# LUMINESCENT PROPERTIES OF CALCIUM HALOPHOSPHATE PHOSPHOR FOR WHITE LIGHT EMITTING DIODE

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Tb<sup>3+</sup> and Eu<sup>3+</sup> activated Ca<sub>5</sub>(PO<sub>4</sub>)Cl phosphors were synthesized by a solid state reaction. From powder X-ray diffraction analysis, Ca<sub>5</sub>(PO<sub>4</sub>)Cl with a hexagonal structure was confirmed. The excitation spectra indicate the phosphor can be excited by near ultraviolet (NUV) light, which makes it attractive for white light emitting diode (WLED) applications. When the phosphor was excited by 394 nm light, it exhibits blue emission, green emission, orange-red emission and red emission at 465 nm, 543 nm, 591 nm and 615 nm, respectively. The phosphor had been found to have chromaticity coordinates of x=0.31 and y=0.28, which was depicted by white near to "ideal white" in chromaticity diagram. The properties shows that Ca<sub>5</sub>(PO<sub>4</sub>)Cl: Eu<sup>3+</sup>, Tb<sup>3+</sup> was a single-phased white-emitting phosphors, which can be excited by NUV chip.

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# 1. Introduction

Since Edison invited incandescent lamp, mankind has entered the bright era. But in the 100 years since incandescent lamp invited, emission efficiency of lamp only increased to 15 lm/W. Incandescent lamp consumes a lot of energy for heating and conversion efficiency of electro-optical is only 10 %. However people are plagued by energy and environment problem now. Many countries want to find illumination source which is energy conservation <sup>[1-3]</sup>. Light Emitting Diode (LED) was invited in the 1960s. It was used as indicator. And blue LED was developed first in the 1990s. The blue LED provided a theoretical possibility of using LED in lighting field. LED was developing fast in lighting field when mankind went into 21 century <sup>[4,5]</sup>. Nearly a decade, with the technology of LED fast developing and emission efficiency improving, and LED especially high-power LED can instead of traditional fluorescent tube light. In addition, the cost of manufacturing the LED is slowly reduced, and the share of the market also increased significantly. LED has been considered the future development trends in next decade <sup>[6,7]</sup>.

WLED have many advantages like small size, low power consumption, fast response, long life and no pollution <sup>[8]</sup>. Based on the above advantages, WLED can be used widely in lighting field. Therefore many developed countries make choice WLED as the first choice of illumination source. WLED have many methods which can be achieved. We can be achieved WLED by red, green, blue chips. But this method is very expensive which is not affordable. People came up another method which is consist of blue chip and yellow fluorescent powder to achieve WLED <sup>[9]</sup>. This method is the most usual in the industry. The defects of this method is instability and low color temperature. Red, green, blue fluorescent powder and UV chip were constituted to achieve WLED which have high color temperature <sup>[10]</sup>. The method also have defected on luminous efficiency and color reduction. In order to avoid the above defects, single white fluorescent powder was prepared which have good luminous efficiency and color reduction <sup>[11-13]</sup>. With respect to other bulk material, phosphate has good thermal, chemical stability and low synthesis temperature. The introduction of chlorine which increased covalent component of the crystal structure further improves the stability

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of the structure. Because of these features, the single white light fluorescent powder has a value of research <sup>[14,15]</sup>.

### 2. Experimental

 $Ca_5(PO4)_3Cl:Eu^{3+},Tb^{3+}$  powder was prepared by a solid-state reaction route. The raw materials used in the synthesis of the phosphor were as follows:  $CaCl_2$  (AR. 99.99%),  $Ca(NO_3)_2$  (AR. 99.99%),  $(NH_4)_2HPO_4$  (AR. 99.99%),  $Eu_2O_3$  (AR. 99.999%),  $Tb_4O_7$  (AR. 99.999%),  $K_2CO_3$  (AR. 99.99%),  $Na_2CO_3$  (AR. 99.99%),  $Li_2CO_3$  (AR. 99.99%). Mix them in the mortar with ethanol as a solvent for mixing. The powder mixture which was mixed well was packed into an alumina crucible and calcined in a resistance furnace. The samples were heated at a high temperature in a range of 900-1200°C for 3-6 h. Then we can get the samples we wanted when the samples were ground evenly.

The measurements of photoluminescence excitation (PLE) and photoluminescence (PL) spectra were performed using a RF-5301PC SHIMADZU fluorescent spectrometer at room temperature. The phase of the product was identified by X-ray diffraction (XRD, Rigaku D/max-2200, Japan) with Cu-K $\alpha$  radiation. We can observe surface of sample by Scanning Electron Microscopy (SEM, Philip Sirion200, Holland).

# 3. Results and discussion

The XRD patterns of  $Ca_5(PO4)_3Cl$  calcined with 3-6 h were shown in Fig. 1. From Fig. 1, it can be observed that the four samples had semblable features and were similar with the Joint Committee on Powder Diffraction Standards (PDF 73-1278). Impurity peak maybe were due to impurities which were leaded into when prepared. When calcination time was 5 h, strength of the impurity peak was lower than others. So the calcination time was chosen 5 h.



