Structural and Luminescent Properties of $Y_2Mo_4O_{15}$:Eu$^{3+}$
Red Phosphor Calcined at Different Temperatures

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The red phosphor $Y_2Mo_4O_{15}$:Eu$^{3+}$ calcined at different temperatures is obtained by a solid-state method, and is investigated in this article. Usage of solid-state method with the combination of five different calcination temperatures (500, 550, 600, 650, and 700 °C) leads to the formation of pure monoclinic phase in all samples apart from the one calcined at the lowest temperature. Crystallite size obtained by Rietveld refinement is in the range of 38–55 nm. Scanning electron microscopy analysis confirms the presence of agglomerates. Luminescence emission spectra and emission decay curves are measured for all pure samples, and parameters derived from these measurements are used for Judd–Ofelt analysis. International commission on illumination (CIE) chromaticity diagram confirms the presence of pure red emission and high quantum efficiency.

1. Introduction

Nowadays, modern phosphor industry is rapidly expanding. Among all the phosphors, the red emitting phosphors show a significant role in the solid-state lighting, especially in white LEDs. Commercialized white LEDs are normally based on InGaN blue chips with yellow-emitting $Y_3Al_5O_{12}$:Ce$^{3+}$ phosphors.[1] White light obtained from blue chip and the yellow-emitting phosphor is cold, with lack of red compound, so it is necessary to complement the warm white light with the addition of the red emission component. Eu$^{3+}$ ions are the most commonly used red phosphor activator due to the strong absorption in the near-visible ultraviolet (NUV) light region.[2] Europium possesses low absorption strength due to the spin- and parity-forbidden nature of their intraconfigurational $[\text{Xe}]4f^6 \rightarrow [\text{Xe}]4f^6$ transitions, but in some lattices (molybdates, tungstates, niobates, and vanadates) these transitions, especially at shorter wavelengths (<400 nm), become rather strong due to admixing with low-lying charge-transfer (CT) band.[3] Rare-earth (RE) molybdates are a wide family of inorganic lattices with potential application as luminescent host lattices, such as REMo$_4$O$_9$, RE$_2$(MoO$_4$)$_3$, RE$_2$Mo$_4$O$_9$, NaSrRE(MoO$_4$)$_3$, Re$_2$MoO$_9$, and Re$_2$MoO$_6$.[4–10] Molybdates with formula $Y_2Mo_4O_{15}$, with dual MoO$_4$ and Mo$_2$O$_7$ groups, are proven to exhibit interesting photoluminescence properties.[11] These materials showed good color saturation, high luminous efficacies, and high external quantum yields and optical thermometric behaviors.[3,12] Generally, luminescent properties of inorganic phosphors are dependent on calcination process. Temperature is highly involved in the crystallization process and in the formation of crystal field around Eu$^{3+}$ ions.

In this work, for the first time, the structural and luminescent properties of $Y_2Mo_4O_{15}$:1 at% Eu$^{3+}$ powders were investigated as a function of calcination temperature. $Y_2Mo_4O_{15}$:1 at% Eu$^{3+}$ powders were synthesized by a conventional solid-state reaction.[13,14] X-ray diffraction (XRD) and scanning electron microscopy (SEM) are used to characterize the phase structure as well as the particle size and morphology of products. Emission spectra and decay curves are used for the application of Judd–Ofelt (JO) theory and intensity of emission parameters, radiative and nonradiative emission probabilities, quantum efficiencies, and asymmetry ratios of Eu$^{3+}$ emission are derived.

