

Optical Properties of Molybdates Containing a Combination of Rare-Earth Elements

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Abstract—We have synthesized new molybdates, $\text{Cs}_2\text{LnZrTi}(\text{MoO}_4)_{6.5}$ ($\text{Ln} = \text{Eu} + \text{Yb}$, $\text{Eu} + \text{Dy}$, and $\text{Gd} + \text{Dy}$ lanthanides), containing pairs of rare-earth elements in the ratio 1 : 1. The synthesized compounds have been shown to be single-phase and isostructural with each other. We have determined their crystallographic characteristics and assessed their thermal stability. In the dysprosium-containing molybdates, the Dy^{3+} luminescence intensity is low as a result of concentration quenching. The molybdate containing the $\text{Eu} + \text{Dy}$ pair of rare-earth elements shows predominant high-intensity luminescence in the red spectral region. In addition to usual infrared emission due to ytterbium, the $\text{Eu} + \text{Yb}$ compound demonstrates emission in the ultraviolet spectral region. We have measured luminescence decay kinetic characteristics at the peak emission wavelengths. In the case of the molybdate containing the $\text{Eu} + \text{Yb}$ pair of rare-earth elements, energy transfer from europium ions to ytterbium has been observed. We have demonstrated high-intensity luminescence that can be excited both on intraconfigurational transitions and in the region of charge transfer bands of oxygen–molybdenum complexes.

Keywords: molybdates, X-ray diffraction, differential scanning calorimetry, optical spectroscopy

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INTRODUCTION

Designing mercury-free luminescent lamps requires novel phosphors suitable for light intensity measurements in the vacuum ultraviolet region. One possible approach to improving the efficiency of phosphors is to utilize the cascade photon emission effect (quantum cutting effect), in which a rare-earth ion excited by one high-energy photon emits a few lower-energy photons. There are various potentially attractive pairs of rare-earth elements (REEs) that exhibit quantum cutting as a consequence of interionic interaction and cross-relaxation processes [1–8]. The quantum yield of phosphors where this mechanism is possible often exceeds 100%. In particular, Kroupa et al. [1] demonstrated that Yb^{3+} -doped metal-halide perovskite thin films offered a quantum yield as high as 190%. Framework structures of borates, tungstates, and molybdates containing trivalent and rare-earth ions can be attractive hosts for phosphors [4–16]. The incorporation of a pair of REEs into such structures is expected to enable the preparation of materials that exhibit cascade photon emission as a consequence of interaction between the rare-earth ions. Tushinova et al. [17] obtained data on phase relations in systems

of cesium, lanthanide, and zirconium molybdates and demonstrated the formation of the $\text{Cs}_2\text{LnZr}_2(\text{MoO}_4)_{6.5}$ ($\text{Ln} = \text{Nd}$, Sm , Tb , Er) phases.

In this paper, we present our results on the optical, crystallographic, and thermal properties of molybdates containing pairs of REEs in the ratio 1 : 1, namely, $\text{Cs}_2\text{LnZrTi}(\text{MoO}_4)_{6.5}$ ($\text{Ln} = \text{Eu} + \text{Yb}$, $\text{Eu} + \text{Dy}$, and $\text{Gd} + \text{Dy}$).

EXPERIMENTAL

The starting chemicals used for the synthesis of the molybdates were Cs_2MoO_4 (pure grade), MoO_3 (reagent grade), Ln_2O_3 (99.9+% purity), and ZrO_2 prepared by calcining pure-grade $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. The $\text{Ln}_2(\text{MoO}_4)_3$ and $\text{Zr}(\text{MoO}_4)_2$ molybdates were prepared by solid-state reactions via stepwise firing in the temperature range from 350 to 750°C for 100 h. Stoichiometric amounts of appropriate reagents were fired with homogenization of the mixture every 50°C. The $\text{Cs}_2\text{LnZrTi}(\text{MoO}_4)_{6.5}$ ($\text{Ln} = \text{Eu} + \text{Yb}$, $\text{Eu} + \text{Dy}$, $\text{Gd} + \text{Dy}$) mixed molybdates were synthesized in the temperature range 350–600°C. The synthesis time was 100 h.

