

# Synthesis and luminescence properties of $\text{Eu}^{2+}$ -activated $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$ for blue-emitting phosphor

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**Abstract.**  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6:\text{Eu}^{2+}$  blue-emitting phosphor was synthesized by the combustion-assisted synthesis method under reductive atmosphere. The products were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and photoluminescence (PL) spectrum. XRD analysis confirmed the formation of  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  pure phase. Photoluminescence results showed that the phosphor can be excited efficiently by UV light range from 230–400 nm, and then exhibited bright blue light with peak wavelength at 431 nm. It is a very promising candidate as a blue-emitting phosphor for potential applications in display devices.

**Keywords.** Optical materials and properties; luminescence; phosphor; orthophosphate.

## 1. Introduction

Divalent europium ion is an important activator ion for luminescence materials, which have been extensively studied. The emission and absorption spectra of  $\text{Eu}^{2+}$  usually consist of broadband due to transitions between the  $^8S_{7/2}$  ( $4f^7$ ) ground state and the crystal field components of the  $4f^65d^1$  excited state configuration. Since the involved  $5d$  orbital is external, the positions of the excitation and emission wavelength of  $\text{Eu}^{2+}$  strongly depend on the host crystal. Thus, the host is critical for determining the optical properties of  $\text{Eu}^{2+}$  ions.

$\text{Eu}^{2+}$  doped alkaline earth metal phosphates are one class of desirable phosphors for UV excitation (Pardo *et al* 2002; Dorenbos 2005; Nakashima *et al* 2005; Balda *et al* 2009) because of excellent thermal stability and water-resistant property. Meanwhile, tetrahedral rigid three-dimensional matrix of phosphate is thought to be ideal for charge stabilization (Tang *et al* 2007; Zu *et al* 2008).  $\text{Ca}_3(\text{PO}_4)_2$ – $\text{Mg}_3(\text{PO}_4)_2$  system is important for a fundamental study of fused calcium magnesium phosphate fertilizers (serpentine fused) or defluorinated tricalcium phosphate with magnesia (Ando 1958).  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  was prepared from appropriate 4 starting chemicals (reagent grade  $\text{CaHPO}_4$ ,  $\text{CaCO}_3$ ,  $\text{MgO}$ , and  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ) (Terpstra *et al* 1984). However, little information is found in literature on  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  for potential application as a phosphor host. In the present study,

we synthesized  $\text{Eu}^{2+}$  doped  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  by the combustion technique followed by post-annealing under reductive atmosphere. It was investigated by excitation and emission spectra measurements. The dependence of luminescence on the  $\text{Eu}^{2+}$  concentration and its potential applications were discussed.

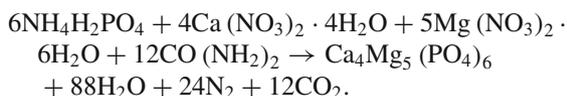
## 2. Experimental

$\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6:\text{Eu}^{2+}$  was prepared by the combustion-assisted synthesis method (Tang and Chen 2009). The starting materials were  $\text{NH}_4\text{H}_2\text{PO}_4$  (analytical reagent),  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (analytical reagent),  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (analytical reagent), and  $\text{Eu}_2\text{O}_3$  (99.99%). For the combustion-assisted synthesis,  $\text{Eu}_2\text{O}_3$  was dissolved in  $\text{HNO}_3$  (analytical reagent) in order to obtain the corresponding nitrate.  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were used as the source of P, Ca and Mg, respectively. Urea (analytical reagent) was used as the fuel.

The stoichiometric chemicals were weighed and thoroughly mixed in an agate mortar and dissolved in a minimum amount of distilled water, then transferred to a porcelain crucible and introduced into a muffle furnace maintained at  $600^\circ\text{C}$ . The refractory lining used in the furnace was lightweight  $\text{MgO}$ . Initially, the solution boiled and underwent dehydration, followed by decomposition with the evolution of large amounts of gases. Then, spontaneous ignition occurred and underwent smouldering combustion. The duration of reaction was  $\sim 3$ – $5$  min and then the product was cooled to room temperature naturally after the combustion in its self-generating atmosphere. For complete

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combustion, the oxidizer/fuel ratio should be equal to 1. The basic combustion reaction can be described as follows:



The foamy precursor was well milled and transferred to a porcelain boat inside a tubular furnace. The samples were heated under a  $\text{H}_2/\text{N}_2$  (5:95) flow (50 mL/min) to  $900^\circ\text{C}$  with a rate of 5 K/min and maintained at this temperature for 5 h. Gas flow was maintained until the furnace was cooled to room temperature.  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6:\text{Eu}^{2+}$  was obtained almost quantitatively as a crystalline and colourless powder.

