



Narrow spectral emission CaMoO_4 : Eu^{3+} , Dy^{3+} , Tb^{3+} phosphor crystals for white light emitting diodes

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ABSTRACT

Alkaline earth metal molybdates are promising candidates as a host material for high efficiency narrow spectral emission phosphors. These phosphors could potentially be used for the fabrication of phosphor-converted light emitting diodes (pc-LEDs). Phosphor crystals of calcium molybdate doped with rare earth dopant Ln^{3+} ($\text{Ln}=\text{Eu}$, Dy , Tb) grown using flux growth method have been shown to exhibit higher excitation efficiency than the powders synthesized by solid-state reaction process. Molybdenum (VI) oxide has been found to be a suitable flux for growing large size optically transparent high quality crystals at a temperature around 1100 °C. Using the excitation wavelengths of 465 nm, 454 nm and 489 nm for CaMoO_4 : Eu^{3+} , CaMoO_4 : Dy^{3+} and CaMoO_4 : Tb^{3+} , respectively, intense emission lines at wavelengths of 615 nm, 575 nm and 550 nm were observed. The optimized doping concentrations of 12%, 2% and 5% for Eu^{3+} , Dy^{3+} and Tb^{3+} , respectively, provided the highest luminescence intensity.

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1. Introduction

Alkaline earth metal molybdates have been used as luminescent materials for various applications such as laser hosts, X-ray detection, etc. This class of compounds is self-activated due to the luminescence from MoO_4 tetrahedral groups in the scheelite host lattice [1]. Also, these serve as excellent host materials for trivalent lanthanide ions, which produce narrow spectral emission lines due to f–f transitions. Narrow line-width emission is particularly important for general lighting applications because it results in high luminous efficacy by preventing light spill over in the wavelengths outside of the human eye sensitivity curve. For example, in order to produce white light with maximum possible luminous efficacy of 400 lm/W at a CRI of 85 and CCT of 3800 K, four narrow-emitting sources at 459 nm, 535 nm, 573 nm and 614 nm, respectively, are needed with the relative power of the sources being 0.18, 0.25, 0.22, 0.36, respectively [2]. For use in solid-state lighting, the phosphors must be excited in the wavelength range of 390–470 nm using near-UV and blue light emitting diodes (LEDs). Molybdate hosts in their powder form have been extensively investigated for narrow line-width emission [3–7]. However, due to large bandgap of these hosts, the phosphor

absorption of the excitation source (395 nm or 465 nm LED) is limited to the narrow f–f transitions of the lanthanide ion. The emission intensity of these phosphors can be improved by using synthetic routes such as sol–gel process [8–11]. In this work, flux crystal growth process has been demonstrated as a way to enhance phosphor excitation efficiency in the near-UV and blue wavelength range leading to improvement of the photo-luminescent intensity of the material. The flux growth process also enabled the growth of optically clear (non-scattering) single crystals of phosphors for improving light extraction efficiency of phosphor-based white LEDs (pc-WLEDs). The effect of flux growth process on phosphor morphology and photo-luminescent excitation and emission properties has been presented in this paper.

2. Experimental details

2.1. Flux crystal growth of phosphors

For the flux growth, the following reagents obtained from Alfa Aesar were used: CaO (99.95% purity), MoO_3 (99.8% purity), Eu_2O_3 (99.9% purity), $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9% purity), $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9% purity) and LiCl (99% purity). The initial reactants were weighed in appropriate stoichiometric ratio and ball milled for 30 min at 600 rpm using Retsch PM 100 Planetary Ball Mill. The homogenized powders were then transferred to alumina crucibles and heated to the reaction temperature inside a box or a tubular furnace in oxygen ambient to form a molten solution containing

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the precursors and the flux. Reaction temperatures in the range of 1000–1300 °C were evaluated. Growth temperatures below 1000 °C produced very small crystallites with extremely weak emission intensity and hence were not analyzed further. For a complete and uniform reaction, the solution temperature was maintained at the reaction temperature for 15–24 h. Then the furnace was cooled down slowly at a rate of 2–3 °C per hour (h) to 650 °C for crystal growth. In the absence of any single crystal seed of these compounds, all the crystal growth experiments were conducted using self-nucleation process. After the growth period, the furnace was rapidly cooled to room temperature at a rate of 350 °C/h. The flux was dissolved in hot water or in mild HCl–water mixture (pH~2) for extracting the crystals without damaging them.

For flux crystal growth, the solubility (or the level of supersaturation) of solute in the flux (solvent) dictates the ratio of solute to solvent and the growth temperature. A higher degree of solubility is desirable for large size crystals and high growth rates. In the experiments conducted, lithium chloride and molybdenum (VI) oxide were used as fluxes for CaMoO₄-based phosphors. For lithium chloride flux, the solubility versus temperature data presented in the literature [12,13] for pure CaMoO₄ was used as the starting point for the estimation of appropriate flux-to-solute ratio and growth temperature. Further optimization of the flux-to-solute ratio and growth temperature was necessary for accounting for the presence of Eu₂O₃ in our solution and crystal. In the absence of any prior literature data for molybdenum (VI) oxide flux, flux-to-solute ratio of 1:1 was used as a starting point. Based on a large number of experimental trials, we could obtain high quality large size crystals for an optimum flux-to-solute ratio and growth temperature, as discussed later in this paper. The crystal growth rate and temperature range for cooling the solution are crucial for avoiding inclusions in the crystals that could lead to undesirable light scattering and absorption in the crystals.