Table 1. Crystallographic characteristics of the $\text{Cs}_2\text{LnZrTi}(\text{MoO}_4)_{6.5}$ (Ln = Eu + Yb, Eu + Dy, Gd + Dy) compounds

Compound	a , Å	c , Å	V , Å ³
$\text{Cs}_2\text{Eu}_{0.5}\text{Yb}_{0.5}\text{ZrTi}(\text{MoO}_4)_{6.5}$	13.2536(6)	11.9521(3)	1818.2(1)
$\text{Cs}_2\text{Gd}_{0.5}\text{Dy}_{0.5}\text{ZrTi}(\text{MoO}_4)_{6.5}$	13.2744(3)	11.9498(7)	1823.5(1)
$\text{Cs}_2\text{Eu}_{0.5}\text{Dy}_{0.5}\text{ZrTi}(\text{MoO}_4)_{6.5}$	13.2879(7)	11.9456(9)	1826.6(1)

Equilibration was ascertained by X-ray diffraction on a Bruker AXS D8 Advance automatic powder diffractometer ($\text{CuK}\alpha$ radiation, diffracted-beam monochromator, VANTEC high-speed position-sensitive detector, maximum angle $2\theta = 100^\circ$, scan step in the range 0.01° – 0.02°).

The unit-cell parameters of the synthesized compounds were determined using crystallographic data for isostructural compounds [17]. Calculations were performed using lines in X-ray powder diffraction patterns of ternary molybdates, the TOPAS 4.2 software suite, and experimental data acquired in the angular range $2\theta = 8^\circ$ – 100° at a temperature of 300 K. Peak positions were determined with EVA software (Bruker).

The molybdates were characterized by thermal analysis using a Netzsch STA 449 F1 Jupiter simultaneous thermal analysis system (argon atmosphere, platinum crucibles). Samples weighing 17–20 mg were heated at a rate of 10 K/min.

Emission, luminescence excitation, and optical density spectra of polycrystalline mixed molybdate samples were measured on a PerkinElmer LS 55 luminescence spectrometer and Lambda 950 spectrophotometer, respectively. During the acquisition of the emission and excitation spectra, the sample was located in a quartz flask, which was placed in a quartz immersion cryostat. In measurements of absorption

spectra, a sample in a quartz ampule was placed in the center of an integrating sphere for the PerkinElmer Lambda 950 spectrophotometer. The excitation, luminescence, and optical absorption spectra were measured in the range from 200 to 2500 nm.

RESULTS AND DISCUSSION

The ceramic samples prepared by us were single-phase and formed a series of isostructural compounds. Using the TOPAS 4.2 software suite, we determined their unit-cell parameters and volume in the triclinic crystal system (Table 1).

Thermal characterization of the molybdates by differential scanning calorimetry (DSC) during heating and cooling showed that all of the compounds exhibited one endothermic event, corresponding to their melting (Fig. 1). The melting points of the $\text{Cs}_2\text{LnZrTi}(\text{MoO}_4)_{6.5}$ (Ln = Eu + Yb, Gd + Dy, Eu + Dy) molybdates are 559, 559, and 557°C, respectively.

We measured the excitation and luminescence spectra of the $\text{Cs}_2\text{Eu}_{0.5}\text{Dy}_{0.5}\text{ZrTi}(\text{MoO}_4)_{6.5}$ sample in the ranges 200–500 and 420–700 nm, respectively (Fig. 2a). The results demonstrate low emission intensity of Dy^{3+} as a result of concentration quenching.

The excitation spectra of the $\text{Cs}_2\text{Eu}_{0.5}\text{Dy}_{0.5}\text{ZrTi}(\text{MoO}_4)_{6.5}$ sample (200–500 nm) are typical of the Eu^{3+} ion and show strong bands at 395 and 465 nm (Fig. 2b). We observe predominant high-intensity luminescence in the red spectral region, due to $\text{Eu}^{3+} f-f$ transitions, with the strongest band at ~617 nm.

