

A Novel Sm³⁺ Activated Orange Emitting Molybdate

F. Baur^{a,*}, A. Katelnikovas^b, R. Petry^c, R. Pöttgen^d, and T. Jüstel^{a,e}

^aDepartment of Chemical Engineering, Münster University of Applied Sciences, Stegerwaldstr. 39, 48565 Steinfurt, Germany

^bDepartment of General and Inorganic Chemistry, Vilnius University, Naugarduko 24, Vilnius, 03225, Lithuania

^cMerck KGaA, Frankfurter Str. 250, 64291 Darmstadt, Germany

^dInstitute of Inorganic and Analytical Chemistry, University Münster, Corrensstr. 30, 48149 Münster, Germany

*Corresponding authors: florian.baur@fh-muenster.de, tj@fh-muenster.de

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Introduction

This work deals with a novel Sm³⁺ doped molybdate, Li₃Ba₂La₃(MoO₄)₈:Sm³⁺, prepared by solid state synthesis, and the characterization of its optical properties. Luminescent materials emitting in the orange to red spectral range are essential for light sources emitting warm-white light. The Sm³⁺ emission spectrum (Fig. 4b) is a suitable for this purpose. Furthermore, Sm³⁺ exhibits broad absorption in the blue spectral range caused by transitions from the ⁶H_{5/2} ground-state to several ⁴I_J multiplets (Fig. 3 and 4a). This allows for excitation by blue emitting LEDs.

Molybdates have been investigated since the 1960's as suitable hosts for "4f-4f" activators such as Sm³⁺. The heavy Mo-atom increases the probability of parity-forbidden transitions resulting in comparatively strong absorption and excitability of the material. The XRD patterns in Fig. 1 indicate the existence of a complete solid solution series. We synthesized the monoclinic α-phase of Li₃Ba₂La₃(MoO₄)₈ where two crystallographic sites are available for Sm³⁺ doping as depicted in Fig. 2.

Crystal Structure and XRD

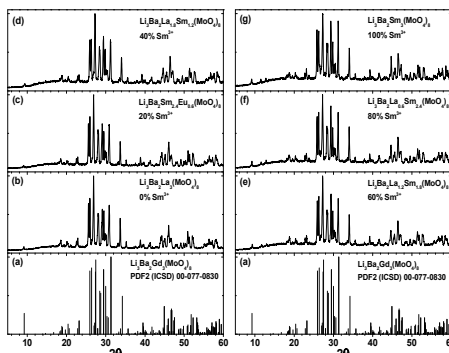


Fig. 1. XRD diagrams of (b-g) Li₃Ba₂La₃Sm_x(MoO₄)₈ and (a) the Li₃Ba₂Gd₃(MoO₄)₈ reference material.

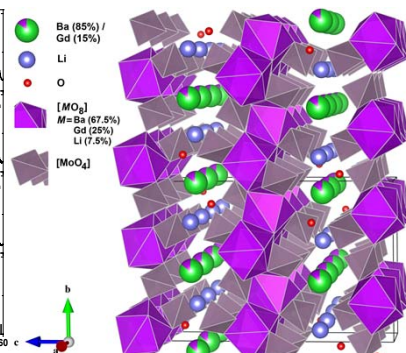


Fig. 2. Crystal structure of monoclinic Li₃Ba₂Gd₃(MoO₄)₈ [1,2].

Results and Discussion

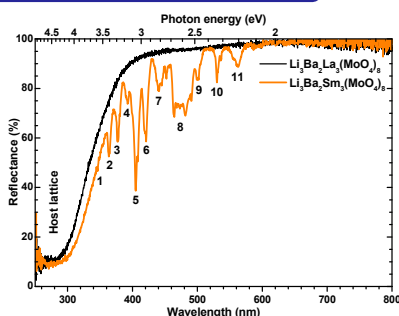


Fig. 3. Reflection spectra of Li₃Ba₂La₃(MoO₄)₈ and Li₃Ba₂Sm₃(MoO₄)₈ with the transitions marked by numbers.

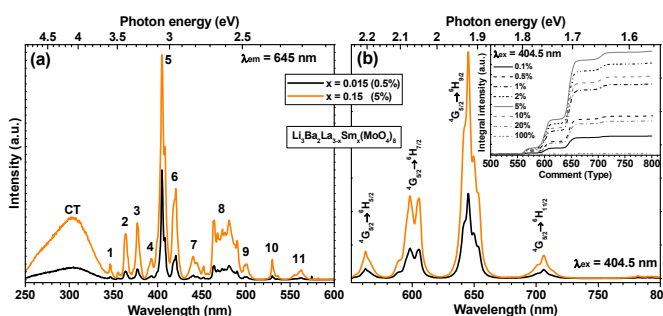


Fig. 4. (a) Excitation and (b) emission spectra of Li₃Ba₂La₃(MoO₄)₈:Sm³⁺ with 0.5% and 5% Sm³⁺ concentration. The inset depicts the integrated emission intensity.

