

Luminescence Study of $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$

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Abstract—The luminescence spectra of $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ ($x = 0.0005, 0.001, 0.01, 0.05, 0.1, 0.5, 1$) scheelite solid solutions are measured under laser excitation at 337.1 nm. The effect of Eu^{3+} concentration on the luminescence behavior of the solid solutions is examined. The highest integrated emission intensity is offered by $\text{LiY}_{0.5}\text{Eu}_{0.5}(\text{MoO}_4)_2$. Eu^{3+} substitution for Y^{3+} has no effect on the symmetry of the emission centers involved. Eu^{3+} is shown to occupy only one site in the structure of the solid solutions. X-ray diffraction and luminescence data indicate that all of the solid solutions have an undistorted scheelite structure.

INTRODUCTION

Rare-earth-activated double molybdates are of practical interest as efficient, high color rendering phosphors. Such molybdates are used as materials for luminescent lamps, gain media, and luminescent display panels (see, e.g., [1]).

Varying the cation composition of $\text{MR}(\text{MoO}_4)_2$ ($M = \text{monovalent metal}$, $R = \text{rare earth}$) molybdates, one can produce phosphors for a broad spectral range. Moreover, rare earths incorporated into the structure of such molybdates can be used to probe the structure of the host material [2]. Europium possesses one of the most distinctive emission spectra among lanthanides. The spectroscopic properties of the Eu^{3+} ion in $\text{KEu}(\text{MoO}_4)_2$ crystals were described in [3, 4]. In particular, the $\text{Eu}^{3+} {}^5D_0 \rightarrow {}^7F_0$ transition was found to be split into three components. This behavior implies that Eu^{3+} occupies at least three inequivalent sites in the host structure, and these sites contribute to the observed spectrum.

Many device applications (e.g., the fabrication of cathode ray tubes and gas panels) require phosphors with low concentration quenching, i.e., with the maximum possible concentration of emission centers and minimum energy losses in the surface layer [5].

In this paper, we report the luminescent properties of $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ solid solutions (undistorted scheelite structure [6]) in a broad range of Eu concentrations ($0.0005 \leq x \leq 1$). Such molybdates are efficient phosphors [7], but the nature of the emission centers in them is still poorly understood.

EXPERIMENTAL

The starting materials used were extrapure-grade lithium carbonate, reagent-grade molybdenum trioxide, and 99.95+%-pure rare-earth oxides (Y_2O_3 and Eu_2O_3). $\text{LiR}(\text{MoO}_4)_2$ ($R = \text{Y, Eu}$) samples were prepared by firing 1 : 4 : 1 mixtures of Li_2CO_3 , MoO_3 , and R_2O_3 at 800–950 K for 50 h. The crystallographic characteristics of the synthesized phases agreed with those reported by Trunov *et al.* [8].

$\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ solid solutions were prepared by the conventional ceramic route from appropriate mixtures of the constituent molybdates, which were thoroughly homogenized and then calcined at 950 K for 30 h with intermediate grindings every 8–10 h.

The phase composition of the reaction products was determined by x-ray diffraction (XRD) on a DRON-UM1 diffractometer (CuK_α radiation).

According to XRD data, $\text{LiY}(\text{MoO}_4)_2$ and $\text{LiEu}(\text{MoO}_4)_2$ form a continuous series of scheelite solid solutions (tetragonal symmetry, sp. gr. $I4_1/a$). In luminescence studies, we used $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ samples with $x = 0.0005, 0.001, 0.01, 0.05, 0.1, 0.5$, and 1. The yttrium-containing host was chosen primarily because the yttrium luminescence in this system is negligible compared to the europium luminescence. Moreover, according to XRD results for the $\text{LiY}(\text{MoO}_4)_2$ – $\text{LiEu}(\text{MoO}_4)_2$ system, the crystal-field symmetry on the rare-earth site is unaffected by Eu content, and, therefore, the energy level diagram of the Eu^{3+} ion must also remain unchanged, which offers the