Figure 3 shows the excitation, luminescence, and optical density spectra of $\text{Cs}_2\text{Eu}_{0.5}\text{Yb}_{0.5}\text{ZrTi}(\text{MoO}_4)_{6.5}$. The excitation spectrum of Yb^{3+} contains bands arising from $4f-4f$ transitions of the europium ions and a broad band at 350 nm, due to transitions of oxygen–molybdenum complexes (Fig. 3a). Yb^{3+} luminescence in the emission spectrum of this compound was observed under excitation in a charge transfer band. Thus, there was energy transfer from europium ions to ytterbium and from oxygen–molybdenum complexes to ytterbium ions. There was high-intensity luminescence (Fig. 3b) arising from transitions within the $4f$ shell of the ytterbium ions. Infrared emission observed at room temperature fell in the range 950–1050 nm. The strong ytterbium ion luminescence and optical density bands correlated with each other.

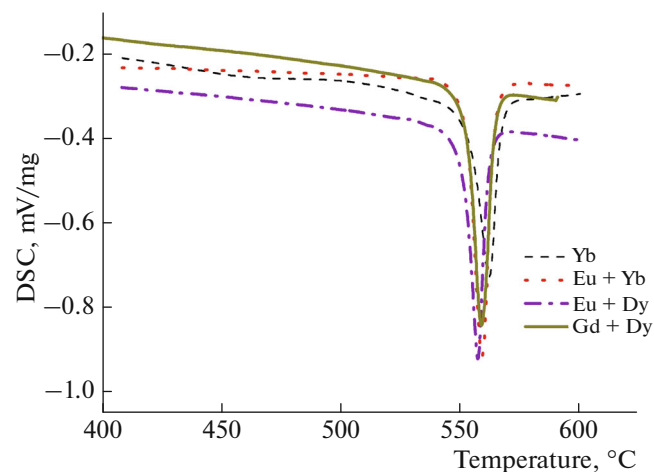


Fig. 1. DSC heating curves of the $\text{Cs}_2\text{LnZrTi}(\text{MoO}_4)_{6.5}$ (Ln = Yb, Eu + Yb, Eu + Dy, Gd + Dy) samples.

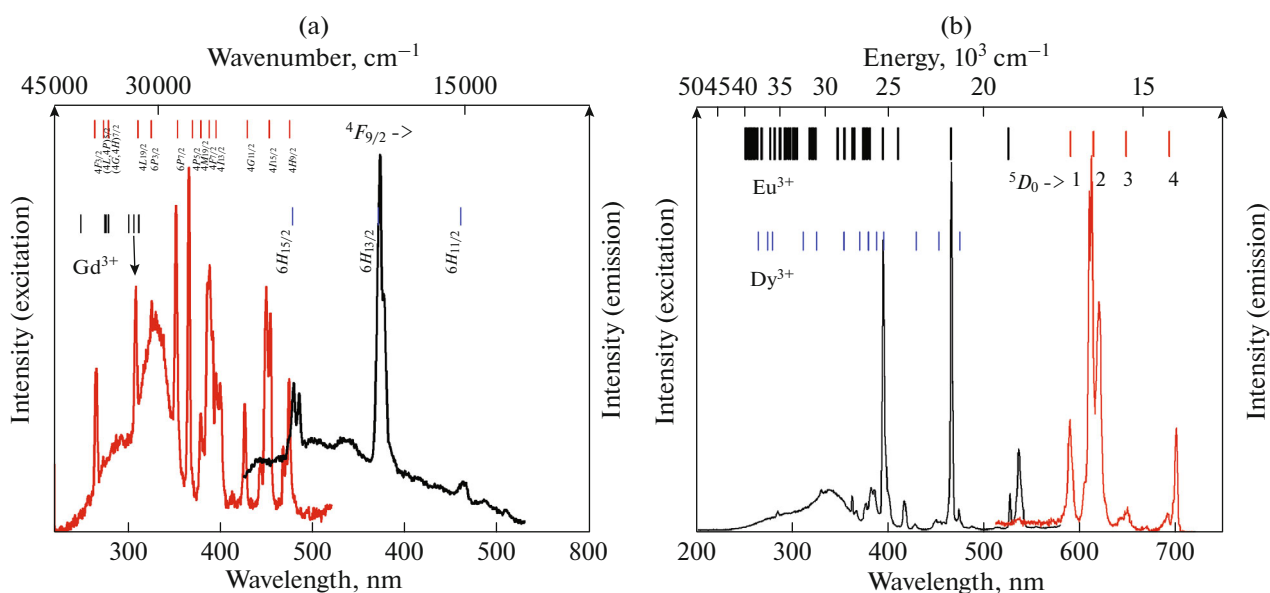


Fig. 2. Excitation and luminescence spectra of $\text{Cs}_2\text{LnZrTi}(\text{MoO}_4)_{6.5}$ with Ln = (a) Gd + Dy and (b) Eu + Dy.

