

Luminescence of Pr³⁺ and Nd³⁺ Ions in Double Molybdates

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Abstract—The optical spectra of samples of double zirconium molybdates activated by rare-earth Pr³⁺ and Nd³⁺ ions are studied. The presence of bands corresponding to the 4*f*–4*f* transitions of Pr³⁺ and Nd³⁺ trivalent ions in the absorption, excitation, and luminescence spectra is shown. A strong dependence of the luminescence intensity of Pr³⁺ ions on temperature is revealed.

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1. INTRODUCTION

Many studies have shown the promises of using molybdates doped with rare-earth ions as lumino-phores, scintillators, and laser media [1–3]. Attention to these materials is due to the wide variation in their physicochemical properties, thermal and chemical stability, and in some cases, extremely low concentration quenching, despite the significant impurity concentrations [4]. The study of the spectral characteristics of double molybdates with various rare-earth ions will make it possible to study the processes of energy transfer and transformation upon the interaction of the crystal matrix with the impurity. This work is concerned with spectroscopic studies of molybdate powders of the compositions Pr₂Zr₃(MoO₄)₉ and Nd₂Zr₃(MoO₄)₉. One of the promising applications of Pr³⁺-doped molybdates is luminescence thermometry, based on quenching of luminescence with increasing temperature [5]. Nd : YAG is a commercial laser material, but, at the same time, numerous investigations are aimed at finding alternative compounds with Nd³⁺ ions, suitable for lasing, including molybdates and tungstates [6, 7].

2. EXPERIMENTAL

Samples of double molybdates were synthesized by ceramic technology by stepwise annealing of a mixture of stoichiometric quantities of Pr₆O₁₁, Nd₂O₃, MoO₃, and ZrO₂ for 150 h up to a maximum temperature of 700°C [8]. X-ray phase analysis of the synthesized compounds was carried out on a D8 Advance Bruker AXS diffractometer (CuK_α radiation). The luminescence spectra were measured using an SDL-1 double monochromator with gratings of 600 lines per mm and

a Hamamatsu H10721-04 photomodule for the range of 400–800 nm. For the region of 800–1100 nm, gratings of 300 lines per mm and a cooled FEU-83 photomultiplier were used. The excitation was performed using a DKsSh-150 high-pressure xenon lamp through an MDR-2 monochromator with a diffraction grating of 1200 lines per mm. The substrate for applying the sample was a polished pure LiF crystal, which was fixed in the holder of a vacuum cryostat. The data obtained were corrected for the spectral characteristics of the device. The absorption spectra were obtained using a Perkin-Elmer Lambda 950 UV/VIS/NIR spectrophotometer equipped with an integrating sphere.

3. RESULTS AND DISCUSSION

The absorption spectra of Pr₂Zr₃(MoO₄)₉ and Nd₂Zr₃(MoO₄)₉ (Fig. 1) consist of a set of narrow intense bands related to 4*f*–4*f* transitions of Pr³⁺ and Nd³⁺ rare-earth ions and a wide absorption band in the region of 300 nm, caused by transitions with a charge transfer in the MoO₄²⁻ group.

The luminescence spectrum of Pr₂Zr₃(MoO₄)₉ (Fig. 2) at 77 K consists of intense thin bands corresponding to the radiative transitions of the trivalent praseodymium ion from the ³P₀ level to the ³H₅ (544 nm), ³H₆ (612 nm), ³F₂ (642 nm), and ³F₄ levels (727 nm). Each band consists of an intense zero phonon line and a wide phonon wing, which is displaced relative to the zero phonon line by 150 cm⁻¹. The excitation spectrum shows bands of 4*f*–4*f* transitions of praseodymium from the ³H₄ ground state to the overlying levels ³P₀ (490 nm), ³P₁ (473 nm), and ³P₂

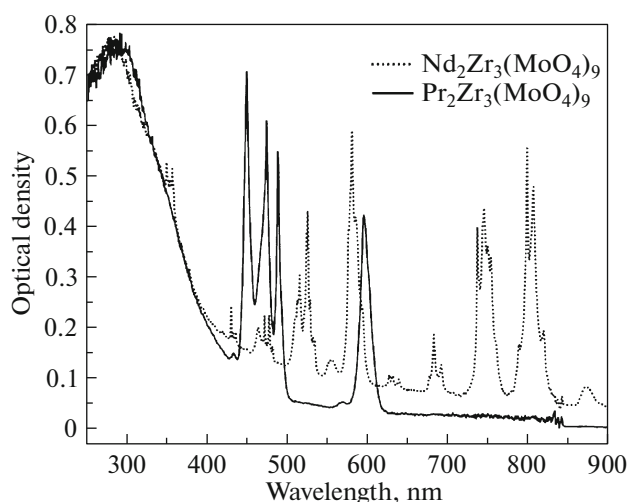


Fig. 1. Absorption spectra of Pr₂Zr₃(MoO₄)₉ and Nd₂Zr₃(MoO₄)₉.

