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ARTICLE

Photoluminescence Studies of CaMoO₄: Eu³⁺ Phosphors

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ABSTRACT

Eu³⁺-doped CaMoO₄ phosphors with a Scheelite structure have been synthesized *via* mechanochemically assisted solid state metathesis reaction at room temperature. The characteristics of the phosphor materials were analyzed by X-ray diffraction, Fourier transform infrared spectroscopy, photoluminescence and diffuse reflectance spectra. The photoluminescence emission spectra of CaMoO₄:Eu³⁺ phosphors showed an intense peak at 615 nm which corresponds to ⁵D₀→⁷F₂ transition of Eu³⁺. Comparing with the earlier reports, it is concluded that Eu³⁺ occupied a lattice site with non-centrosymmetric environment in the scheelite phase. The excitation spectra displayed that these phosphors could be effectively excited by near ultraviolet (394 nm) light and so they could be used as red components for white light-emitting diodes.

KEYWORDS

Photoluminescent phosphor, Eu³⁺ activator, Solid state metathesis reaction.

INTRODUCTION

Currently, more research interest is focused on phosphor converted white light emitting diodes (pc-WLEDs) technique [1]. Many reports on Eu³⁺ doped molybdates or tungstate based phosphors have been published. Most of them were synthesized by a conventional solid-state reaction approach, which usually requires high temperature, time consuming heating process *etc.* The mechanochemically assisted solid state metathesis reaction at room temperature is one of the most important techniques for the synthesis of various inorganic materials as it offers many advantages over conventional solid state method in the synthesis of fine powders, in terms of reaction rate, with little or no need for external energy. The high lattice energy of the coproduced salt (*e.g.*, NaCl) makes the reaction feasible at low temperature [2]. In this paper, synthesis of Eu³⁺ activated calcium molybdate (CaMoO₄) phosphors were prepared by mechanochemically assisted solid state metathesis reaction at room temperature and their luminescent properties were investigated.

EXPERIMENTAL

The red phosphors of CaMoO₄:xEu³⁺ (x = 0.05, 0.1, 0.2) were prepared by mechanochemically assisted solid state metathesis reaction at room temperature by using AR grade

$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, CaCl_2 and $\text{EuCl}_3 \cdot \text{H}_2\text{O}$ (99.9 %) as the starting materials and used without any further purification. The appropriate stoichiometric mixtures of CaCl_2 , $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and EuCl_3 were mixed and grounded using a planetary ball mill of grinding bowl capacity of 12 mL and the speed of 450 rpm by using tungsten carbide balls for a period of 2 h. The resultant powder was washed with water to remove sodium chloride that was the by product of the reaction and dried around 100°C for 3 h.

The X-ray diffraction spectra of these phosphors were identified by a Pan Analytical X'pert pro X-ray diffractometer. Fourier transform infrared spectroscopy (FT-IR) data were collected on a Nicolet 6700 FT-IR spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$. The excitation and emission spectra were measured on a Jobin Yvon Fluorolog-3-11 spectrofluorometer at room temperature. Diffuse reflectance spectra were recorded Varian 5000 UV-visible spectrophotometer.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of $\text{CaMoO}_4:\text{xEu}^{3+}$ ($x = 0.05, 0.1, 0.2$) phosphors (Fig. 1) are similar to each other and they compare very well with standard XRD data (JCPDS card 062219). This indicates that the doped Eu^{3+} ions have no obvious influence on the structure of the host. It shows that the products are single phase.

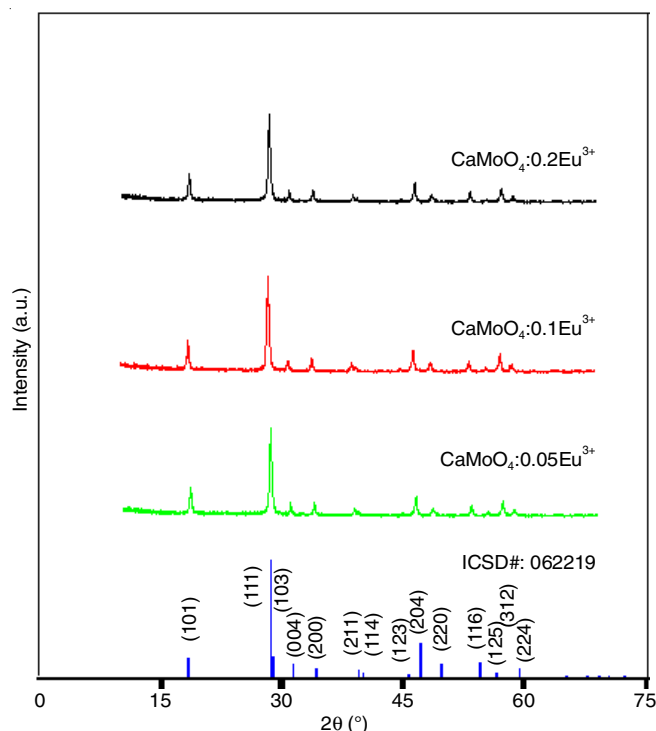


Fig. 1. XRD patterns of $\text{CaMoO}_4:\text{xEu}^{3+}$ ($x=0.05, 0.1, 0.2$) phosphors

