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# Phase evolution induced color-tunable emission for Calcium-phosphate based phosphors

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## ABSTRACT

In this paper, color-tunable emission of  $\text{Eu}^{2+}$  doped Calcium-phosphate based phosphors resulted from the phase evolution of luminescent host was demonstrated. Red emission peaked at 675 nm was tuned to blue emission peaked at 480 nm as the Calcium-phosphate luminescent host evolved from  $\text{Ca}_4(\text{PO}_4)_2\text{O}$  (TTCP) to  $\alpha\text{-Ca}_3(\text{PO}_4)_2$  ( $\alpha$ -TCP) by increasing calcination temperature from 1400 °C to 1500 °C. The phase transformation and the resultant color-tunable emission as well as the dependence of emission on phase composition for Calcium-phosphate based phosphors were investigated in detail. The results presented a promising approach to tailor the luminescent properties for phosphors materials by means of phase evolution of hosts.

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## 1. Introduction

Phosphors have been widely developed and applied in lighting, display and labeling [1,2]. Particularly in solid state lighting, abundant phosphor systems were exploited in the past decades, such as aluminate, silicate, sulfide and (oxy)nitride [3–5]. Phosphate hosted phosphors were identified as an important group of luminescent materials due to their excellent thermal stability and charge stabilization, representative by  $\text{NaCaPO}_4:\text{Mn}^{2+}$  [6],  $\text{LiSrPO}_4:\text{Eu}^{2+}$  [7],  $\text{Sr}_8\text{MgLn}(\text{PO}_4)_7:\text{Eu}^{2+}$  (Ln=Sc, Y, La) [8],  $\text{Ca}_9\text{Gd}(\text{PO}_4)_7:\text{Eu}^{2+}$ ,  $\text{Mn}^{2+}$  [9]. Phosphors with color-tunable characters are highly desired to meet the different application requirements. Typical phosphors usually consist of a host and activators, which offer two approaches to tune the luminescent properties through manipulating either the host or the activator. Activator-tuned luminescence could be easily traced for activator species, e.g. a shift of  $\text{Ce}^{3+}/\text{Tb}^{3+}/\text{Mn}^{2+}$  doped in  $\text{Ca}_3\text{YGaO}_3(\text{BO}_3)_4$  leads to diversified emissions of blue/green/red light [10]. The same activator but with varied valence may be also responsible for the color change, e.g.  $\text{Eu}^{2+}$  doped in  $\text{LaAlO}_3$  emits blue light whereas  $\text{Eu}^{3+}$  emits red light [11]. The activator concentration could induce distinct wavelength shift, e.g. emission peak of  $\alpha\text{-Ca}_2\text{SiO}_4:\text{Eu}^{2+}$  phosphor shifts from 560 nm to 650 nm by increasing of  $\text{Eu}^{2+}$  content [12]. Meanwhile, host-tuned luminescence were also widely reported, especially for the phosphors doped with host-sensitive 5d–4f transition activators, such as  $\text{Ce}^{3+}$  or  $\text{Eu}^{2+}$ . The

famous case is the adjustable emission throughout whole visible light range for  $\text{Eu}^{2+}$  in varied composition-structure hosts [13]. Even in a host, luminescence of  $\text{Ce}^{3+}$  or  $\text{Eu}^{2+}$  could be effectively tuned by solid solution modification [14]. Host phase transformation was developed as a facile color-tuning strategies recently, e.g. blue emission of  $\text{Ce}^{3+}$  in  $\beta\text{-Ca}_2\text{SiO}_4$  could be tuned to yellow emission as the host transforms into  $\gamma\text{-Ca}_2\text{SiO}_4$  [15]. As a member of phosphate phosphors, Calcium-phosphate based phosphors were exploited as potential candidates in solid state lighting [16,17]. Particularly, TTCP, TCP and hydroxyapatite (HAP) hosted phosphors were proposed to have promising application prospect in vivo imaging because of their nontoxicity and biocompatibility [18–21]. It was well recognized that Calcium-phosphate based phosphors with color-tunable characters would broaden or heighten its application value in either solid-state lighting or vivo imaging.