The phase purity of the phosphor was checked by powder X-ray diffraction (XRD) analysis collected on a Bruker D8 diffractometer (Bruker Co. Ltd., Karlsruhe, Germany) operating at 40 kV, 40 mA with Bragg–Brentano geometry using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). Powder morphology and dimension were studied in detail using transmission electron microscopy (TEM) (Tecnai G20, FEI Co. Ltd., Eindhoven, The Netherlands). Chemical analysis was performed in TEM using energy-dispersive X-ray spectroscopy (EDS) point scans. Fluorescence emission and excitation spectra were recorded on a Perkin-Elmer LS55 spectrometer (Perkin-Elmer Co. Ltd., Wellesley, USA) at room temperature. The obtained data have been corrected for emission and excitation with respect to the Xe plasma excitation source.

### 3. Results and discussion

The phase identification for  $\text{Ca}_{4(1-x)}\text{Mg}_5(\text{PO}_4)_6:4x\text{Eu}^{2+}$  ( $x = 0.005\text{--}0.03$ ) samples characterized by XRD are portrayed as a profile as shown in figure 1. All the patterns are the same as the JCPDS Card No. 11–0231. No impurity

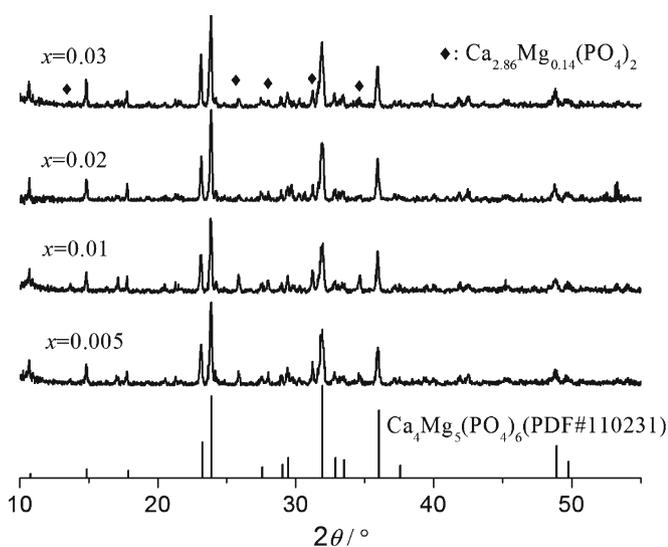


Figure 1. XRD patterns of  $\text{Ca}_{4(1-x)}\text{Mg}_5(\text{PO}_4)_6:4x\text{Eu}^{2+}$ .

lines were observed, and all the reflections could be well indexed to a  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  single phase except a trace amount of impurity phase,  $\text{Ca}_{2.86}\text{Mg}_{0.14}(\text{PO}_4)_2$  (JCPDS #70–0681). Therefore, we conclude that the  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  can be synthesized by the suggested method. It also indicates that the  $\text{Eu}^{2+}$  doping ions do not make the phosphor form new phases in the synthesized process. Moreover,  $\text{Eu}^{2+}$  atoms probably occupy the  $\text{Ca}^{2+}$  sites in  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$ , because ionic radii,  $\text{Eu}^{2+}$  and  $\text{Ca}^{2+}$ , are very close in size, such as  $\text{Eu}^{2+}$  ( $r = 0.117 \text{ nm}$  with  $\text{CN} = 6$  and  $r = 0.120 \text{ nm}$  with  $\text{CN} = 7$ ) and  $\text{Ca}^{2+}$  ( $r = 0.100 \text{ nm}$  with  $\text{CN} = 6$  and  $r = 0.106 \text{ nm}$  with  $\text{CN} = 7$ ) (Shannon 1976; Ju *et al* 2009).

Figure 2a displays TEM image of  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6:\text{Eu}^{2+}$  as-prepared. The powders appear weakly agglomerated. The  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6:\text{Eu}^{2+}$  phosphors consist of fine particles with a mean size of about  $1 \mu\text{m}$  in length. Energy disperse spectrometry (EDS) analysis was employed to determine composition of the  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6:\text{Eu}^{2+}$  phosphors. The corresponding EDS spectrum (figure 2b) shows that it mainly