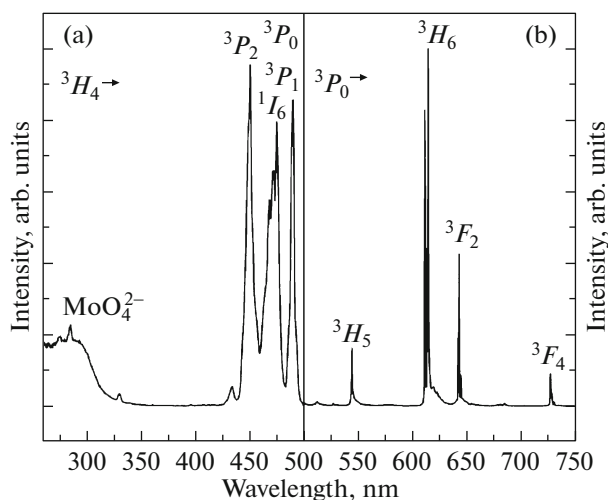


Fig. 2. (a) Excitation and (b) luminescence spectra of Pr₂Zr₃(MoO₄)₉ at excitation wavelengths of 490 nm (³H₄–³P₀) and detection of 612 nm (³P₀–³H₆), respectively.

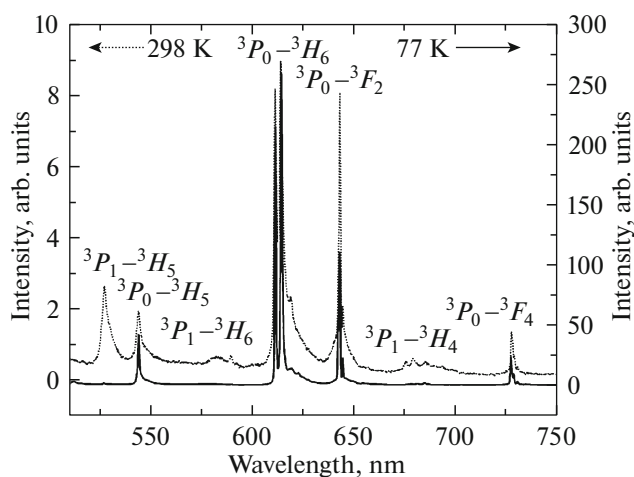


Fig. 3. Luminescence spectra of Pr₂Zr₃(MoO₄)₉ with excitation of 490 nm (³H₄–³P₀) at different temperatures.

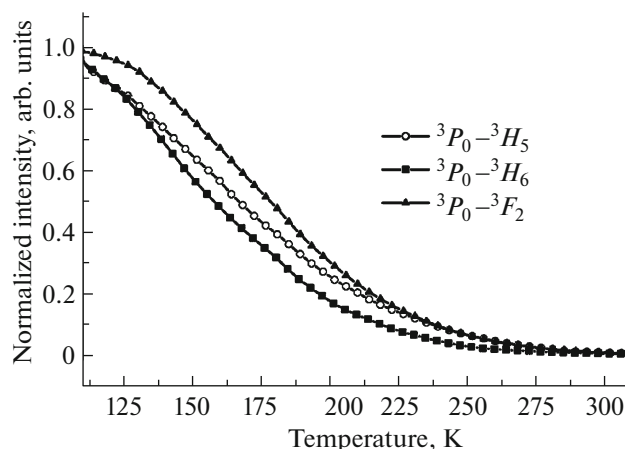


Fig. 4. Normalized temperature dependences of the luminescence intensity of different bands of Pr₂Zr₃(MoO₄)₉ upon excitation of 473 nm (³H₄–³P₁).

(450 nm). Also, there is a wide excitation band related to transitions inside the MoO₄²⁻ complex (300 nm) with the subsequent excitation of a rare-earth ion. Figure 3 shows a comparison of the luminescence spectra of Pr₂Zr₃(MoO₄)₉ at liquid nitrogen and room temperatures. Upon cooling the sample, the integral emission intensity of the main Pr₂Zr₃(MoO₄)₉ bands increases more than tenfold. Also, upon cooling the sample, the integral luminous intensity of strongly forbidden transitions from the upper excited level ³P₁ of the Pr³⁺ ion decreases by a factor of 1.4. Figure 4 shows the temperature dependence of the intensities of the Pr₂Zr₃(MoO₄)₉ main luminescence bands upon exci-

tation into the ³H₄–³P₁ band (473 nm). A sharp decrease in the emission intensity of the 4*f*–4*f* transitions of Pr³⁺ is observed with an increase in temperature in the range of 110–230 K. An analysis of the data obtained has shown that the process of quenching of luminescence in Pr₂Zr₃(MoO₄)₉ has a complex character, which includes several overlapping processes associated with concentration and temperature effects.