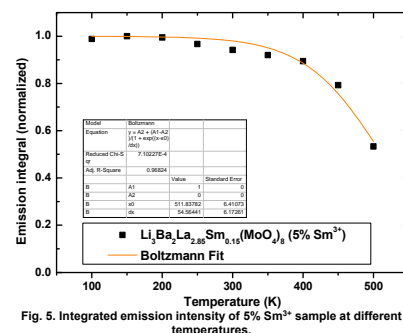


Fig. 5. Integrated emission intensity of 5% Sm³⁺ sample at different temperatures.

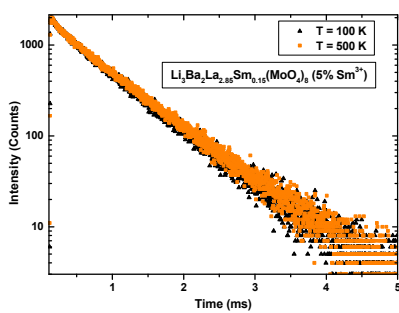


Fig. 6. Decay 5% Sm³⁺ sample at 100 K and 500 K.

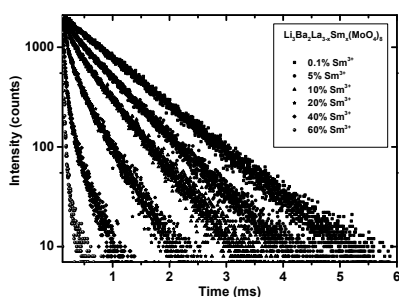


Fig. 7. Decay of Li₃Ba₂La₃Sm_x(MoO₄)₈ with different Sm³⁺ concentrations.

Fig. 3 shows the reflection spectra of the undoped material (black line) and the 100% Sm³⁺ sample (orange line). The broad absorption in the UV-range is the host absorption caused by charge transfer from oxygen ligands to the Mo⁶⁺ central atoms. Additional absorption lines are clearly visible in the Sm³⁺ sample which originate from 4f-4f transitions. Table 1 translates the assigned numbers to the respective transitions. The same transitions show up in the excitation spectrum in Fig. 4 (a). The width of the lines correlates with the number of transitions involved (see Table 1). Additionally, each multiplet can split into up to J+1/2 Stark sublevels, resulting in further broadening.

Emission can be observed in the range of 550-720 nm (Fig. 4 (b)). The emission intensity depends on the Sm³⁺ concentration and was highest for the 5% sample (Fig. 4 (inset)). This concentration quenching is attributed to cross-relaxation between the Sm³⁺ ions. From temperature dependent emission measurements a TQ_{1/2} of 511 K ± 6 K (Fig. 5) was calculated. However, the decay time remained constant (Fig. 6) up to 500 K. The decay time is proportional to the internal quantum efficiency (QE). Therefore, the internal QE remains constant while the external QE strongly decreases at temperatures higher than 400 K. This indicates that the host material is responsible for the TQ_{1/2}, oxygen defects caused by partial reduction of Mo⁶⁺ being a likely explanation.

The decay of the samples strongly depends on the Sm³⁺ concentration (Fig. 7). At very low concentrations (e.g. 0.1%) a mono-exponential decay can be observed. With increasing concentration the decay curve becomes multi-exponential. This can be caused by Sm³⁺ ions occupying more than one crystallographic site and energy transfer occurring between the sites. With increasing concentration, occupation of different sites and cross-relaxation becomes more probable. Additionally, the decay time decreases as non-radiative relaxation processes are in the nanosecond range while Sm³⁺ radiative relaxation is in the ms range.

Table 1. The optical transitions of Sm³⁺ and the numbers used to indicate them in the spectra.

Transition	⁶ H _{5/2} →
1	⁴ D _{7/2} + ⁴ D _{9/2}
2	⁴ D _{3/2} + ⁴ P _{3/2}
3	⁴ D _{1/2} + ⁴ L _{17/2} + ⁶ P _{17/2}
4	⁴ H _{11/2} + ⁶ M _{15/2} + ⁴ M _{21/2}
5	⁴ L _{13/2} + ⁶ P _{3/2} + ⁴ F _{7/2}
6	⁴ M _{19/2} + ⁶ P _{5/2}
7	⁴ I _{15/2} + ⁴ G _{9/2} + ⁴ M _{17/2}
8	⁴ I _{13/2} + ⁴ I _{11/2} + ⁴ I _{9/2} + ⁴ M _{15/2}
9	⁴ G _{7/2}
10	⁴ F _{3/2}
11	⁴ G _{5/2}

Table 2. Decay times of Sm³⁺ at different activator concentrations.

Sm ³⁺	Decay times (μs)		
0.1%	928 (100%)		
5%	132 (4%)	720 (96%)	
10%	106 (8%)	588 (92%)	
20%	46.8 (9%)	158 (20%)	437 (71%)
40%	8.63 (8%)	47.6 (36%)	247 (56%)
60%	1.85 (16%)	16.0 (46%)	75.7 (38%)