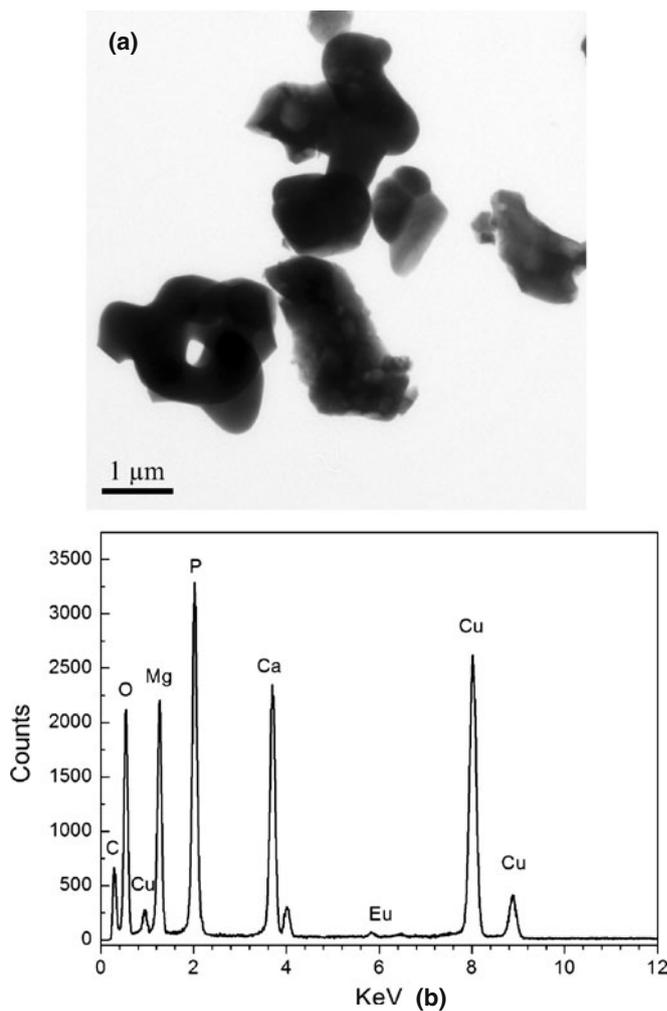
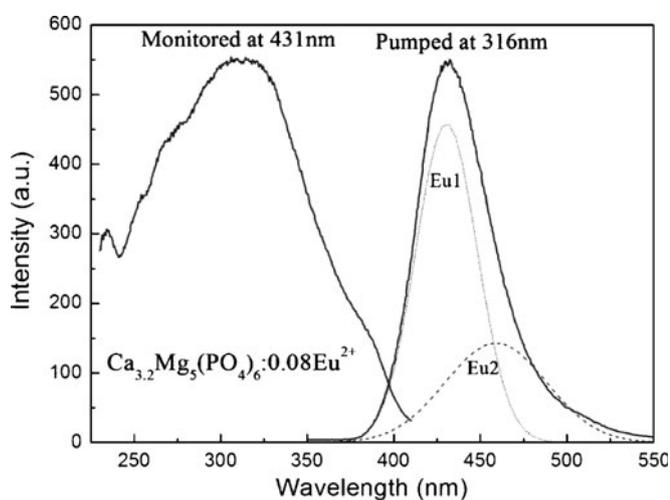


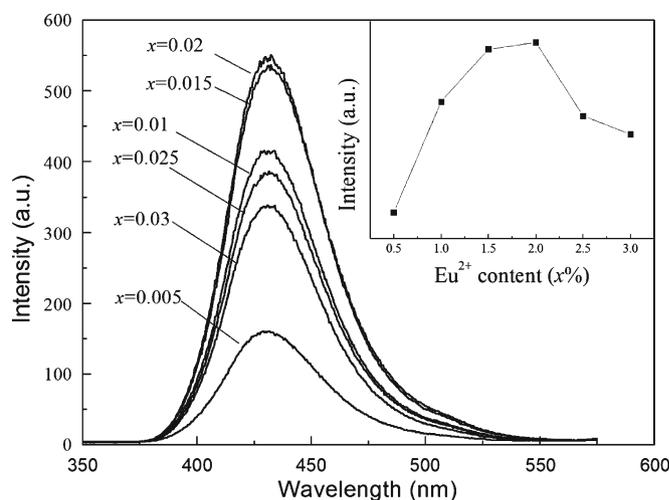
Figure 2. TEM image of  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6:\text{Eu}$  particles synthesized at  $900^\circ\text{C}$  (a) and EDS analysis for particles synthesized at  $900^\circ\text{C}$  (b).

composed of Ca, Mg, O and P atoms, and no other impurity is detected except a small amount of Eu, indicating the Eu elements are successfully doped in the  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  crystals. In this spectrum, signals corresponding to Cu arise from TEM grid. To improve conductivity during EDS analysis, carbon was attached on the bottom of the samples and was detected.