The luminescence and excitation spectra of Nd₂Zr₃(MoO₄)₉ at the liquid nitrogen temperature are shown in Fig. 5. The luminescence spectrum consists of intense narrow bands corresponding to the radiative

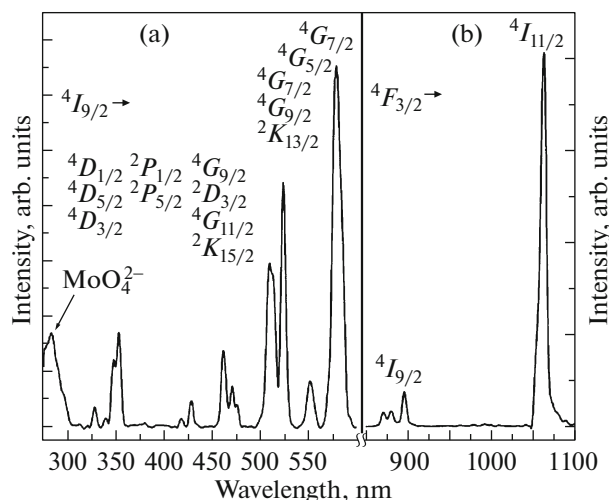


Fig. 5. (a) Excitation and (b) luminescence spectra of $\text{Nd}_2\text{Zr}_3(\text{MoO}_4)_9$ at the wavelengths of excitation at 580 nm ($^4I_{9/2} \rightarrow ^2G_{7/2}$) and detection at 1060 nm ($^4F_{3/2} \rightarrow ^4I_{11/2}$), respectively.

transitions of the trivalent neodymium ion from the $^4F_{3/2}$ level to the $^4I_{9/2}$ (880 nm) and $^4I_{11/2}$ (1060 nm) levels. The excitation spectrum contains a set of overlapping $4f-4f$ Nd^{3+} transitions from the $^4I_{9/2}$ ground state to the overlying level groups 4G , 2G , 4P , 2P , 4F , 4S , and 2H with different total angular momentum of the electron. The excitation band with charge transfer has a low intensity, and its position does not differ from the band in the spectrum of $\text{Pr}_2\text{Zr}_3(\text{MoO}_4)_9$. The intensity and shape of the bands in the temperature range 77–300 K varies only slightly.

In [9], it was shown that $\text{Tb}_2\text{Zr}_3(\text{MoO}_4)_9$ and $\text{Eu}_2\text{Zr}_3(\text{MoO}_4)_9$ compounds have an effective mechanism of the transfer of excitation from MoO_4^{2-} complexes to rare earth ions with subsequent intensive $4f-4f$ luminescence. In the compounds studied in this work, the excitation efficiency in a charge-transfer band is significantly weaker than the direct $4f-4f$ excitation of a rare-earth ion. It is also worth noting a strong dependence of the luminescence of $\text{Pr}_2\text{Zr}_3(\text{MoO}_4)_9$ on temperature, which was not observed in our studies for other rare-earth ions in the matrices of double molybdates.

4. CONCLUSIONS

In this work, we have studied the spectral characteristics of Pr^{3+} and Nd^{3+} rare-earth ions in matrices of zirconium double molybdates. The luminescence of $\text{Pr}_2\text{Zr}_3(\text{MoO}_4)_9$ is detected in the range of 500–750 nm and is associated with radiative transitions in $4f$ shells of Pr^{3+} rare-earth ions. The luminescence of $\text{Nd}_2\text{Zr}_3(\text{MoO}_4)_9$ is also associated with $4f-4f$ transi-

tions in the near infrared region (850–1100 nm), typical of Nd^{3+} . The bands in the excitation and absorption spectra are of the same nature and are related to the excitation of MoO_4^{2-} complexes (300 nm) and $4f$ shells of rare-earth ions. The presence of the mechanism of excitation transfer from the matrix to the rare-earth ion in these compounds upon excitation to a band with charge transfer has been shown. The strong temperature dependence of the luminescence of $\text{Pr}_2\text{Zr}_3(\text{MoO}_4)_9$ complex has a complex nature, and additional research is needed to reveal the reasons for the luminescence quenching.

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