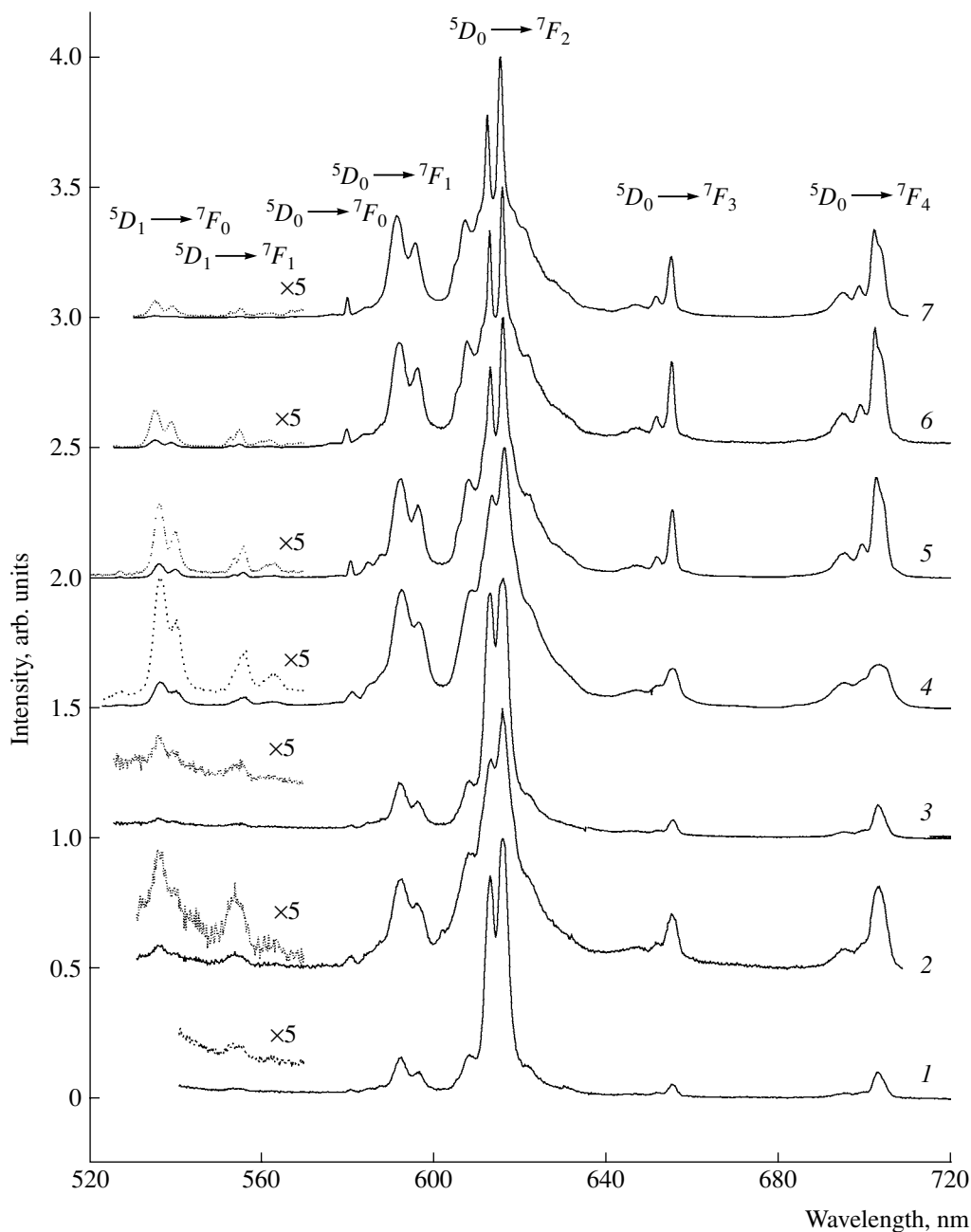


Fig. 1. Room-temperature luminescence spectra of $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ with $x = (1)$ 0.0005, (2) 0.001, (3) 0.01, (4) 0.05, (5) 0.1, (6) 0.5, and (7) 1; $\lambda_{\text{ex}} = 337.1$ nm.

possibility of assessing the interaction between the activator and host ions with high accuracy.

