Luminescence properties of Eu\(^{3+}\) doped CaMoO\(_4\) nanoparticles

Abdul Kareem Parchur, a Raghumani Singh Ningthoujam,*b Shyam Bahadur Rai, a Gunadhor Singh Okram, c Ram Asaray Singh, d Mohit Tyagi, a S. C. Gadkari, a Raghvendra Tewari f and Rajesh Kumar Vatsa b

Received 25th Feb 2011, Accepted 17th May 2011
DOI: 10.1039/c1dt10878f

When Eu\(^{3+}\) ions occupy Ca\(^{2+}\) sites of CaMoO\(_4\), which has a body centered tetragonal structure with inversion symmetry, only the magnetic dipole transition (\(5D_0 \rightarrow 7F_1\)) should be allowed according to Judd–Ofelt theory. Even if there are a few distortions in the Eu\(^{3+}\) environment, its intensity should be more than that of the electric dipole transition (\(5D_0 \rightarrow 7F_2\)). We report here the opposite effect experimentally and ascribe this to the polarizability effect of the MoO\(_4\) tetrahedron, which is neighboring to EuO\(_2\) (symmetric environment). The contribution of the energy transfer process from the Mo–O charge transfer band to Eu\(^{3+}\) and the role of Eu\(^{3+}\) over the surface of the particle could be distinguished when luminescence decay processes were measured at two different excitations (250 and 398 nm). Further, the luminescence intensities and lifetimes increase significantly with increasing heat-treatment temperature of the doped samples. This is attributed to the reduction of H\(_2\)O from the surface of the particles and a non-radiative process after heat treatment.

1. Introduction

Rare-earth ion doped calcium molybdate (CaMoO\(_4\)) has attracted much interest due to its wide luminescence applications. These include optical filters, solid state lasers, LED (light emitting diodes), scintillators, microwave dielectrics, cryogenic detectors and fluorescent lamps. Moreover, some of its attractive features include a high melting point (1445–1480 °C), refractive index (1.98), effective average decay time (14 μs), photo electron yield (9%) and it is also chemically resistant and non-hygrosopic. CaMoO\(_4\) shows a broad blue and/or green luminescence emission peak in the range 350–650 nm with a peak maximum around 500 nm. The peak maximum however varies with particle size and oxygen vacancies in the lattice. It is related to the electron-hole recombination after excitation through the band gap of the charge transfer (CT) from O to Mo (2p → 4d orbital) in the MoO\(_4\)\(^{2-}\) complex tetrahedron cluster itself. Liu et al. calculated the band gap of pure CaMoO\(_4\) crystal using a density functional theory calculation as 3.6 eV. Nearly consistently, Ryu et al. found it to be 3.41 eV using a linearized-augmented-plane-wave technique. The experimentally measured value was slightly higher.

In fact, when a rare-earth dopant like Eu\(^{3+}\) is doped in calcium molybdate, what is predicted to happen to the luminescence? In our study, the crystal structure of CaMoO\(_4\) has inversion symmetry. Eu\(^{3+}\) ions occupy Ca\(^{2+}\) sites and thus only magnetic dipole transition should be allowed because Eu\(^{3+}\) ions have inversion symmetry according to Judd–Ofelt theory. In many reported papers, it is suggested that Eu\(^{3+}\) ions have an asymmetric environment. This has been claimed because the electric dipole transition intensity is higher than the magnetic dipole transition of Eu\(^{3+}\) in the observed spectra. However, the relationship between crystal structure and luminescence behavior has not been reported. The unusual behaviour in this compound has not been discussed in earlier literature so far, to the best of the authors’ knowledge. This is explained based on the polarizability effect of the MoO\(_4\) tetrahedron, which is sharing with EuO\(_2\)/CaO\(_2\) through an O atom in this work. The effect of particle size on luminescence behavior and lifetime are also studied.