Herein, color-tunable emission is demonstrated for Calcium-phosphate based phosphors by carefully controlling the host phase evolution between TTCP and  $\alpha$ -TCP. The phase evolution and the resultant color tunable emission as well as the dependence of emission on phase composition are investigated in detail. The results presented in this work show a promising approach to tailor the luminescent properties of phosphors.

## 2. Experimental

$\text{Eu}^{2+}$  doped Calcium-phosphate phosphors based were prepared by the high temperature solid-state synthesis procedure. Chemicals of  $\text{CaCO}_3$  (99.9%),  $\text{NH}_4\text{H}_2\text{PO}_4$ (99.9%),  $\text{Eu}_2\text{O}_3$  (99.99%) with the stoichiometry of TTCP: 0.03  $\text{Eu}^{2+}$  and 2.5 wt%  $\text{NH}_4\text{Cl}$

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flux were mixed well by using an agate mortar and subsequently subjected to firing at different reaction temperatures of 1400, 1460, 1480 and 1500 °C respectively in a reducing atmosphere of H<sub>2</sub> (8%) and N<sub>2</sub>(92%) for 10 h. X-ray powder diffraction (XRD) patterns were recorded on a Rigaku Ultima-III diffractometer to identify the phase component. Thermogravimetry-differential analysis was obtained on a NETZSCH STA 449C simultaneous thermal analyzer. Photoluminescence (PL) and photoluminescence of excitation (PLE) spectra for phosphor samples were recorded on a Hitachi F-4600 spectrometer. The fluorescence photographs of phosphor particles were taken using a DFM-40C fluorescence microscope. CIE chromaticity coordinates were traced on an EVERINE PMS-50 Plus UV-vis-Near IR spectro-photocolorimeter.

### 3. Results and discussion

Fig. 1(a) presents the XRD patterns of Eu<sup>2+</sup> doped Calcium-phosphate based phosphor samples prepared at different sintering temperatures. It is observed that all the diffraction peaks of sample prepared at 1400 °C can be indexed to standard data of TTCP (JCPDS card no.70-1379). Weak diffraction peaks of  $\alpha$ -TCP phase (JCPDS card no.70-0364) are detected when the calcination temperature up to 1460 °C and tends to be stronger with further temperature increasing. And then  $\alpha$ -TCP phase is identified as the dominant phase when the calcination temperature up to 1500 °C. As the TTCP (Ca/P ratio = 2) phase evolves into  $\alpha$ -TCP (Ca/P ratio = 1.5), the missing Ca will be presented in the form CaO secondary phase. But the existence of CaO is hard to be detected in XRD because of its small amount. The phase content of the prepared phosphor samples is quantitative analysis by an XRD *K*-value method and calculated results show that the content of TTCP phase was in 100%, 82.4%, 66.4% and 8% for the samples fired at 1400, 1460, 1480 and 1500 °C respectively. Fig. 1 (b) shows schematically the crystal structure of  $\alpha$ -TCP and TTCP phases. Phosphorus atoms are tetrahedral coordinated by oxygen atoms in both structure, the formed isolated P–O tetrahedral structures are coordinated by Ca<sup>2+</sup> ions in  $\alpha$ -TCP lattice, while those are coordinated by Ca<sup>2+</sup> and discrete oxygen atoms in TTCP lattice, respectively. The average Ca–O bond for TTCP and  $\alpha$ -TCP lattices was about 2.36 Å and 2.38 Å, respectively, indicating an occurrence of stronger crystal field splitting in TTCP lattice than in  $\alpha$ -TCP lattice.

Fig. 2 depicts the simultaneous TG/DSC measurement for the well mixed raw material before calcination. TG curve displays three mass loss processes at 130, 190 and 750 °C, which is assigned

to the decomposition of NH<sub>4</sub>Cl, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and CaCO<sub>3</sub>, respectively. Three endothermic peaks were recorded at 130, 190 and 750 °C in DCS curve, corresponding to the decomposition processes as mentioned above. Furthermore, endothermic peak at 1160 °C without mass loss is observed, most likely owing to the crystallization reaction of TTCP. It is worth to note that an endothermic peak at 1458 °C is traced in the inset picture. By combing with the XRD results, this endothermic peak may be assigned to the formation reaction of  $\alpha$ -TCP. Transformation temperature from TTCP to  $\alpha$ -TCP was larger than 1600 °C depicted in the CaO–P<sub>2</sub>O<sub>5</sub> binary phase diagram. [22] Lower transformation temperature was observed at 1458 °C in our case owing to the introduction of NH<sub>4</sub>Cl flux.