2. Results and Discussion

2.1. Structure and Morphology

Crystal structure of $Y_2Mo_4O_{15}$ belongs to a monoclinic structure and could be written as $Y_2[MoO_4]_2[MoO_2]$, where there are two different molybdate groups, ortho-anionic [MoO$_4$]$^{2-}$ and pyroanionic oxodimolybdate(VI) units [Mo$_2$O$_7$]$^{5-}$.[15,16] The Y atom is surrounded by seven oxygen atoms to form a YO$_7$ polyhedron with ten faces and the Y–O distances range from 0.224 to 0.243 nm. The Mo(1) coordination polyhedron and the Mo(2) coordination polyhedron are almost regular tetrahedron formed with four oxygen atoms.[17] $Y_2Mo_4O_{15}$:1 at% Eu$^{3+}$ powders calcined at different temperatures (500, 550, 600, 650, and 700 °C) showed pure monoclinic...
phase, with the exception of the powder calcined at 500 °C. (Figure 1). After calcination at 500 °C, there is the formation of monoclinic phase, but this temperature is insufficient for the formation of pure phase; there are still impurities present, such as Y₂O₃ and MoO₃. The crystal lattice of Y₂Mo₄O₁₅ is shown in Figure 1b. Structural parameters (average crystal size, unit cell parameters, and strain) of the calcined samples were estimated by structural Rietveld refinement based on the Y₂Mo₄O₁₅ structural data (COD 7054112) and the calculated values are shown in Table 1.

Calcination temperature had a large impact on the crystal growth and the strain of crystal lattice. With higher calcination temperature, crystallites of Y₂Mo₄O₁₅ gradually increase their size up to calcination temperature of 650 °C, and then slightly decrease. The strain of crystal lattice unbalanced this trend: the strain first increases with calcination temperature 500–600 °C, then it decreases to the smallest strain at 650 °C, and at the end there is a slight increase in strain at calcination temperature of 700 °C.

Figure 2 represents SEM images of Y₂Mo₄O₁₅:Eu³⁺ powders calcined at different temperatures. The main conclusion is that particles are in the range of 80–1500 nm and represent between 2–3 and 30 agglomerates of single crystallite. With higher calcination temperature, particles become more spherical, and the most spherical particles are obtained at a calcination temperature of 650 °C. Calcination higher than 650 °C led to the small cracking formation.

2.2. Photoluminescence Studies

The excitation spectra of Y₂Mo₄O₁₅:1 at% Eu³⁺ powder calcined at 650 °C are shown in Figure 3. Excitation spectra are recorded in the spectral range of 350–575 nm, with λ_em = 614 nm, and present characteristic Eu³⁺ absorption bands centered at 362 nm (²F₀→²D₄), 383 nm (²F₀→²G₂), 395 nm (²F₀→²L₆), 417 nm (²F₁→²L₆), 466 nm (²F₀→²D₂), and 534 nm (²F₁→²D₁).

Photoluminescence spectra of pure Y₂Mo₄O₁₅: 1 at% Eu³⁺ powders calcined at different temperatures (550, 600, 650 and 700 °C) are shown in Figure 4. All spectra are normalized to the intensities of the ³D₀→²F₁ magnetic dipole electronic transition as required by the JO theory (which assumes that magnetic dipole transitions in lanthanide ions are practically independent of the ion’s surroundings and can be well calculated by theory).¹⁸

Table 1. Structural parameters of Y₂Mo₄O₁₅:Eu³⁺ powders calcined at different temperatures (500, 550, 600, 650, and 700 °C) obtained by Rietveld refinement of XRD data.

| 500 °C | 550 °C | 600 °C | 650 °C | 700 °C |
|--------|--------|--------|--------|--------|
| Crystallite size [Å] | 378 (6) | 427 (6) | 414 (6) | 552 (7) | 518 (7) |
| Strain [%] | 0.11 (4) | 0.12 (2) | 0.13 (2) | 0.06 (3) | 0.101 (19) |
| Rwp [%] | 23.4 | 6.25 | 5.57 | 5.87 | 5.78 |
| Rp [%] | 14.54 | 4.79 | 4.20 | 4.08 | 4.40 |
| Rs [%] | 2.90 | 2.93 | 2.84 | 2.91 | 2.91 |
| GOF | 8.0685 | 2.1336 | 1.9641 | 2.0178 | 1.9862 |
| a | 6.822 (3) | 6.8197 (2) | 6.8204 (3) | 6.8178 (3) | 6.81677 (18) |
| b | 9.574 (4) | 9.5837 (3) | 9.5830 (4) | 9.577 1 (3) | 9.5806 (3) |
| c | 10.517 (4) | 10.5235 | 10.5236 (4) | 10.5184 (5) | 10.5200 (3) |