2. Experimental details

The nanoparticles of CaMoO\(_4\): Eu\(^{3+}\) (Eu\(^{3+}\) = 0, 1, 3, 5, 7, 10 at. %) were prepared at low temperature (150 °C for 3 h) using urea hydrolysis in ethylene glycol. Finally, the as-prepared sample was annealed at 500 and 900 °C for 4 h each. The photoluminescence (PL) spectra of these powder phosphors were recorded using Hitachi F-4500 spectrometer with a 150 W Xe lamp as a source at the spectral resolution of 3 nm. All the measurements were carried out at room temperature. PL decay was recorded with an Edinburgh instrument F920 equipped with 100 W μs flash xenon lamp as the excitation source.
3. Results and discussion

3.1 Luminescence study

Fig. 1 shows excitation and emission spectra of as-prepared, 500 and 900 °C heated samples of pure CaMoO4. The emission wavelength is monitored at 450 nm and excitation wavelength is fixed at 250 nm because Mo–O absorption occurs at 250–300 nm. In the excitation spectra, a rise in intensity starts below 300 nm. In the emission spectra, a broad peak at 360–600 nm is observed. The peak maximum changes from 405 to 420 nm as heat-treatment temperature (particle size) increases, consistent qualitatively with earlier reports. The increase in intensity is such that the 500 and 900 °C heated samples show a 2 and 10 fold increase, respectively, as compared to that of the as-prepared sample. It is due to reduction of the surface effect, unwanted H2O molecules and an organic moiety (EG) adsorbed on the surface of particles compared to the as-prepared sample.

![Fig. 1](image1.png)

Fig. 1 Excitation (monitoring emission at 450 nm), (b) emission (after excitation at 250 nm) spectra of as-prepared, 500 and 900 heated pure CaMoO4 samples.

Fig. 2 shows excitation spectra of as-prepared, 500 and 900 °C heated samples of 5 at. % Eu³⁺ doped CaMoO4 nanoparticles. The emission wavelength is monitored at 615 nm. In the excitation spectra, there is a broad peak at 220–300 nm and sharp peaks with low intensity at 320–500 nm. The broad peak arises from Eu–O and Mo–O charge transfers (CT). This can be clearly seen in the inset of Fig. 2 for the 900 °C heated sample and its data are fitted with a Gaussian distribution (discussed later). Two main peaks could be resolved. The calculated peaks at 247 and 272 are assigned to Eu–O and Mo–O CT bands, respectively. These peaks could not be distinguished clearly in the case of as-prepared or 500 °C heated samples. This is possibly due to a quenching effect from the surface or H2O over the particles. The sharp intense peaks at 398 (5D⁰ → 7F₁) and 468 nm (5D⁰ → 7F₂) are due to the f–f transitions of Eu³⁺, respectively. The relative intensity of Eu³⁺ with respect to the host increases with increasing heat-treatment temperature. This is related to extent of reduction of quenching effect from surface or H2O over particles with heat treatment.

![Fig. 2](image2.png)

Fig. 2 Excitation spectrum (monitoring emission at 615 nm) of 5 at. % Eu³⁺ doped CaMoO₄ as-prepared, 500 and 900 °C heated samples. Inset (a) shows expansion of excitation spectrum of 900 °C heated sample in the range 220–300 nm and fitting to data in the range 220–300 nm after base line correction. Inset (b) shows expansion of excitation spectrum of 900 °C heated sample in the range 325–500 nm.

Fig. 3 shows emission spectra of as-prepared, 500 and 900 °C heated samples of 5 at. % Eu³⁺ doped CaMoO₄ nanoparticles. The excitation wavelength used is 250 nm. In the emission spectra, a broad peak at 360–500 nm and sharp peaks at 592 and 614 nm could be observed. The broad peak is assigned to the emission due to host CaMoO₄. The sharp peaks at 592 and 614 nm are assigned to the magnetic (5D⁰ → 7F₁) and electric (5D⁰ → 7F₂) dipole transitions of Eu³⁺, respectively. The relative intensity of Eu³⁺ with respect to the host increases with increasing heat-treatment temperature. This is related to extent of reduction of quenching effect from surface or H2O over particles with heat treatment.

As-prepared nanoparticles of 5 at. % Eu³⁺ doped CaMoO₄ were excited at four different excitation wavelengths at 240, 250, 300 and 398 nm to choose the optimum excitation wavelength (Fig. 4a). The intensity increases in the following order of excitations: 300, 398, 250 and 240 nm. Thus, excitation at 240 nm gives the highest emission intensity. In the case of same sample heated at 500 or 900 °C (Fig. 4b, 4c), the intensity increases in the following order of excitations: 398, 300, 250 and 250 nm. This order is different from the as-prepared sample. It means that energy transfer process from the host or Eu–O to Eu³⁺ shifts to
higher wavelength (from 240 to 250 nm) with increasing heat-treatment temperature. For 500 or 900 °C heated samples, Mo–O charge transfer excitation peak (300 nm) dominates over the direct Eu³⁺ (398 nm) excitation. There is large gap between emission intensities from different excitation wavelengths in the case of the as-prepared sample. However, this gap reduces with heat-treatment temperature up to 900 °C. This is related to the extent of reduction of the non-radiative process arising from dangling bonds, H₂O and the organic moiety (EG) on the particles.