The FTIR spectra of $\text{CaMoO}_4:\text{xEu}^{3+}$ ($x = 0.05, 0.1, 0.2$) phosphors (Fig. 2) display a very weak band around 430 cm^{-1} which is related to the $\text{F}_2(\nu_4)$ bending modes of vibration and a very broad absorption band around 810 cm^{-1} is assigned to $\text{F}_2(\nu_3)$ antisymmetric stretch vibrations of molybdate group [3]. The band around 3400 cm^{-1} is assigned to O-H stretching vibration and the bands around 1630 cm^{-1} are assigned to H-O-H bending vibration of absorbed water from air [4].

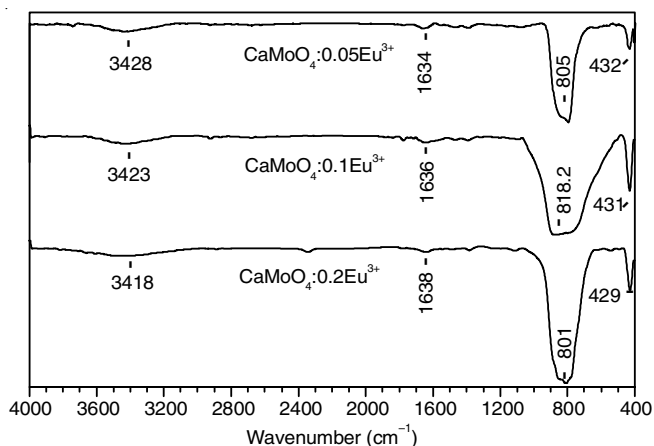


Fig. 2. FTIR spectra of the $\text{CaMoO}_4:\text{xEu}^{3+}$ ($x = 0.05, 0.1, 0.2$) phosphors

The photoluminescence excitation spectrum of $\text{CaMoO}_4:0.05\text{Eu}^{3+}$ phosphor monitored at 615 nm (Fig. 3) may be divided in to two regions: (i) The intense broad band centered at 297 nm is attributed to the charge-transfer (CT) transition between oxygen and molybdenum [5] and (ii) In the range from 350 nm to 500 nm , the sample shows the characteristic intra configurational $4f\text{--}4f$ transitions of the Eu^{3+} : ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$ transition at 359 nm , the ${}^7\text{F}_0 \rightarrow {}^5\text{G}_6$ transition at 378 nm , the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition at 394 nm , the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_3$ transition at 415 nm and the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition at 464 nm . The lines at 394 and 464 nm are the two strongest of these observed lines and match well with the near-UV and the blue LED chips well.

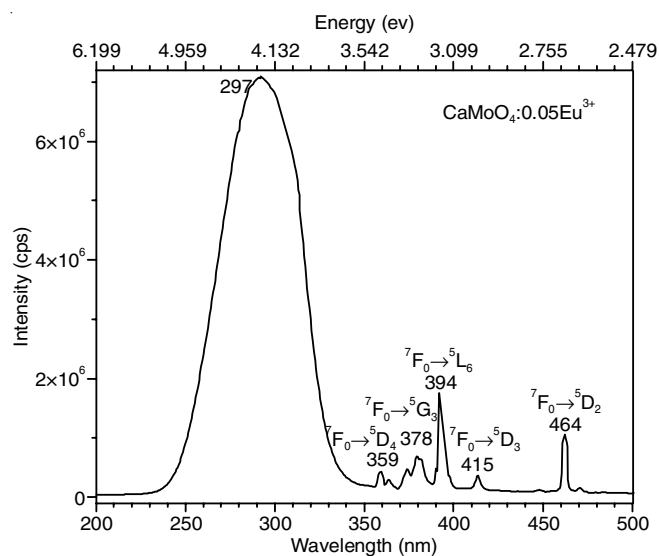


Fig. 3. Excitation spectrum of $\text{CaMoO}_4:0.05\text{Eu}^{3+}$ phosphor monitored at 615 nm

The photoluminescence emission spectrum of $\text{CaMoO}_4:0.05\text{Eu}^{3+}$ phosphor under near-UV 394 nm excitation is shown in Fig. 4. It consists of several sharp lines between 570 nm and 710 nm , which are associated with the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($J = 1, 2, 3, 4$) transitions from the excited Eu^{3+} to the ground state. The strongest emission peak is the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions of Eu^{3+} at 615 nm ; other transitions from ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ located in the range of 570 to 710 nm are weak.