Luminescence spectra were recorded using an SDL-1 monochromator, fitted with a set of interchangeable diffraction gratings, and an FEU-136 photomultiplier. Excitation was provided by an LGI-21 nitrogen laser ($\lambda_{\text{ex}} = 337.1$ nm). In front of the entrance slit of the monochromator, we placed cut-off filters in order to exclude higher diffraction orders. The entrance and exit slits of the monochromator and the voltage applied to

the FEU-136 were adjusted so as to measure the entire luminescence spectrum (520–720 nm) with the highest possible resolution. The measurements were made at ~80 and 300 K. In low-temperature measurements, the sample was contained in a vacuum cryostat, which was evacuated to 0.1 Pa using rough and adsorption pumps.

RESULTS AND DISCUSSION

Figure 1 displays the room-temperature luminescence spectra of $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ solid solutions

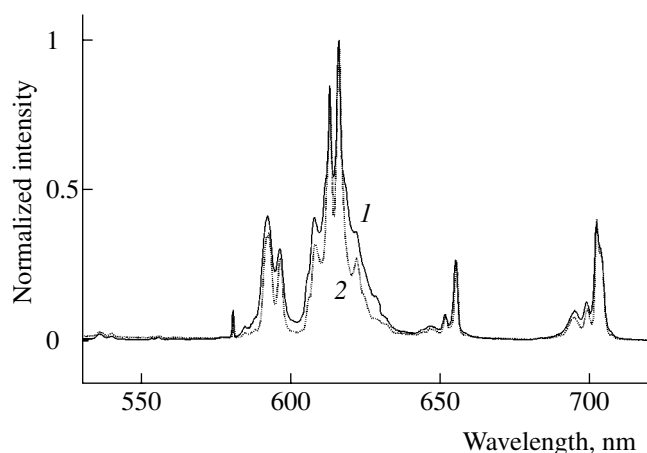


Fig. 2. Luminescence spectra of $\text{LiY}_{0.5}\text{Eu}_{0.5}(\text{MoO}_4)_2$ at (1) ≈ 300 and (2) 80 K; $\lambda_{\text{ex}} = 337.1$ nm.

($\lambda_{\text{ex}} = 337.1$ nm). The observed emission bands are due to Eu^{3+} [2], which exhibits bright red luminescence. All of the spectra show five emission bands characteristic of transitions from the excited, metastable state $\text{Eu}^{3+} {}^5D_0$ to 7F_J ($J = 0-4$) levels: 579–581 (${}^5D_0 \rightarrow {}^7F_0$), 588–600 (${}^5D_0 \rightarrow {}^7F_1$), 610–630 (${}^5D_0 \rightarrow {}^7F_2$), 640–662 (${}^5D_0 \rightarrow {}^7F_3$), and 681–710 nm (${}^5D_0 \rightarrow {}^7F_4$). These bands have a well-defined fine structure. The electric-dipole transition ${}^5D_0 \rightarrow {}^7F_2$ has the highest intensity, with a maximum at 616 nm. The ${}^5D_0 \rightarrow {}^7F_0$ transition, highly forbidden by selection rules, has a low intensity. In addition, the spectra contain weak emission bands in the range 535–560 nm, attributable to the $\text{Eu}^{3+} {}^5D_1 \rightarrow {}^7F_0$ (535–540 nm) and ${}^5D_1 \rightarrow {}^7F_1$ (555–559 nm) transitions [4].