In order to see the optimum concentration of Eu³⁺ in CaMoO₄ samples for the highest luminescence, luminescence spectra were recorded for as-prepared, 500 and 900 °C heated samples at four different excitation wavelengths 240 (host or Eu–O CT), 250 (host or Eu–O CT), 300 (Mo–O CT) and 398 nm (direct Eu³⁺). Typical emission spectra of 900 °C heated samples are shown in Fig. 5.

In order to compare emission intensity, the Gaussian equation is used.\(^{23-30}\) The data are fitted in range 583 to 630 nm in which magnetic dipole and electric dipole allowed transitions (592 and 614 nm) occur. The parameters such as area \((A)\) and full width at half maximum intensity \((FWHM, W)\) for the magnetic dipole and electric dipole allowed transitions are characterized by \((A₁, W₁)\) and \((A₂, W₂)\), respectively. One typical fit to data of 5 at. % Eu³⁺ doped CaMoO₄ is shown as inset of Fig. 3 using a Gaussian equation after background correction. The fitting parameters are shown in Fig. 3, inset. Since electric dipole transition is sensitive to the asymmetric environment of Eu³⁺, only the variations of \(A₂\) and \(W₂\) with Eu³⁺ concentrations are discussed here.

In Fig. 6a, \(A₂\) of the as-prepared samples decreases with Eu³⁺ up to 10 at. %. The decrease in luminescence with Eu³⁺ is due the concentration quenching effect. It was reported that 8 at. % Eu³⁺ gave the optimum luminescence intensity in CaMoO₄.\(^{18}\) In lower Eu³⁺ doping (1 and 3 at. %), the luminescence intensity increases in the following order of excitation wavelengths 398, 300, 240 and 250 nm. For 5 at. % Eu³⁺ doping, luminescence intensity increases in the following order of excitation wavelengths 300, 398, 250 and 240 nm. This variation in emission intensity with excitation wavelength can be correlated with appearance of extra phases (MoO₃) and Eu–O–Mo for 5 at. % Eu³⁺ doping in the XRD patterns wherein 1 and 3 at. % Eu³⁺ doped CaMoO₄ samples show substitution of Ca³⁺ by Eu³⁺. In Fig. 6a (inset), \(W₂\) of as-prepared samples increases from 7.5 to 13 nm with increasing of Eu³⁺ concentration up to 10 at. %. Larger \(W₂\) means a broader peak and usually, a less luminescence intensity. This corroborates with a decrease in luminescence for 7 to 10 at. % Eu³⁺ doping (Fig. 6a).
Fig. 6 Variation of $A_2$ and $W_2$ for (a) as-prepared, (b) 500 and (c) 900 °C heated CaMoO$_4$ : Eu nanophosphors at different excitations.

The asymmetric environment of europium ion (Eu$^{3+}$) in the host lattice can be calculated by measuring the ratio of the electric to the magnetic dipole transitions (known as asymmetric factor ($A_{21}$)).$^{23–30} A_{21}$ values for the as-prepared samples at different excitation wavelengths (240, 250, 300 and 398 nm) are calculated. For lower concentration of Eu$^{3+}$ (1, 3, 5 at. %), $A_{21}$ is found to be maximal (7–9) while for 7 to 10 at. % Eu$^{3+}$ it is minimal (1–2). This is related to variation in $A_2$. In highly Ln$^{3+}$ doped samples and/or systems with highly quenching environment such as H$_2$O, C–H groups or surface dangling bonds, the following can be concluded: (1) intensities of the magnetic and electric dipole transitions are dominated by cross-relaxation among Ln$^{3+}$ ions and quenching environment and thus, intensity is reduced significantly. (2) Their intensity ratio ($A_{21}$) is close to 1 or 2. In this situation, occupancy of Ln$^{3+}$ ions in asymmetric environment could not be determined by observing the $A_{21}$ alone. (3) Their FWHM ($W_1$ and $W_2$) are very large as compared to that of diluted Ln$^{3+}$ doping or crystalline samples having reduction of quenching effect from surrounding or surface of particles. For example, equal values of intensity in $A_1$ and $A_2$ or FWHM in $W_1$ and $W_2$ are shown by as-prepared sample with 10 at. % Eu$^{3+}$ dopant after different excitation wavelengths (Fig. 4d). Their intensities ($A_1$ or $A_2$) are very weak due to the concentration quenching effect and the presence of H$_2$O over particles.

