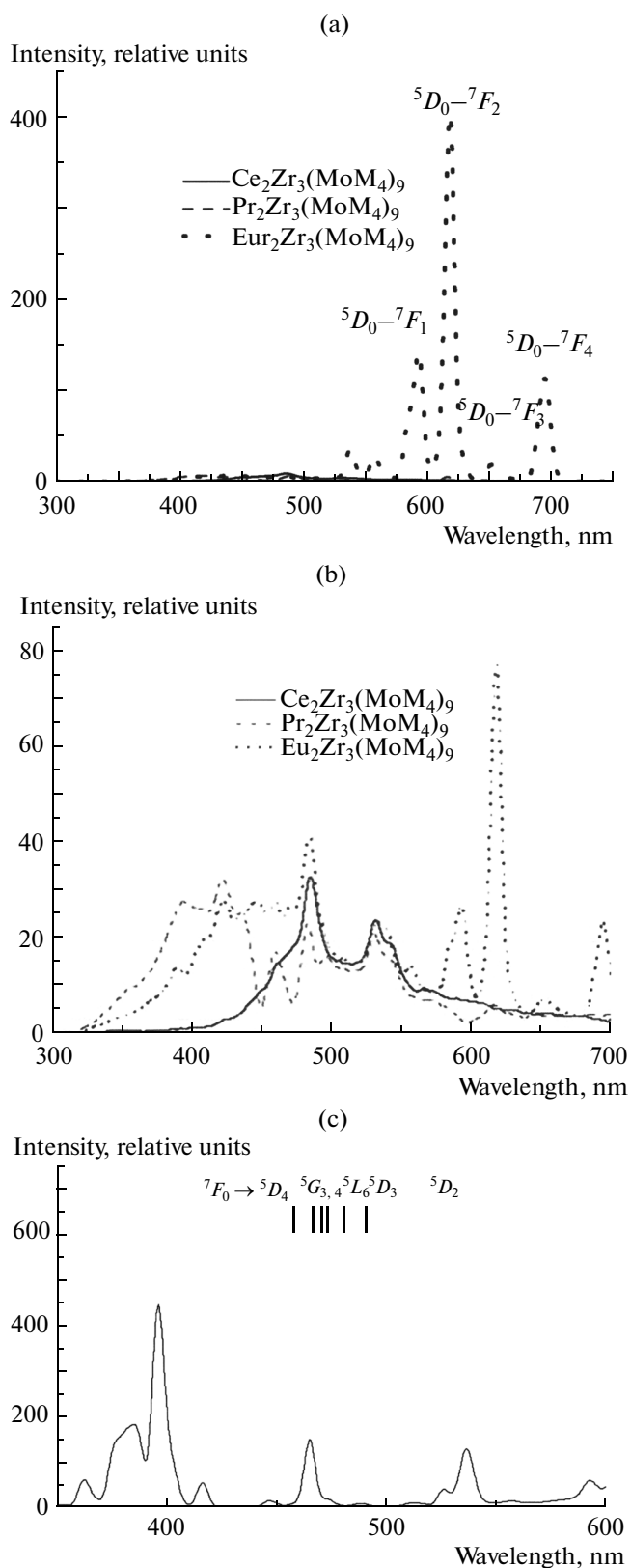
Fig. 3. DSC curves of  $\text{Ln}_2\text{Zr}_3(\text{MoO}_4)_9$  ( $\text{Ln} = \text{Ce}, \text{Pr}, \text{Eu}$ ).

rose at 10 K/min. Annealed  $\text{Al}_2\text{O}_3$  served as a reference sample.

Samples were heated to a temperature of  $1050^\circ\text{C}$ , at which large losses of mass and releases of heat were observed. DSC curves of the synthesized compounds were characterized by a single endothermic effect (Fig. 3). Melting temperatures of  $\text{Ln}_2\text{Zr}_3(\text{MoO}_4)_9$  where  $\text{Ln} = \text{Ce}, \text{Pr}$ , and  $\text{Eu}$  were 996.5, 989.0, and  $964.6^\circ\text{C}$ , respectively. The volume of elementary cells grew along with ionic radius according to Shannon [10]. The enthalpies of melting for  $\text{Ce}_2\text{Zr}_3(\text{MoO}_4)_9$ ,  $\text{Pr}_2\text{Zr}_3(\text{MoO}_4)_9$ , and  $\text{Eu}_2\text{Zr}_3(\text{MoO}_4)_9$  were 222.6 kJ/mol,  $-194.7$  kJ/mol, and 183.2 kJ/mol, respectively.