As seen in Fig. 1, the position, number, and relative intensities of the Stark components in the Eu^{3+} luminescence bands vary insignificantly with Eu content, which implies that Eu^{3+} substitution for Y^{3+} in $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ ($0.0005 \leq x \leq 1$) has little effect on the site symmetry of the emission centers involved, in line with the conclusion drawn from XRD data that all of the solid solutions have an undistorted scheelite structure.

The luminescence spectrum of the solid solution offering the highest emission intensity, $\text{LiY}_{0.5}\text{Eu}_{0.5}(\text{MoO}_4)_2$, was also measured at liquid-nitrogen temperature (Fig. 2) (the actual sample temperature in the cryostat was about 80 K). Cooling the sample from room temperature to about 80 K improves the spectral resolution only slightly: the full width at half maximum of the bands decreases and the bands shift to longer wavelengths by about 0.2 nm. The number of observed lines remains unchanged, and their relative intensities differ little from those at room temperature. These findings indicate that cooling from 300 to 80 K has no effect on the symmetry of the emission centers in the solid solution in question. Raising the temperature from 80 to 300 K leads to only a slight reduction in emission intensity. Thus, in the temperature range under consideration the thermal quenching of luminescence in this material is insignificant.

The $\text{Eu}^{3+} {}^5D_0 \rightarrow {}^7F_0$ transition is of great interest in studying the structure of luminescent materials. Since the crystal field does not split the 5D_0 and 7F_0 levels, the luminescence spectrum must show only one line related to this transition. Some crystals may, however, exhibit more than one line in the region of the ${}^5D_0 \rightarrow {}^7F_0$ transition. Several lines in this region typ-

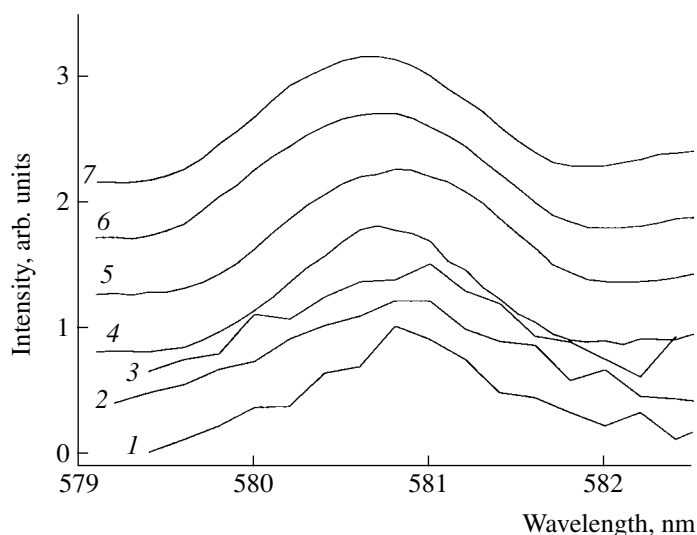


Fig. 3. Room-temperature luminescence spectra of $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ in the region of the ${}^5D_0 \rightarrow {}^7F_0$ transition: $x =$ (1) 0.0005, (2) 0.001, (3) 0.01, (4) 0.05, (5) 0.1, (6) 0.5, (7) 1; $\lambda_{\text{ex}} = 337.1$ nm.

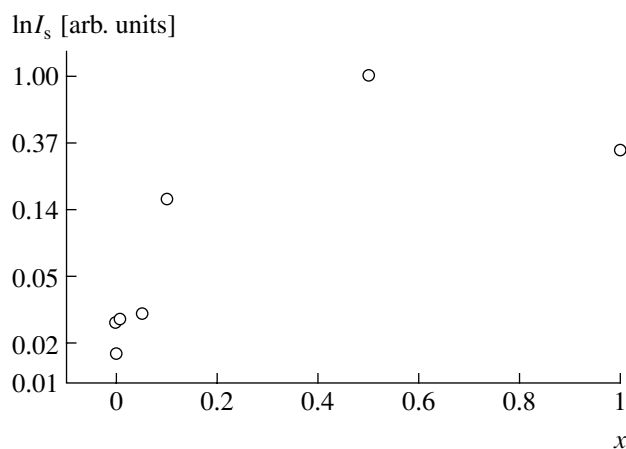


Fig. 4. Integrated luminescence intensity as a function of Eu^{3+} content for $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ solid solutions.

ically appear if Eu^{3+} occupies several inequivalent sites in the host structure [2].