Fig. 6b shows the variations of $A_2$ and $W_2$ of 500 °C heated samples at different excitation wavelengths. $A_2$ increases with Eu$^{3+}$ up to 3 at. % and decreases with further increase of Eu$^{3+}$. This is related to the concentration quenching effect above 3 at. % Eu$^{3+}$. $W_2$ increases from 7.2 to 10 nm with increasing of Eu$^{3+}$. $A_{21}$ values are found in the range 2–10 depending on Eu$^{3+}$ concentration and excitation wavelength. Fig. 6c shows the variations of $A_2$ and $W_2$ of 900 °C heated samples at different excitation wavelengths. $A_2$ increases with Eu$^{3+}$ up to 5 at. % and decreases with further increase of Eu$^{3+}$. $W_2$ decreases from 7.4 to 7 nm with increasing Eu$^{3+}$. $A_{21}$ values are found in the range 4.2–10. From heat-treatment study, it can be concluded that $A_2$ or $A_{21}$ increases, whereas $W_2$ decreases with heat-treatment.

It is worth mentioning that CaMoO$_4$ has a tetragonal structure, with space group I4$_1$/a (C$_{4h}$).$^{11}$ This structure has body centered symmetry, similar to the reported one.$^1$ In CaO$_4$, there are two different Ca–O bond lengths, but with inversion symmetry. Likewise, there is only one Mo–O bond length with no inversion symmetry in MoO$_3$ (tetrahedron structure). It is expected that only the magnetic dipole transition should be allowed if Eu$^{3+}$ ions occupy Ca$^{2+}$ sites according to Judd–Ofelt theory.$^{14,15,31}$ If there is a slight distortion from symmetry, distribution of magnetic and electric dipole transitions of Eu$^{3+}$ could be observed. From the...
Table 1  Parameters obtained after bi-exponential equation fitting to the decay data of as-prepared, 500 and 900 °C heated samples at 250 and 398 nm excitations

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<th>τ₁ (μs)</th>
<th>I₂(%)</th>
<th>τ₂ (μs)</th>
<th>τₐv (μs)</th>
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χ² = Σ [w_k (X_k - F_k)²]/n, where w_k is a weighting factor for data points (w_Fk = 1/√F_k), X_k is the fitted data and F_k is the luminescence decay data.

XRD study, there is substitution of Ca²⁺ sites by Eu³⁺ up to 3 at. %. If Eu³⁺ ions do not occupy Ca²⁺ sites (and instead occupy a grain boundary), broadening in the XRD peak could be observed. This was not observed. We feel that the intensity of the magnetic dipole transition should be more than an electric dipole transition even if there is a slight distortion from symmetry. However, the opposite effect is observed. Similar unusual luminescence observations with respect to structural model were reported in REPO₄ : Lₙ³⁺ (RE = Y, La, Gd; Lₙ³⁺ = Eu³⁺, Dy³⁺, Tb³⁺).²⁴⁻²⁶⁻³⁴ A possible way to answer this is due to MoO₄ polarization in luminescence. This polarization changes the crystal field of EuO₆ and should be considered when Judd–Ofelt parameters are calculated.²⁸⁻³⁹

3.2 Luminescence decay study

The luminescence decay curves of the level ¹D₅ (615 nm) has been measured for as-prepared, 500 and 900 °C heated samples of Eu³⁺ doped CaMoO₄. Fig. 7, 8 and 9 show the decay curves for ¹D₅ → ³F₂ emission for these samples when excited at 250 and 398 nm. The decay curves are not well fitted by the mono-exponential equation (I = I₁ e⁻ⁿ/τₙ). Fig. 10a shows the mono-exponential curve fitting of 5 at. % Eu³⁺ doped CaMoO₄. The fitted parameter are given in the figure itself with χ² = 19.35. The definition of χ² is given in Table 1. The fitting behavior can be clearly understood by plotting ln(I) vs. t, which is shown in Fig. 10a (inset). The fitted straight line does not match with the decay data points. This suggests that the environment of the Eu³⁺ ions in the lattice are not the same in different positions.

