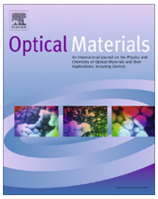
Optical Materials 39 (2015) 173–177

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat



# Synthesis and photoluminescence properties of a cyan-emitting phosphor $Ca_3(PO_4)_2$:$Eu^{2+}$ for white light-emitting diodes

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ARTICLE INFO

*Article history:*
Received 12 June 2014
Received in revised form 3 November 2014
Accepted 18 November 2014
Available online 12 December 2014

*Keywords:*
Cyan-emitting
White LED
$Eu^{2+}$
Calcium triphosphate
Phosphor

ABSTRACT

In this paper, a cyan-emitting phosphor $Ca_3(PO_4)_2$:$Eu^{2+}$ (TCP:$Eu^{2+}$) was synthesized and evaluated as a candidate for white light emitting diodes (WLEDs). This phosphor shows strong and broad absorption in 250–450 nm region, but the emission spectrum is prominent at around 480 nm. The emission intensity of the TCP:$Eu^{2+}$ was found to be 60% and 82% of that of the commercial $BaMgAl_{10}O_{17}$:$Eu^{2+}$ (BAM) under excitation at 340 nm and 370 nm, respectively. Upon excitation at 370 nm, the absolute internal and external quantum efficiencies of the $Ca_3(PO_4)_2$:1.5%$Eu^{2+}$ are 60% and 42%, respectively. Moreover, a white LED lamp was fabricated by coating TCP:$Eu^{2+}$ with a blue-emitting BAM and a red-emitting $CaAlSiN_3$:$Eu^{2+}$ on a near-ultraviolet (375 nm) LED chip, driven by a 350 mA forward bias current, and it produces an intense white light with a color rendering index of 75.

## 1. Introduction

Much attention has recently been paid to the development of white-light emitting diodes (WLEDs) because of their advantages and wide applications in consumer electronics as well as in solid state lighting (SSL) [1–4]. Conventional methods to obtain white light using LEDs involve precoating a yellow phosphor, such as cerium-doped yttrium aluminum garnet (YAG:$Ce^{3+}$), on top of the blue LED chip. However, this approach causes several serious problems, such as thermal quenching, a narrow visible range and a low color rendering index (CRI) [5,6]. An alternative approach involves the manufacture of near-UV LED chips by blending red-, green-, and blue-emitting phosphors together on top of an *n*-UV LED chip to assemble WLEDs [7,8]. The fabrication of white LEDs using this method can yield a CRI of Ra > 80, and the color temperature may be easily controlled. Additionally, the blending of cyan and red-emitting phosphors together is also practical for *n*-UV LED chips to produce white light according to Commission Internationale de l'Eclairage (CIE) chromaticity diagram. For display applications, the introduction of a cyan-emitting phosphor could enlarge the display gamut [6,9], so the images of the device may be more colorful and natural, because the display characteristics of field emission displays strongly depend on the emission colors of the phosphors. Hence, it is important to develop new RGB phosphors that can be efficiently excited by *n*-UV LED chips for the fabrication of white LEDs.

Rare earth (RE) element-doped phosphates have been studied for use in white LEDs, because of their low sintering temperature, high quantum efficiency and nice thermal stability [10,11]. Herein, our attention is focused on $Ca_3(PO_4)_2$ (Tricalcium Phosphate, TCP) as a host. As we known, $Ca_3(PO_4)_2$ possesses at least four polymorphs: the low-temperature $\beta$-TCP, and the high-temperature forms, $\alpha$-, $\alpha'$- and $\alpha''$-TCP. The structural characteristics of the first three polymorphs were reported [12,13]. The $\alpha'$-TCP only exists at temperatures >~1430 °C and reverts to $\alpha$ phase when cooling below the transition temperature [13]. In contrast, $\alpha$- and $\beta$-TCP is stable at room temperature [14], and both of which are biocompatible and currently used in several clinical applications in dentistry, maxillo-facial surgery and orthopaedics [15,16]. Ttrivalent RE ions doped $\beta$-TCP luminescent materials as bioprobe are investigated [17–19]. Very recently, $Eu^{2+}$ ion doped whitlockite-type phosphates also have attracted many attentions due to their potential applications in WLEDs, such as $Ba_2Ca(PO_4)_2$:$Eu^{2+}$ [20], $Sr_{1.75}Ca_{1.25}(PO_4)_2$:$Eu^{2+}$ [21], $Ca_{3-x}Sr_x(PO_4)_2$:$Eu^{2+}$ [22], and $Ca_3(PO_4)_2$:$Eu^{2+}$,$Mn^{2+}$ [23]. $\beta$-$Ca_3(PO_4)_2$:$Eu^{2+}$ emits blue light at about 420 nm, when codoping

