Photoluminescence of Eu³⁺ Doped Rare Earth Molybdates

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Introduction

Light sources based on phosphor converted light emitting diodes (pcLEDs) are going to replace conventional light sources, viz. incandescent and gas discharge lamps within the next decade. The most widely applied phosphor in white pcLEDs is cerium doped yttrium aluminum garnet (YAG:Ce). It possesses high quantum efficiency (>90%), good chemical and photochemical stability, and has a broad emission spectrum peaking at 560 nm. Moreover, the spectral width and position of its absorption band is very suitable to overcome the binning problem of blue-emitting LEDs. However, a combination of yellow phosphor and a blue emitting LED yields an insufficient color rendering index (CRI), i.e. some colors, in particular the red ones, are poorly reproduced under illumination by such a pcLED light source. Another drawback of such combination is the rather high color temperature (CCT > 4500 K) due to the deficiency in the red spectral range. Therefore, the quest of red emitting phosphors that can be pumped by near-UV or blue emitting LEDs gains a lot of attention.

Crystal Structure

Fig. 1. Crystal structure of Li₃Ba₂Gd₃(MoO₄)₈.

Results

Li₃Ba₂La₃(MoO₄)₈ and Li₃Ba₂Eu₃(MoO₄)₈ are going to replace conventional light sources, viz. incandescent and gas discharge lamps within the next decade. The most widely applied phosphor in white pcLEDs is cerium doped yttrium aluminum garnet (YAG:Ce). It possesses high quantum efficiency (>90%), good chemical and photochemical stability, and has a broad emission spectrum peaking at 560 nm. Moreover, the spectral width and position of its absorption band is very suitable to overcome the binning problem of blue-emitting LEDs. However, a combination of yellow phosphor and a blue emitting LED yields an insufficient color rendering index (CRI), i.e. some colors, in particular the red ones, are poorly reproduced under illumination by such a pcLED light source. Another drawback of such combination is the rather high color temperature (CCT > 4500 K) due to the deficiency in the red spectral range. Therefore, the quest of red emitting phosphors that can be pumped by near-UV or blue emitting LEDs gains a lot of attention.

Fig. 2. Reflection spectra of Li₃Ba₂La₃(MoO₄)₈ and Li₃Ba₂Eu₃(MoO₄)₈.

Fig. 3. Excitation spectra of Li₃Ba₂La₃(MoO₄)₈ doped with 10 and 100% of Eu³⁺.

Fig. 4. Emission spectra of Li₃Ba₂La₃(MoO₄)₈ doped with 10 and 100% of Eu³⁺.

Fig. 5. Thermal quenching of Li₃Ba₂Eu₃(MoO₄)₈.

Fig. 6. Quantum efficiencies of Li₃Ba₂La₃-xEux(MoO₄)₈ phosphors (λₑₓ = 465 nm).

Fig. 7. CIE 1931 chromaticity diagram with color points of Li₃Ba₂La₃-xEux(MoO₄)₈ phosphors.

Conclusions

- Single phase target materials can be prepared by annealing the blend of respective oxides and/or carbonates at 800 °C for 10 h in air. Solid solution forms at any La/Eu ratio.
- Optical band gap of Li₃Ba₂La₃(MoO₄)₈ and Li₃Ba₂La₃(MoO₄)₈ is about 340 nm (≈ 3.65 eV). The phosphors can be efficiently excited in the near-UV and blue spectral regions.
- The dominant emission lines (≈ 615 nm) originates from the ⁵D₀ → ⁷F₂ transition. The strongest emission intensity was achieved if samples were doped with about 90% of Eu³⁺.
- The emission intensity decreases at elevated temperatures.

Li₃Ba₂Eu₃(MoO₄)₈ loses only about 15% of efficiency at 400 K (127 °C) what makes the investigated phosphors attractive for application in pcLEDs.
- Quantum efficiency of the phosphors increases with increasing Eu³⁺ concentration. Almost 100% efficiency was obtained for the samples doped with 70, 80, and 90% of Eu³⁺. Sample containing 100% of Eu³⁺ showed a slight decrease in quantum efficiency.
- The colour points of the investigated phosphors are located in the red region of CIE 1931 chromaticity diagram. The increase of Eu³⁺ concentration has led to a slight shift of colour points to the red. The luminous efficacies were 330 and 312 lm/W for 10 and 100% Eu³⁺ doped samples, respectively.