¹⁰Rwp = regression sum of weighted squared errors of fit, ⁰Rp = profile factor, ¹⁰Rs = regression sum of relative errors of fit, ²⁰GOF = goodness-of-fit (GOF = Rwp/Rs).
The peaks are centered at around 590 nm ($^{5}D_{0} \rightarrow ^{7}F_{1}$), 613 nm ($^{5}D_{0} \rightarrow ^{7}F_{2}$), 657 nm ($^{5}D_{0} \rightarrow ^{7}F_{3}$), and 704 nm ($^{5}D_{0} \rightarrow ^{7}F_{4}$). The emission peaked at 613 nm derived from the electric dipole transition is the strongest, implying that $\text{Eu}^{3+}$ ions occupy low-symmetry sites in $\text{Y}_{2}\text{Mo}_{4}\text{O}_{15} : \text{Eu}^{3+}$ phosphor. Due to the similar ionic radii of $\text{Eu}^{3+}$ with $\text{Y}^{3+}$, the incorporation of $\text{Eu}^{3+}$ will be promoted to $\text{Y}^{3+}$ site, which presents one symmetry site as confirmed by the presence of only one peak at ($^{5}D_{0} \rightarrow ^{7}F_{0}$), as shown in the inset of Figure 4.

Lifetime values for all calcined samples are shown in Figure 5. For each sample, a series of spectra were acquired as a function of time delay in respect to the stop of the excitation pulse. The lifetime $\tau$ was then calculated by fitting the time-dependent intensity logarithm to a simple linear model connected to the single exponential one, as given in Equation (1).

$$I(t) = I_0 e^{-t/\tau}; \quad \ln(I(t)) - \ln(I_0) = \frac{t}{\tau}$$  \hspace{1cm} (1)

For all calcined samples, the measured lifetime values are in less than 2% range, showing there is no significant influence of calcination temperature on this parameter.

2.3. JO Analysis of $\text{Y}_{2}\text{Mo}_{4}\text{O}_{15} : \text{Eu}^{3+}$

To obtain more insight into the photoluminescence properties and the relevant annealing temperature-induced changes, the JO parameters and derived quantities have been evaluated by the JOES application software\cite{19} using the emission spectra of $\text{Y}_{2}\text{Mo}_{4}\text{O}_{15} : \text{Eu}^{3+}$ (Table 2). For the calculations, the true correct refractive index values are needed. Due to the considerably smaller particle size than the wavelength of emission light, the refractive index value of the bulk material, 2.85,\cite{20} must be corrected for the volume of air filling the gaps between crystallites. The effective refractive index is given by\cite{21}

$$n_{\text{eff}} = x(n_{\text{bulk}} - 1) + 1$$ \hspace{1cm} (2)

where $x$ is the optical filling factor, a fraction of space occupied by nanoparticles, which can be calculated by dividing the nanocomposite and the bulk material densities: $x = 2.1235 \text{g cm}^{-3}/
4.013 g cm$^{-3}$ = 53%. Thus, the effective refractive index value, approximately independent on the wavelength on the measured range, is equal to 1.98.