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http://dx.doi.org/10.1016/j.optmat.2014.11.021
0925-3467/

with Ba or Sr atoms in it, the emission wavelength significantly redshifts to 450 nm even 518 nm. Xia et al. have investigated the structure–property relationship in detail. In the case of $\beta$-$Ca_3(PO_4)_2$:$Eu^{2+}$,$Mn^{2+}$, we tuned the emission color from blue (418 nm) to red (650 nm) via the energy transfer of $Eu^{2+}$ and $Mn^{2+}$ ions. The detailed structure of the fourth polymorph $\alpha''$-TCP is not yet known. However, $\alpha''$-TCP, as a phosphate, may be a suitable host matrix for RE ions doping and is expected to exhibits good photoluminescent properties for SSL applications [24]. In this study, we therefore synthesized $\alpha''$-TCP:$Eu^{2+}$ phosphors through a conventional solid-state reaction, and investigated their morphology, absorption, photo-excitation and emission, absolute quantum efficiency and temperature- dependent photoluminescence, with an aim to explore new phosphors for *n*-UV LEDs.

## 2. Experimental

The $\alpha''$-$Ca_{3(1-x)}(PO_4)_2$:$xEu^{2+}$ (TCP:$xEu^{2+}$, $x = 0.2\%$, 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, 3.0%) powder samples were synthesized by conventional solid-state reaction at high temperature. The starting materials were $CaCO_3$ (A. R.), $NH_4H_2PO_4$ (A. R.) and $Eu_2O_3$ (99.99%), with molar ratios of $3(1-x)$:2.1:$3x/2$. Typically, the raw materials were thoroughly grounded, and the mixture was then heated at 1400 °C for 6 h in a reducing ambient atmosphere of 15% $H_2$/85% $N_2$. Finally the as-synthesized samples were cooled to room temperature (RT).

WLED lamps were fabricated by integrating a mixture of optical grade transparent silicon resin and phosphors blending of cyan-emitting TCP:1.5%$Eu^{2+}$, blue-emitting $BaMgAl_{10}O_{17}$:$Eu^{2+}$ (BAM) commodity and red-emitting $CaAlSiN_3$:$Eu^{2+}$ (CASN) commodity on a 375 nm *n*-UV chip.

The phase purity of the products was examined by X-ray diffraction (XRD) using a Bruker D8 ADVANCE powder diffractometer with Cu K$\alpha$ radiation ($\lambda = 1.54059$ Å) at RT. The morphology and elemental composition of the as-prepared products were measured using scanning electron microscopy (SEM, FEI Quanta 400). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and selected area electron diffraction (SAED) analyses were performed on a JEOL 2010 instrument. Diffuse reflectance spectra (DRS) were taken on a Cary 5000 UV–vis–NIR Spectrophotometer. The photoluminescence (PL), photoluminescence excitation (PLE) spectra and luminescence decay curves were recorded on an Edinburgh FLS920 Time Resolved and Steady State Fluorescence Spectrometer at RT, which was equipped with a time-correlated single-photon counting (TCSPC) card and a thermoelectric cooled red sensitive photomultiplier tube (PMT). A 450 W Xenon lamp was used as the excitation source. The excitation photons for the luminescence decay curves determining were provided by a 150 W nF900 flash lamp. Quantum efficiency (QE) measurements were conducted based on an integrating sphere technique [25,26].