Fig.1 XRD patterns of  $Ca_5(PO_4)_3Cl$  samples prepared for different calcination time

The size and morphology of  $Ca_5(PO_4)_3Cl$  phosphor synthesized by solid state reactions calcined at 900-1200°C were observed by SEM. As shown in Fig. 2(a) the size of powder particles calcined at 900°C was not uniform and form was irregular. When the temperature was 1000°C, the powder particles was as same as 900°C which was shown in Fig. 2(b). However the powder particles in Fig. 2(c) which were calcined at 1000°C, we can observe uniform, regular and laminar powder particles. Agglomerated particles were shown in Fig. 2(d). The particles were calcined at 1200°C. From these figures, the size of powder particles were more regular when the temperature rose from 900°C to 1100°C. But when the temperature increased to 1200°C, the crystalline grain grow so big that made the particles bigger. So we chose the temperature was 1100°C.



Fig. 2 SEM images of  $Ca_5(PO_4)_3Cl$ :  $Eu^{3+}$ ,  $Tb^{3+}$  syntheses at different calcination temperature

The effect of doped Eu<sup>3+</sup> concentration on the emission of Ca<sub>5</sub>(PO4)<sub>3</sub>Cl phosphor was investigated first. The emission spectra of Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Eu<sup>3+</sup> phosphors prepared at various concentrations of Eu<sup>3+</sup>(0.5%, 1%, 2%, 4%) under 394 nm excitation were shown in Fig. 3. The emission spectrum of our obtained samples were composed of a series of sharp emission lines, corresponding to transitions from the excited states <sup>5</sup>D<sub>0</sub> to the ground state <sup>7</sup>F<sub>3</sub>:<sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>1</sub>(591 nm),<sup>5</sup>D<sub>0</sub>-<sup>7</sup>F<sub>2</sub>(613 nm). The peak intensity increased with the concentration of Eu<sup>3+</sup> increasing until the maximum intensity reached 1%, and then it decreased due to concentration quenching. At first with the concentration of Eu<sup>3+</sup> increasing, luminescent centers increased which made the PL peak intensity increased. However, the energy went into quenching center when luminescent center was too close as the amount increasing. We can see the best concentrations of Eu<sup>3+</sup> was 1% from Fig. 3.



Fig.3 Emission spectras of  $Ca_5(PO_4)_3Cl$ :  $Eu^{3+}$  with different concentrations of  $Eu^{3+}$ 

Fig. 4 showed the emission of  $Ca_5(PO_4)_3Cl$ :  $Eu^{3+}$ ,  $Tb^{3+}$ , doped with  $Li^+$ ,  $Na^+$ ,  $K^+$  respectively as charge compensator. Charge compensator can improve the stability and fluorescence properties. The PL peak intensity of  $Ca_5(PO_4)_3Cl$ :  $Eu^{3+}$ ,  $Tb^{3+}$ ,  $Li^+$  was higher than others and the PL peak intensity of  $Ca_5(PO_4)_3Cl$ :  $Eu^{3+}$ ,  $Tb^{3+}$ ,  $Li^+$  was the smallest. Because  $Li^+$  had the smallest ionic

radius, it can easy get into the lattice of  $Ca_5(PO4)_3Cl$  and do not effect the lattice drastically. Therefore we chose  $Li^+$  as the charge compensator.



Fig. 4 Emission spectras of  $Ca_5(PO_4)Cl:Eu^{3+}$ ,  $Tb^{3+}$  with different charge compensator ( $Li^+$ ,  $Na^+$ ,  $K^+$ )



Fig. 5 Emission spectras of  $Ca_5(PO_4)Cl:Eu^{3+}$  with different concentrations of  $Tb^{3+}$ 

The emission spectras of Ca<sub>5</sub>(PO4)<sub>3</sub>Cl doped with 1% Eu<sup>3+</sup> and different concentrations of Tb<sup>3+</sup>(0.5%, 1%, 2%, 4%) under 394 nm excitation were shown in Fig. 5. We can see the peaks located at 465 nm, 540 nm, 590 nm, 613 nm. The peaks of 465 nm, 540 nm correspond to  ${}^{5}D_{3} \rightarrow {}^{7}F_{2}$ ,  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  of Tb<sup>3+</sup> and 590 nm, 613 nm correspond to  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ,  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ . The peak which located at 540 nm was small and with the concentrations of Tb<sup>3+</sup>, the intensity of other peaks increased. Tb<sup>3+</sup> transfered energy to Eu<sup>3+</sup>. Considering all PL peaks intensity, we chose the concentrations of Tb<sup>3+</sup> which was 2% as the best.

Fig. 6 illustrated the CIE chromaticity diagram for the emissions of  $Ca_5(PO_4)Cl$ . We can see that the point was located at (0.31, 0.28) which was near to "ideal white" in chromaticity diagram.



Fig. 6 Chromaticity diagram

### 4. Conclusions

In this work,  $Ca_5(PO_4)Cl$  phosphors were synthesized by a solid state reaction method, which had good thermal stability and strong luminescent intensity. The  $Ca_5(PO_4)Cl$  phosphors belonged to hexagonal by XRD and the best calcination time was 5 h. The best calcination temperature was 1100°C through analyzed SEM photos. And the emission spectra was shown that the best charge compensator was Li<sup>+</sup> and the best concentration of doped ions was 1%(Eu<sup>3+</sup>) and 2%(Tb<sup>3+</sup>). Chromaticity coordinates of the  $Ca_5(PO_4)Cl:Eu^{3+},Tb^{3+}$  was located at (0.31,0.28) that was near to "ideal white" in chromaticity diagram. In summary,  $Ca_5(PO_4)Cl:Eu^{3+},Tb^{3+}$  was a kind of promising single phase white light fluorescent powder.

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