Fig. 3(a) expresses the PLE and PL spectra of phosphor samples prepared at different firing temperatures. TTCP:Eu<sup>2+</sup> phosphor obtained at 1400 °C presents a broad red emission band peaked at 675 nm pumped by 325 nm. And the dominant  $\alpha$ -TCP:Eu<sup>2+</sup> sample obtained at 1500 °C presents a broad blue emission band positioned at 480 nm. Apparently, the 5*d*–4*f* transition of Eu<sup>2+</sup> activators doped in TTCP/ $\alpha$ -TCP host is responsible for the broad red/blue emissions. The distinguished blue-shift of Eu<sup>2+</sup> emission in  $\alpha$ -TCP host comparing with the emission of Eu<sup>2+</sup> in TTCP host is ascribed to a weaker crystal field splitting effect of TCP lattice owing to the longer average atomic distance of Ca–O bond. Crystal

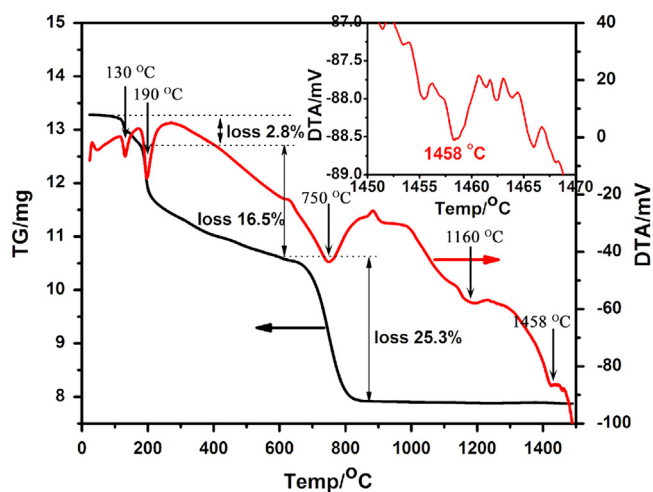


Fig. 2. Simultaneous TG/DSC profiles for the well mixed raw material.

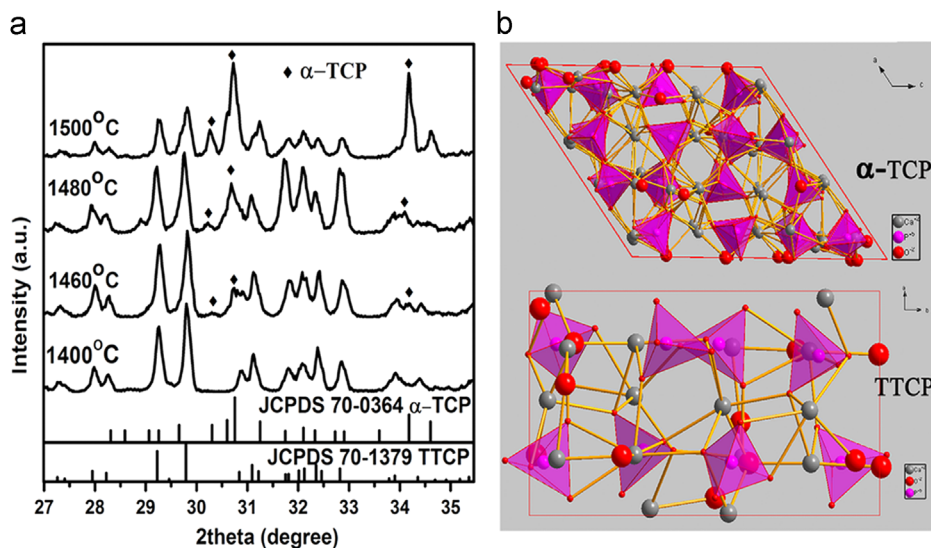


Fig. 1. (a) XRD profiles of samples; (b) crystal structure of TTCP and  $\alpha$ -TCP.

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