## 3. Results and discussion

### 3.1. Phase characterization

The composition and phase purity of the as-prepared powder samples were first examined by XRD. Fig. 1 shows XRD patterns of TCP:$xEu^{2+}$ samples annealed at 1400 °C for 6 h. It is obvious that all the diffraction peaks of these samples can be exactly assigned to pure orthorhombic phase $Ca_3(PO_4)_2$ according to JCPDS file 09-0348. No other phase or impurity can be detected, indicating that the $Eu^{2+}$ ions were completely dissolved in the $Ca_3(PO_4)_2$ host without inducing significant changes of the crystal structure. These XRD patterns are similar to each other except for a slight peak shift. The diffraction peak position at $2\theta = 30.75°$ for the TCP host gradually shifts to a lower $2\theta$ value with the increase of $Eu^{2+}$ doping concentration, for example, $2\theta = 30.67°$ for $x = 3.0\%$, due to the larger ion radius of $Eu^{2+}$ ($r = 1.31$ Å for CN = 6) with respect to $Ca^{2+}$ ($r = 1.14$ Å for CN = 6).

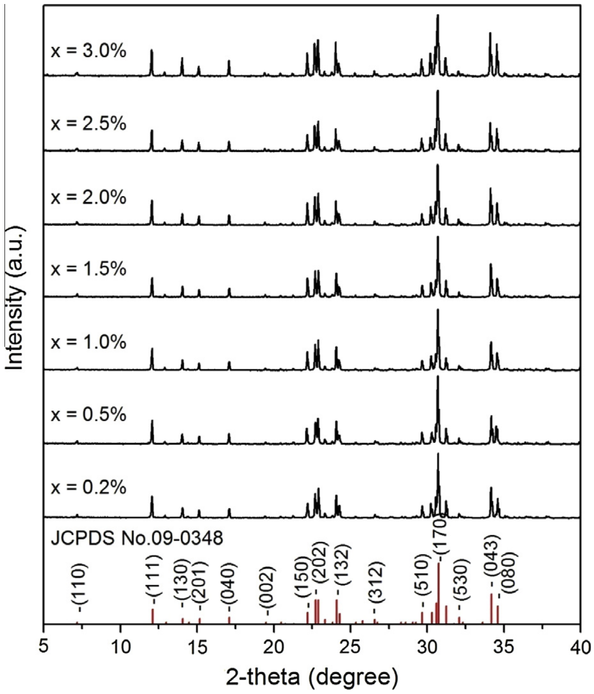

**Fig. 1.** XRD patterns of TCP:$xEu^{2+}$ phosphors, the standard data of $Ca_3(PO_4)_2$ (JCPDS No. 09-0348) is shown as reference.

### 3.2. Microstructural analyses

Based on the SEM images shown in Fig. 2a, it is clear that the surface of TCP:$Eu^{2+}$ particles is smooth, with diameter of about 10 μm in size. Energy-dispersive X-ray (EDX) spectroscopy was employed to characterize the elemental composition of the as-prepared TCP:$Eu^{2+}$ product, as presented in Fig. 2b. It confirms the existence of the elements Ca, P, O and Eu, with atomic ratios of 21.12:16.28:62.29:0.31. Further TEM observation shows the surface of TCP:$Eu^{2+}$ is very coarse (Fig. 2c). A lot of pores can be clearly seen in the surface of as-fabricated TCP:$Eu^{2+}$ particles, with size of around 15 nm. The formation of these nanopores could be resulted from the production of nano-bubbles during the reaction between $CaCO_3$ and $NH_4H_2PO_4$ raw materials, because both which decompose and then produce gas ($CO_2$ and $NH_3$) at high temperature. High-resolution TEM (HRTEM) image with the corresponding FFT pattern taken from the selected micro-particle at the edge was shown in Fig. 2d. The interplanar spacings of 0.42 and 0.514 nm correspond to (022) and (040) planes of orthorhombic $Ca_3(PO_4)_2$, respectively. Significantly, selected area electron diffraction (SAED) pattern (Fig. 2e) taken from the circled area on the particle (Fig. 2c) exhibits highly single-crystalline feature, and can be indexed to the orthorhombic structure of $\alpha''$-$Ca_3(PO_4)_2$.

### 3.3. Optical band gap energy

Fig. 3 shows the diffuse reflection spectra (DRS) of undoped, 1.5% and 3.0%$Eu^{2+}$-doped TCP phosphors. The band at about 200 nm belongs to the intrinsic absorption of the host compound. There is no considerable change when some activators are introduced. In comparison with TCP host, the DRS of $Eu^{2+}$ singly doped