The spectra of all the $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ solid solutions studied here show only one line in the region of the ${}^5D_0 \rightarrow {}^7F_0$ transition (Fig. 3), indicating that Eu^{3+} occupies only one site. In addition, it can be seen in Fig. 3 that increasing the Eu^{3+} content of $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ slightly shifts the ${}^5D_0 \rightarrow {}^7F_0$ transition to shorter wavelengths, by about 0.3 nm. It is well known [9] that the energy of the ${}^5D_0 \rightarrow {}^7F_0$ transition typically decreases with decreasing Eu–O bond length. Since the ionic radius of yttrium ($r_{\text{VIII}} = 1.019 \text{ \AA}$) is smaller than that of europium ($r_{\text{VIII}} = 1.066 \text{ \AA}$) [10], the R–O bond distance in the solid solutions under consideration increases with europium content, which correlates with the slight shift of the ${}^5D_0 \rightarrow {}^7F_0$ transition to shorter wavelengths with increasing Eu concentration in $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$.

In the spectra of the $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ solid solutions, the integrated intensity I_s in the region of Eu luminescence (total area under the spectral curve in the range 530–710 nm) rises rapidly as x increases from 0.0005 to 0.001 (Fig. 4). At slightly higher Eu concentrations, the integrated intensity rises more gradually, which is due to the concentration quenching of Eu^{3+} luminescence. In the range $0.05 < x < 0.1$, however, I_s rises sharply again. It seems likely that, at these relatively high Eu^{3+} concentrations, a europium sublattice begins to form, influencing the variation of the luminescence yield with Eu^{3+} concentration. Increasing x to above 0.5 reduces the integrated luminescence intensity. Note that, with increasing europium concentration, the emission lines broaden (Fig. 1). For $x \geq 0.05$, the linewidths increase systematically with Eu^{3+} concentration. Contributions to the broadening come from both

homogeneous and inhomogeneous components. The inhomogeneous broadening may be due to random cation site occupancy in the scheelite structure.

CONCLUSIONS

We studied the luminescent properties of $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ ($x = 0.0005, 0.001, 0.01, 0.05, 0.1, 0.5, 1$) scheelite solid solutions. The luminescence is shown to be due to Eu^{3+} optical transitions. The brightest emission is due to the ${}^5D_0 \rightarrow {}^7F_2$ electric-dipole transition.

Eu^{3+} substitution for Y^{3+} in the solid solutions has little effect on the symmetry of the emission centers involved.

The spectra of all the $\text{LiY}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ solid solutions show only one, narrow line in the region of the ${}^5D_0 \rightarrow {}^7F_0$ transition, indicating that Eu^{3+} occupies only one site in the host structure. With increasing Eu^{3+} concentration, the emission lines broaden and slightly shift, predominantly to shorter wavelengths.

The luminescence spectrum of $\text{LiY}_{0.5}\text{Eu}_{0.5}(\text{MoO}_4)_2$ was measured at 300 and 80 K. The number of observed lines remains unchanged on cooling, and their relative intensities differ little from those at room temperature.

The present results suggest that the molybdate solid solutions studied here have good color rendering properties and that $\text{LiY}(\text{MoO}_4)_2$ is stable to changes in cation composition, which makes it a convenient host for various activators, potentially attractive for producing efficient phosphors.

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