The radiative transition probabilities of induced electric dipole and magnetic dipole transition are, respectively, given by\textsuperscript{[22,23]}

\[
A_l = \frac{64\pi^2\tilde{\nu}_l^3 n(n^2 + 2)^2}{9\hbar^2} \tilde{\nu}_l^2 \Omega_l \lambda^2
\]

\[
A_{MD} = 9.6 \times 10^{-42} \text{esu}^4 \text{cm}^2 \times 64\pi^2\tilde{\nu}_{MD}^3 n^4/3\hbar, \quad \lambda = 2, 4, 6
\]

where $\hbar$ is the Planck constant and $\tilde{\nu}$ is the transition barycenter.
Table 2. Judd–Ofelt intensity parameters, radiative lifetimes, quantum efficiencies, and branching ratios of Y$_2$Mo$_4$O$_{15}$:Eu$^{3+}$ calcined at various temperatures.

| $T$ [°C] | $\Omega_2$ [cm$^2$] ($\times 10^{-20}$) | $\Omega_4$ [cm$^2$] ($\times 10^{-20}$) | $\tau_{\text{rad}}$ [ms] | $\eta$ | $\beta_1$ | $\beta_2$ | $\beta_3$ |
|----------|--------------------------------------|--------------------------------------|--------------------------|--------|----------|----------|----------|
| 550      | 13.02                                | 4.20                                 | 0.795                    | 0.94   | 0.089    | 0.787    | 0.124    |
| 600      | 11.84                                | 4.27                                 | 0.855                    | 0.90   | 0.096    | 0.796    | 0.135    |
| 650      | 12.18                                | 4.44                                 | 0.832                    | 0.94   | 0.093    | 0.770    | 0.137    |
| 700      | 12.08                                | 4.12                                 | 0.846                    | 0.90   | 0.095    | 0.777    | 0.129    |

3. Conclusion

To conclude, red phosphor Y$_2$Mo$_4$O$_{15}$:Eu$^{3+}$ is prepared by solid-state method and calcined at five different temperatures (500, 550, 600, 650, and 700 °C). Calcination temperature showed influence on structural, morphological, and optical properties. With higher calcination temperature, molybdate particles begin to be more spherical, and the most spherical particles are obtained at a calcination temperature of 650 °C; after 650 °C, small cracking formation is observed. Lifetime values are uniform, and they are in the range of 752–786 μs. JO analysis demonstrated that higher annealing temperature led to the increasing site symmetry of the Eu$^{3+}$ ions. It can be observed that both the emission intensity and quantum efficiency are highest for the sample annealed at 550 °C. Quantum efficiency (high values of 90–94%) and pure red colors are recommendations for consideration of Y$_2$Mo$_4$O$_{15}$:Eu$^{3+}$ annealed at various temperatures as red phosphor in white or RGB LEDs.

4. Experimental Section

The stoichiometric amounts of Y$_2$O$_3$ (99.99%; Tailorlux), Eu$_2$O$_3$ (99.99%; Tailorlux), and (NH$_4$)$_2$Mo$_4$O$_{24} \times 4$H$_2$O (99+%; Acros Organics) were thoroughly mixed in an agate mortar using some acetone as the grinding medium. The blends of starting materials were dried, transferred to the porcelain crucibles, and sintered at 500, 550, 600, 650, and 700 °C for 4 h in air.

XRD measurements were performed using a Rigaku SmartLab diffractometer with X-ray lamp working on 40 V/30 mA. Diffraction data were collected at 10°–90° 2θ range with a step of 0.01° and counting of 1 min$^{-1}$. The results of structural analysis (unit cell parameter, crystal coherence size, microstrain values, and data fit parameters) were obtained by PDXL Integrated X-ray powder diffraction software. After a deposition of a thin gold layer on the sample surface, a TESCAN MIRA 3 XMU field emission scanning electron microscope (FE-SEM), operated at 20 keV, was used to analyze the morphology of particles. As an excitation source for luminescence measurements and emissions, the VIASHO laser system consisting of a 532 nm diode-pumped solid-state laser with corresponding driver was used. On the detection side, the FHR1000 monochromator (Horiba Jobin Yvon) and iCCD camera (Horiba Jobin Yvon 3771) were utilized for spectra acquisition. All the measurements were done at room temperature.

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**Conflict of Interest**
The authors declare no conflict of interest.

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