2.2. Solid state synthesis of phosphor powders

The precursor materials used in these experiments were also obtained from Alfa Aesar. The following reactants in powder form were used: CaO (99.95% purity), MoO₃ (99.8% purity), Eu₂O₃ (99.9% purity), DyCl₃·6H₂O (99.9% purity) and TbCl₃·6H₂O (99.9% purity). The powders were weighed in appropriate stoichiometric ratio and ball milled for 30 minutes at 600 rpm. After proper mixing, the powders were transferred to quartz crucibles and heated in the range of 1000–1300 °C in a tubular or box furnace in oxygen ambient. Powders synthesized below 1000 °C resulted in extremely weak emission intensity and hence were not analyzed further. For a complete and uniform reaction, the synthesis temperature was maintained for 15–24 h and then the furnace was cooled down to room temperature at a rate of 350 °C/h. The powders could be extracted out of the crucible in free flowing form. The use of quartz crucibles was found to be satisfactory for the solid-state reaction in contrast to the flux growth wherein the quartz reacted severely with the flux. However, for synthesis temperature beyond 1200 °C, the quartz crucibles degraded and could not be used beyond two or three experiments.

2.3. Characterization

Powder x-ray diffraction (XRD) patterns were recorded on Bruker D8 Discover Diffractometer running on Cu K α radiation at 40 kV and 40 mA. These data were used to determine the crystal structure of the synthesized phosphors and to calculate their lattice constants. Excitation and emission spectrum measurements were done using Flourollog Tau-3 lifetime measurement system. For all these measurements, fine powders of the phosphor

samples were used. The crystals were mechanically grinded using a mortar and pestle to form the powder.

3. Results and discussion

3.1. Excitation spectra of CaMoO₄: Ln³⁺ (Ln=Eu, Dy, Tb) phosphors

Fig. 1(a–c) shows the excitation spectra of CaMoO₄: Eu³⁺, CaMoO₄: Dy³⁺, CaMoO₄: Tb³⁺ phosphors monitored at 615 nm, 575 nm and 550 nm emission wavelengths, respectively. The excitation spectrum of the phosphors comprises a broad band (the Charge Transfer Band, CTB) from 270 to 320 nm and narrow excitation peaks from 320 nm to 550 nm. The broad excitation band (CTB) originates from the charge transfer excitation of MoO₄²⁻ groups and the narrow excitation peaks originate from Ln³⁺ f–f transitions [3,6,7,14].

3.2. Emission spectra of CaMoO₄: Ln³⁺ (Ln=Eu, Dy, Tb) phosphors

Fig. 2(a–c) shows the dominant peaks in the emission spectra of CaMoO₄: Ln³⁺ (Ln=Eu, Dy, Tb) phosphors at specific excitation wavelengths, as indicated next to the curves in the figure. These narrow excitation wavelengths shown in Fig. 1 were chosen from the blue region.

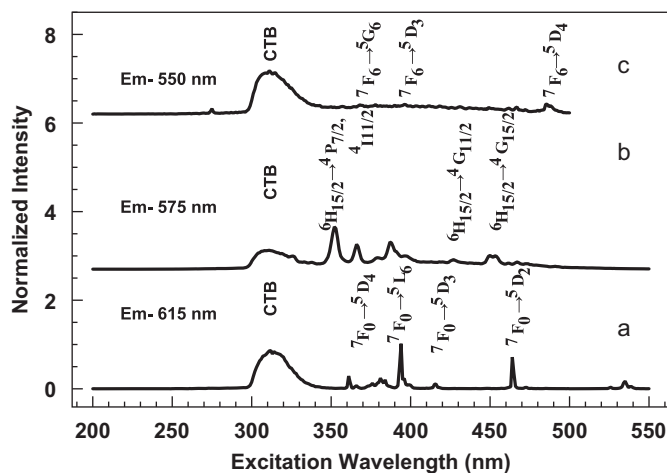


Fig. 1. Excitation spectra of (a) CaMoO₄: Eu³⁺, (b) CaMoO₄: Dy³⁺ and (c) CaMoO₄: Tb³⁺ for emission wavelengths of 615 nm, 575 nm and 550 nm, respectively.

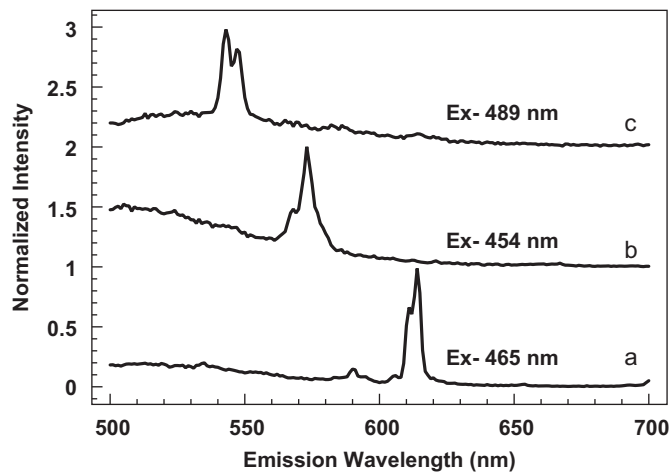


Fig. 2. Emission spectra of (a) CaMoO₄: Eu³⁺, (b) CaMoO₄: Dy³⁺ and (c) CaMoO₄: Tb³⁺ at excitation wavelengths of 465 nm, 454 nm and 489 nm respectively.

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