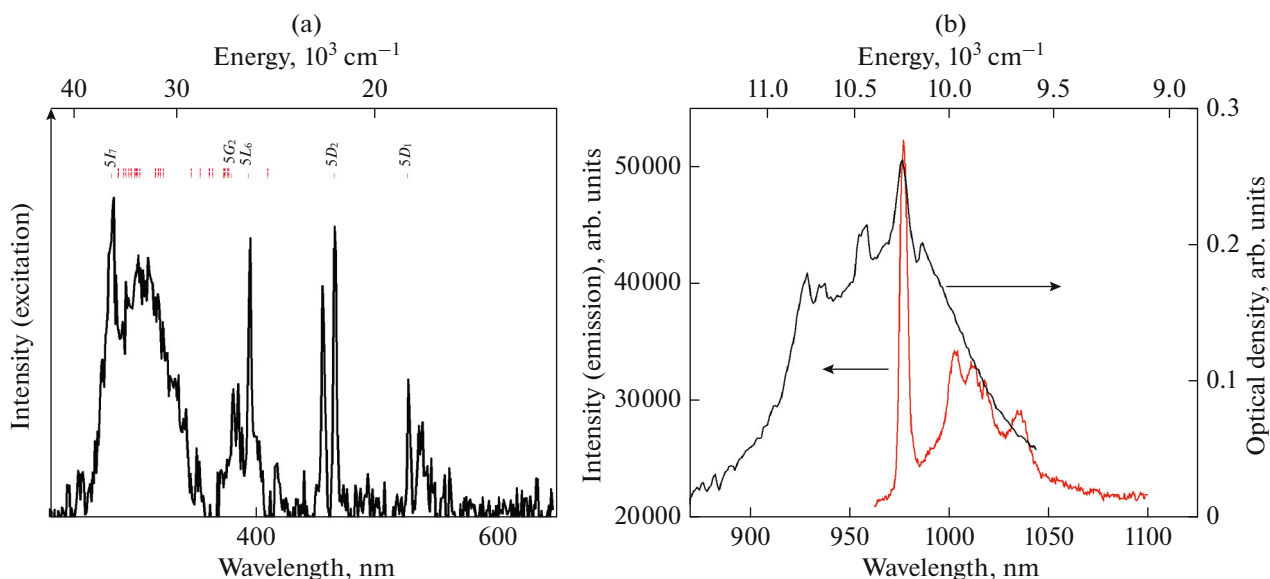


Fig. 3. (a) Excitation, (b) luminescence, and optical density spectra of $\text{Cs}_2\text{Eu}_{0.5}\text{Yb}_{0.5}\text{ZrTi}(\text{MoO}_4)_{6.5}$.

The $\text{Cs}_2\text{YbZrTi}(\text{MoO}_4)_{6.5}$ and $\text{Cs}_2\text{Eu}_{0.5}\text{Yb}_{0.5}\text{ZrTi}(\text{MoO}_4)_{6.5}$ samples have different structures of the broad bands in the range 250–370 nm, arising from charge transfer transitions. The excitation spectra of Yb^{3+} f - f luminescence in $\text{Cs}_2\text{YbZrTi}(\text{MoO}_4)_{6.5}$ show only one band, corresponding to slow intrinsic emission, without a fast blue emission band (Fig. 4a).

At a temperature of 77 K, we studied in detail the excitation and luminescence spectra of the Eu + Yb

sample. The spectra had two types of intrinsic luminescence bands excited in a charge transfer band: fast emission, with a band at 440 nm (Fig. 4b), and slow emission, in the range 570–670 nm (Fig. 4c).