### OPTICAL SPECTROSCOPY

The luminescence and excitation and absorption spectra of polycrystalline samples of double molybdates were measured on PerkinElmer LS 55 and Lambda 950 optical spectrometers, respectively. When photographing the luminescence and excitation spectra, the powder was contained in a quartz flask placed in a floodable quartz cryostat. When measuring the absorption spectra, samples contained in a quartz flask were placed in the center of an integrating sphere



**Fig. 4.** Luminescence spectra of  $\text{Ln}_2\text{Zr}_3(\text{MoO}_4)_9$  ( $\text{Ln} = \text{Ce}, \text{Pr}, \text{Eu}$ ): (a)  $\lambda_{\text{exc}} = 280$  nm, (b)  $\lambda_{\text{exc}} = 200$  nm. (c) Excitation spectrum of  $\text{Eu}_2\text{Zr}_3(\text{MoO}_4)_9$  ( $\lambda_{\text{lum}} = 616$  nm).

attachment (diameter, 50 mm) for a PerkinElmer Lambda 950 spectrometer.

Among the studied compounds, we found that the one of greatest interest was  $\text{Eu}_2\text{Zr}_3(\text{MoO}_4)_9$ , which displayed the most intense photoluminescence in the red end of the spectrum at an excitation of  $\lambda_{\text{exc}} = 280$  nm.  $\text{Eu}^{3+}$  ions are characterized by  $f-f$  transitions with a maximum band at 616–617 nm, corresponding to  $^5D_0-^7F_2$  electron transitions (Fig. 4a). A comparison of the luminescence spectra of  $\text{Ln}_2\text{Zr}_3(\text{MoO}_4)_9$  ( $\text{Ln} = \text{Ce}, \text{Pr}, \text{Eu}$ ) at  $\lambda_{\text{exc}} = 200$  nm shows that the luminescence of the main matrix of molybdates lies within the 300–550 nm range of wavelengths (Fig. 4b).

At excitation energies of 2.2–3.5 eV, the excitation spectra of our samples were similar and typical of  $f-f$  transitions in  $\text{Eu}^{3+}$  ions; we determined their nature for two intense bands (Fig. 4c). The positions of these bands at 395 and 465 nm in the excitation spectrum corresponds to the wavelengths normally used for excitation of the luminophores in light emitting diodes. A comparison of the absorption and excitation spectra for  $\text{Eu}_2\text{Zr}_3(\text{MoO}_4)_9$  revealed a correlation between the main peaks.

## CONCLUSIONS

We have confirmed the structure of double molybdates  $\text{Ln}_2\text{Zr}_3(\text{MoO}_4)_9$  ( $\text{Ln} = \text{Ce}, \text{Pr}$  and  $\text{Eu}$ ) with trigonal sigony (spatial group,  $R\bar{3}c$ ;  $Z = 6$ ) at 700°C. The structure consists of ( $\text{Ln}, \text{Zr}$ ) rods arranged relative to one another in rhombohedral order and connected via the common oxygen vertices of bridged  $\text{MoO}_4$  tetrahedrons.

Melting temperatures of  $\text{Ln}_2\text{Zr}_3(\text{MoO}_4)_9$  are 964.6°C (Eu), 989.0°C (Pr), and 996.5°C (Ce). Elementary cell volume grows along with the ionic radius of lanthanide.

It was established that at an excitation of  $\lambda_{\text{exc}} = 280$  nm, intense photoluminescence characterized by  $f-f$  transitions can be observed in the red end of the  $\text{Eu}_2\text{Zr}_3(\text{MoO}_4)_9$  spectrum. Luminescence of the main matrix of molybdates is observed within the 300–550 nm range of wavelengths. The positions of the bands at 395 and 465 nm in the excitation spectrum correspond to the wavelengths normally used for excitation of the luminophores in light emitting diodes. A correlation was shown between bands in the absorption and excitation spectra of  $\text{Eu}_2\text{Zr}_3(\text{MoO}_4)_9$ .

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