The transition of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ belongs to a forced electric dipole transition and its intensity is very sensitive to the site

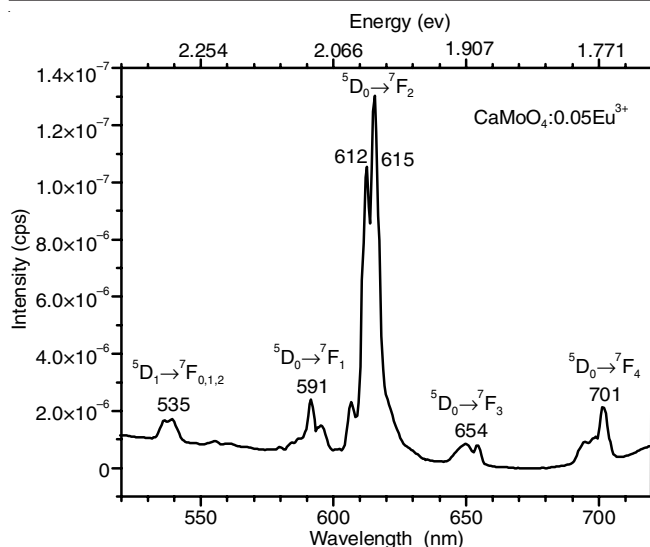


Fig. 4. Photoluminescence emission spectrum of $\text{CaMoO}_4:0.05\text{Eu}^{3+}$ phosphor under 394 nm excitation

symmetry of the Eu^{3+} ions. The transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ is much stronger than the transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, which suggests that the Eu^{3+} located in a distorted (or asymmetric) cation environment [6].

The photoluminescence emission intensity of $\text{CaMoO}_4:x\text{Eu}^{3+}$ ($x = 0.05, 0.1, 0.2$) enhances with the increase in Eu^{3+} concentration and reaches maximum at $x = 0.1$ (Fig. 5). When the Eu^{3+} concentration is higher than $x = 0.1$, the luminescence intensity reduces contrarily due to the concentration quenching effect of the dopant [7]. The spectral peak position and the photoluminescence intensity of 615 nm emission of $\text{CaMoO}_4:\text{Eu}^{3+}$ phosphors prepared by both solid state metathesis reaction and solid state reaction do not show any appreciable differences.

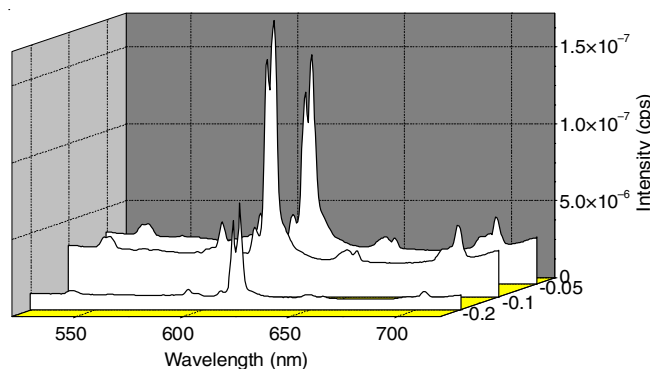


Fig. 5. Photoluminescence ($\lambda_{\text{exc}} = 394$ nm) spectra of phosphors $\text{CaMoO}_4:x\text{Eu}^{3+}$ ($x = 0.05, 0.1, 0.2$)

To investigate the energy absorption, the diffuse reflectance spectra of $\text{CaMoO}_4:x\text{Eu}^{3+}$ ($x = 0.05, 0.1, 0.2$) phosphors

were measured (Fig. 6). The absorption band from 220 to 350 nm corresponds to the (O-Mo) ligand to metal CT in the MoO_4^{2-} group. The absorptions at 394 and 464 nm are ascribed to the $f-f$ electron transitions of Eu^{3+} ions, which is consistent with the conclusion of the excitation spectrum analysis.

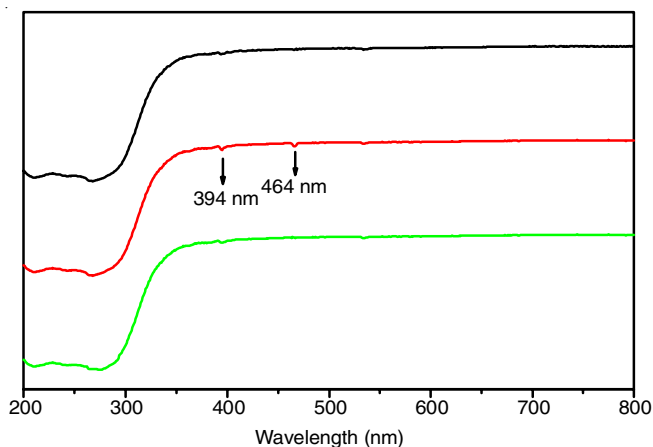


Fig. 6. Diffuse reflectance spectra of $\text{CaMoO}_4:x\text{Eu}^{3+}$ ($x = 0.05, 0.1, 0.2$) phosphors

Conclusion

$\text{CaMoO}_4:\text{Eu}^{3+}$ phosphor powders have been synthesized by simple solid state metathesis reaction at room temperature and their luminescent properties have been investigated. Upon 394 nm near-UV excitation, the $\text{CaMoO}_4:0.1\text{Eu}^{3+}$ phosphor showed strong red emission lines at 615 nm correspond to the forced electric dipole transitions. All these favourable properties indicate that $\text{CaMoO}_4:\text{Eu}^{3+}$ phosphor might be a useful compound as the red component.

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