All decay data are fitted by using bi-exponential decay equation, which is expressed as

\[ I = I₁ e^{⁻tn₁} + I₂ e^{⁻tn₂}, \]  

(a) 2.5x10⁻⁴  

(b) 6x10⁻⁴  

250 nm As-prepared  

1 at.%  

3 at.%  

5 at.%  

10 at.%  

398 nm As-prepared  

1 at.%  

3 at.%  

5 at.%  

Fig. 7  Luminescence decay spectra of as-prepared Eu³⁺ doped CaMoO₄ (Eu³⁺ = 1, 3, 5 and 10 at. %) nanoparticles at (a) 250 and (b) 398 nm excitations.
Fig. 8 Luminescence decay spectra of 500 °C heated Eu3+ doped CaMoO4 (Eu3+ = 1, 3, 5 and 10 at. %) nanoparticles at 250 and 398 nm excitations. where $I_1$ and $I_2$ are the intensities at different time intervals and $\tau_1$ and $\tau_2$ their corresponding lifetimes. The average lifetime can be calculated using the equation,

$$\tau_{av} = \frac{I_1 \tau_1 + I_2 \tau_2}{I_1 + I_2}$$

Typical plot of $I$ versus time for as-prepared 5 at. % Eu3+ doped CaMoO4 fitted using bi-exponential decay is shown in Fig. 10b with goodness of fitting parameter $\chi^2 = 2.36$. Bi-exponential decay behavior is observed when energy transfer takes place from donor/host to activator. It is observed that lifetime value decreases with increasing Eu3+ concentration. This is due to concentration quenching effect. The average lifetime ($\tau_{av}$) values for the $^1D_0$ level are 291, 175, 146 and 94 μs for 1, 3, 5 and 10 at. % Eu3+ ion concentration, respectively under 250 nm excitation. Moreover, the lifetime value measured for as-prepared samples of Eu3+ doped CaMoO4 at 398 nm excitation is shorter as compared to that at 250 nm excitation (see Table 1). This is due to decrease in luminescence intensity at 398 nm excitation compared to that at 250 nm excitation. Longer lifetime value or higher intensity after excitation at 250 nm is related to the high population of excited photons at the $^1D_0$ level due to energy transfer from the host or Eu-O CT band to Eu3+.

Table 1 gives the parameters ($\tau_1$, $I_1$, $\tau_2$, $I_2$) obtained after bi-exponential equation fitting to data of as-prepared, 500 and 900 °C samples. In the as-prepared sample (1 at. % Eu3+), $\tau_1$ ($I_1$ %) is found to be 731 μs (61%), which is two times $\tau_1$ ($I_1$ %) = 304 μs (39%) after excitation at 250 nm. The same sample after excitation at 398 nm gives $\tau_1$ ($I_1$ %) = 403 μs (95%), which is 134 times $\tau_1$ ($I_1$ %) = 3 μs (5%). Thus, $\tau_1$ from 250 nm excitation has a contribution (39%) in the average lifetime value while $\tau_2$ with lower contribution from 398 nm excitation arises from either surface Eu3+ or inhomogeneity. The reported lifetime values of Eu3+ (5 at.%) in CaMoO4 were 494 and 455 μs.11,18 Some reported lifetimes values of other Eu3+ doped compounds: Y2O3:Eu, Gd2O3:Eu, YVO4:Eu, GdVO4:Eu, YPO4:Eu, GdPO4:Eu and LaPO4:Eu are 1.6, 1.3, 0.247, 0.583, 2.07, 1.0 and 3.56 ms, respectively.23,24,30,33,36–38 In the case of 500 or 900 °C heated samples, the lifetime value is longer than that of the as-prepared samples. This is related to the increase of particle size and reduction of surface to volume ratio and surface defects after heat-treatment.

4. Conclusions

Luminescence intensity increases with Eu3+ up to 5 at. % and decreases with further increase of Eu3+. The decrease of luminescence with increasing Eu3+ is related to a concentration quenching effect. The luminescence intensity improves with heat-treatment due to a reduction in non-radiative processes from the surface and O–H groups. From luminescence decays on direct excitation at 398 and indirect excitation at 250 nm, energy transfer process from Mo–O CTB to Eu3+ and surface contribution to lifetime could be...
from the polarizability effect of the MoO$_4$ tetrahedron. This can be explained due to the crystal structure having inversion symmetry. The intensity of the electric dipole transition is more pronounced in the as-prepared Eu$^{3+}$ doped CaMoO$_4$ nanoparticles. The fitted parameters from the bi-exponential model are shown in their figures. Inset of (a) shows the ln(I) vs. t plot.

Acknowledgements

A. K. Parchur acknowledges the financial support provided by University Grants Commission, Govt. of India through the D. S. Kothari Post Doctoral Fellowship. The authors thank Dr. T. Mukherjee, Chemistry Group and Dr D. Das, Chemistry Division, BARC for their support and encouragement during this work.

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