Figure 3 shows the excitation and emission spectra of  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6:\text{Eu}^{2+}$  measured on the luminescence spectrometer at room temperature. The excitation spectra present a broad absorption bands which peaked from 230 to 400 nm, which were ascribed to the  $4f-5d$  transitions of  $\text{Eu}^{2+}$  ions. Under the excitation of 316 nm, the phosphor shows a blue emission band peaking at 431 nm with a shoulder in the long wavelength at 460 nm. The asymmetric emission spectrum shows that  $\text{Eu}^{2+}$  have more than one emission centre in the lattice (Blass 1985). Consequently, it was deconvoluted into two Gaussian components peaking at 430 nm (Eu1) and 460 nm (Eu2), respectively. The Eu1 centre may act as the main luminescence centre because of its relatively high intensity. The  $4f^7 \rightarrow 4f^65d^1$  transition of  $\text{Eu}^{2+}$  is strongly dependent on the host lattice because the outermost  $5d$  shell is involved. Different local structures around  $\text{Eu}^{2+}$  ions produce separate emission spectra even in a single host structure. Therefore, there are at least two sites (Ca and Mg sites) available at which  $\text{Eu}^{2+}$  can be accommodated.  $\text{Eu}^{2+}$  ions mainly occupy  $\text{Ca}^{2+}$  sites and form the corresponding emission centre (Eu1). The intensity ratios of both deconvoluted Gaussian peaks show no significant change with  $\text{Eu}^{2+}$  doping content. This implies that  $\text{Eu}^{2+}$  at Ca and Mg sites was not affected by the  $\text{Eu}^{2+}$  doping content but was consistent, regardless of the  $\text{Eu}^{2+}$  doping content. No emission peaks of  $\text{Eu}^{3+}$  were observed in the spectra, indicating that  $\text{Eu}^{3+}$  ions



**Figure 3.** Room temperature  $\text{Ca}_{3.2}\text{Mg}_5(\text{PO}_4)_6:0.08\text{Eu}^{2+}$  emission spectrum excited at 316 nm and excitation spectrum monitoring emission at 431 nm. The emission spectrum was decomposed by two Gaussian components at 430 nm (Eu1) and 460 nm (Eu2), respectively.



**Figure 4.** Emission spectra of  $\text{Ca}_{4(1-x)}\text{Mg}_5(\text{PO}_4)_6:4x\text{Eu}^{2+}$  ( $\lambda_{\text{ex}} = 316$  nm); inset shows dependence of emission intensity on  $\text{Eu}^{2+}$  concentration.

in the matrix have been reduced to  $\text{Eu}^{2+}$  completely under the reducing  $\text{H}_2$  atmosphere.

A series of  $\text{Ca}_{4(1-x)}\text{Mg}_5(\text{PO}_4)_6:4x\text{Eu}^{2+}$  phosphor with various  $\text{Eu}^{2+}$  concentrations ( $x = 0.005-0.03$ ) were prepared and the effect of doped  $\text{Eu}^{2+}$  concentration on the emission intensity was investigated. The emission spectra of  $\text{Ca}_{4(1-x)}\text{Mg}_5(\text{PO}_4)_6:4x\text{Eu}^{2+}$  with different  $\text{Eu}^{2+}$  concentrations are shown in figure 4. The phosphors invariably emitted blue luminescence with a peak wavelength predominating at 431 nm when excited at 316 nm. The positions of the emission peak are not influenced by the  $\text{Eu}^{2+}$  concentration, indicating that the crystal structure of  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  remains unchanged by substitution of divalent calcium by  $\text{Eu}^{2+}$  ions. The inset of figure 4 represents the dependence of emission intensity on the  $\text{Eu}^{2+}$  doping concentrations. The luminescence intensity of  $\text{Ca}_{4(1-x)}\text{Mg}_5(\text{PO}_4)_6:x\text{Eu}^{2+}$  increases with  $\text{Eu}^{2+}$  content increasing until a maximum intensity of about  $x = 0.02$  is reached, and then it decreases because of conventional concentration quenching process. The emission spectra show the presence of a broad band, whose broadness indicates the existence of an interaction between the host and the activator, which can be attributed to the presence of excited electrons in the outer shell of the  $\text{Eu}^{2+}$  ions. According to Dexter's (1953) theory, the probability of energy transfer among the  $\text{Eu}^{2+}$  ions increases as the  $\text{Eu}^{2+}$  concentration increases.

#### 4. Conclusions

In summary,  $\text{Eu}^{2+}$ -doped  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  phosphors have been synthesized for the first time using combustion-assisted synthesis method. The photoluminescence spectra show that the phosphor can be excited efficiently by UV light (230–400 nm) and exhibits a strong blue emission located at

431 nm with some asymmetric on the long wavelength side. This finding has enlarged the host of the family of the potential phosphor.

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