Figure 5 shows photoluminescence decay kinetic characteristics at the peak emission wavelengths under excitation at $\lambda_{\text{ex}} = 280$ and 325 nm. The decay time of the luminescence (fast emission at $\lambda_{\text{em}} = 440$ nm) in the ytterbium + europium sample ranges up to 500 ns.

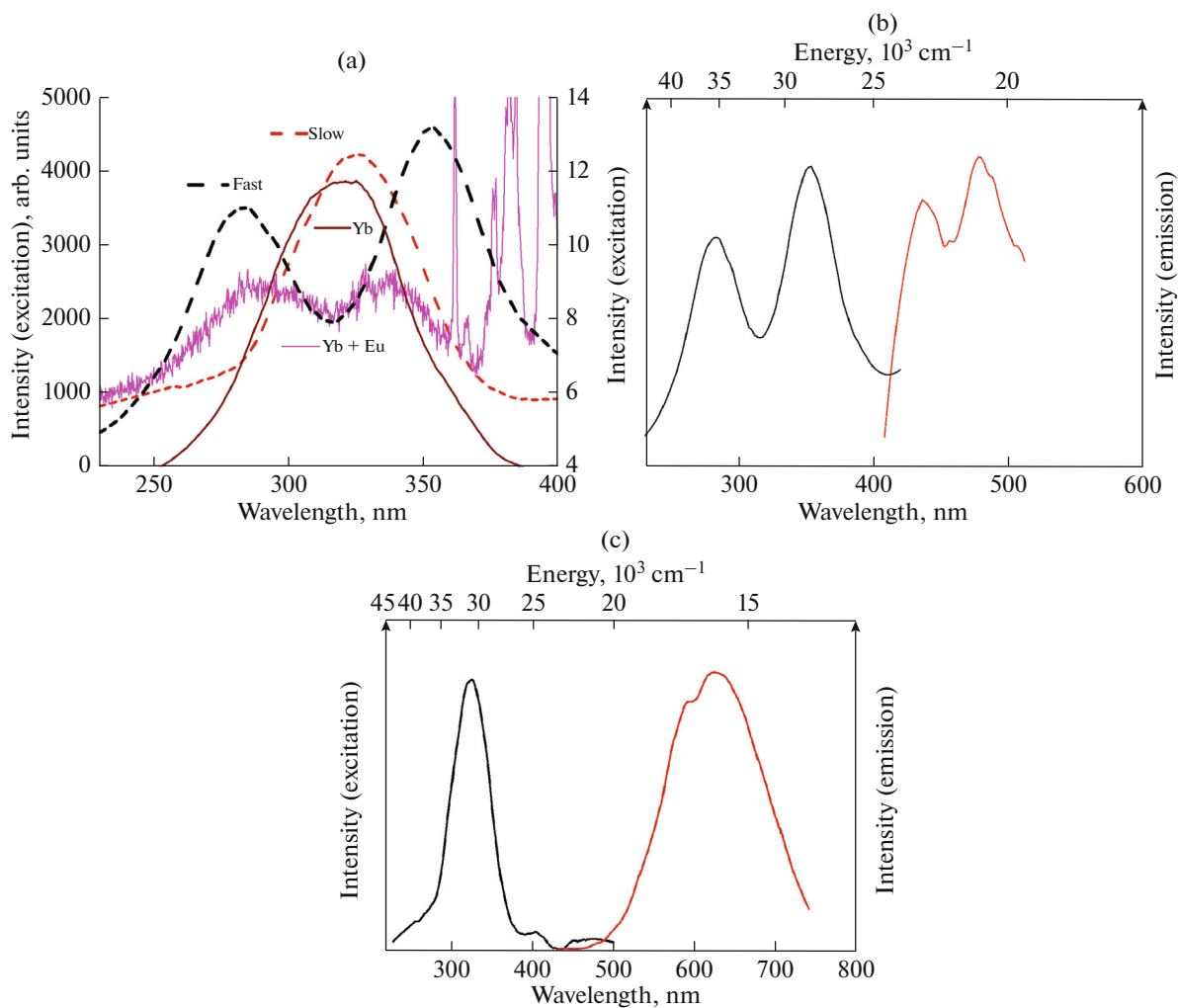


Fig. 4. (a) Excitation spectra of $\text{Cs}_2\text{YbZrTi}(\text{MoO}_4)_{6.5}$ and $\text{Cs}_2\text{Eu}_{0.5}\text{Yb}_{0.5}\text{ZrTi}(\text{MoO}_4)_{6.5}$ and (b, c) excitation and luminescence spectra of $\text{Cs}_2\text{Eu}_{0.5}\text{Yb}_{0.5}\text{ZrTi}(\text{MoO}_4)_{6.5}$: (b) fast and (c) slow emission components.

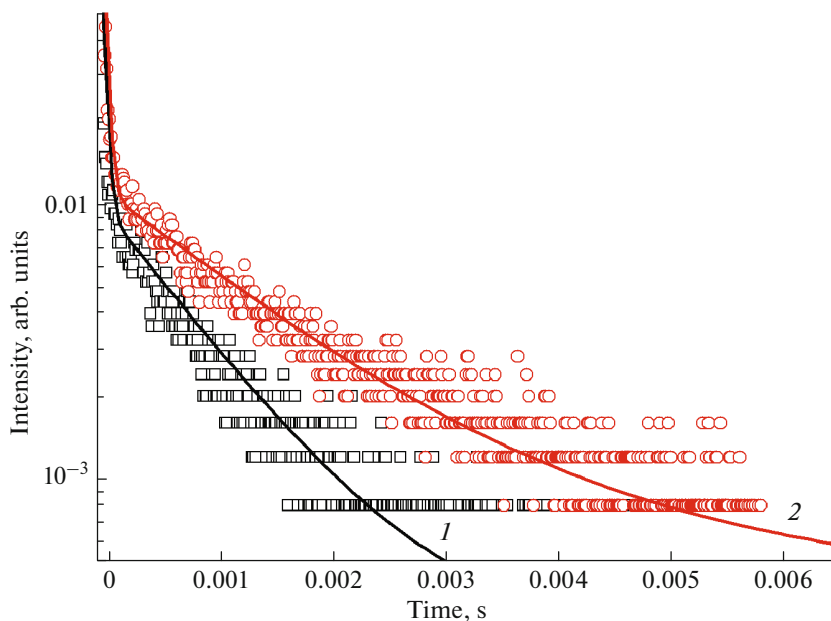


Fig. 5. Luminescence decay kinetics: (1) fast and (2) slow emission components.

The decay time of the slow emission ($\lambda_{em} = 625$ nm) at an excitation wavelength of 325 nm is ~ 13 ms.

CONCLUSIONS

We have synthesized new molybdates containing pairs of REEs in the ratio 1 : 1, namely, $Cs_2LnZrTi(MoO_4)_{6.5}$ ($Ln = Eu + Yb, Eu + Dy, \text{ and } Gd + Dy$), which form a series of isostructural compounds; determined their trigonal cell parameters (sp. gr. $R\bar{3}, Z = 6$); and assessed their thermal stability.

The molybdates have been shown to exhibit high-intensity luminescence that can be excited both on intraconfigurational transitions and in the region of a charge transfer band of oxygen–molybdenum complexes. The $Cs_2LnZrTi(MoO_4)_{6.5}$ ($Ln = Eu + Yb, Eu + Dy$) phases, containing Eu^{3+} ions, demonstrate bright red luminescence excited in the charge transfer band. In the Dy-containing molybdates, the Dy^{3+} luminescence intensity is considerably lower as a result of concentration quenching. Yb^{3+} luminescence in the $Cs_2Eu_{0.5}Yb_{0.5}ZrTi(MoO_4)_{6.5}$ Yb-containing molybdate can be excited in a charge transfer band, with excitation transfer from Eu^{3+} ions.

The synthesized molybdates show two types of broadband intrinsic luminescence excited in a charge transfer band: fast (blue) and slow (red) emission components.

Polycrystalline hosts based on molybdates with framework structures and containing pairs of RE ions with efficient energy transfer between them are expected to be attractive for use in UV-pumped light emitting diodes.

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