



## Synthesis and Photoluminescence of Blue Emitting $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ Phosphor

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**Abstract**— A simple procedure to prepare  $\text{Eu}^{2+}$  activated chlorapatite phosphor  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$  is described. Sample was synthesized by simple low temperature wet chemical method which is efficient than conventional high temperature solid state reaction. Photoluminescence (PL) results showed that the phosphor can be efficiently excited by UV-visible light from 220 to 430 nm, and exhibited bright blue emission around 449 nm when excited by 385 nm near-ultraviolet light. The developed phosphor emits in blue and hence could provide one of the three primary colour components in phosphor converted LED producing white light.

**Keywords**— Solid State Lighting, wet chemical synthesis, blue phosphor, photoluminescence

### 1. INTRODUCTION

Solid state lighting have a very bright future in various lighting applications because of their high energy efficiency and cost effectiveness compared to incandescent bulbs. It has the potential to make much more progress over the coming decade. A very effective way to produce white light from UV/blue LED is by coating on LED suitable phosphors excitable by LED light, so that white light is produced either by mixing of basic colours or complementary colours. Blue is at the short-wavelength (high-energy) end of the visible spectrum, it proved possible to “down convert” blue light into green, yellow and even red light using passive phosphorescent and fluorescent materials [1].

$\text{Eu}^{2+}$  activated phosphors gives bright blue luminescence when excited by near UV radiations.  $\text{Eu}^{2+}$  emission arises from the lowest band of  $4f^65d^1$  configuration to  $8S^{7/2}$  state of  $4f^7$  configuration. The excitation arises from the transition from  $8S^{7/2}$  state of  $4f^7$  configuration to the states belonging to  $4f^65d^1$  configuration. The ground state of  $\text{Eu}^{2+}$  is  $8S^{7/2}$ .

Stoichiometric rare earth phosphates have gained a special attention because of their interesting physical properties, such as optical properties [2, 3]. Several solid solutions of alkaline earth halophosphates like  $\text{Ca}_2\text{PO}_4\text{Cl}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$  are known [4]. The substitution of  $\text{Eu}^{2+}$  for  $\text{Ca}^{2+}$  is facilitated by the similarity in ionic radii. These phosphors are normally synthesized by solid state reaction which requires very high temperature and it is time consuming also. This prompted us to look for alternative method for the synthesis of such phosphors which would be easy, needs low temperature and less time consuming than solid state reaction. In the present work we

synthesized  $\text{Eu}^{2+}$  activated chlorapatite phosphor  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$  and analyzed for photoluminescence.

### 2. EXPERIMENTAL

Sample was prepared by wet chemical method dissolving stoichiometric amount of  $\text{CaCO}_3$ ,  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{Eu}_2\text{O}_3$  in HCl. Excess acid was then boiled off and the solutions were evaporated to dryness. The resulting mass was dried at 475 K for 2 h in air, crushed to fine powder and then annealed for 1 h at 975 K in a reducing atmosphere provided by burning charcoal so as to reduce the activator to divalent state. An alumina crucible containing the compound was placed in another crucible. The annular space was filled with charcoal. A tight fitting lid covered the outer crucible. This treatment was found sufficient to yield bright phosphor exhibiting intense  $\text{Eu}^{2+}$  emission. No nitrogen/ $\text{H}_2$  circulation was needed. The annealed powders were quickly sandwiched between quartz plates and transferred to photoluminescence (PL) cell. Photoluminescence spectra were recorded at the room temperature in the spectral range 220–700 nm on Hitachi F-4000 spectro-fluorimeter with spectral slit widths of 1.5 nm. Samples were also found to be stable against UV irradiation that was used for the PL measurements. No changes in spectral positions or intensities were observed during several, successive PL runs.

### 3. RESULT AND DISCUSSION

As the result is related to PL of  $\text{Eu}^{2+}$ , general features of the emission are first briefly mentioned.  $\text{Eu}^{2+}$  emission arises from the lowest band of  $4f^65d^1$  configuration to  $^8S_{7/2}$  state of  $4f^7$  configuration. The excitation arises from the transition from  $8S^{7/2}$  state of  $4f^7$  configuration to the states belonging to  $4f^65d^1$  configuration. The ground state electronic configuration of  $\text{Eu}^{2+}$  is  $4f^7$ . This results in a  $^8S_{7/2}$  level for the ground state. The next  $f^7$  manifold ( $^6P_j$ ) lies approximately  $28,000 \text{ cm}^{-1}$  higher. The lowest lying

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$4f^65d$  levels begin near  $34,000\text{ cm}^{-1}$  and are labeled  $^8H_J$  for the free ion. The  $4f^65d$  levels experience much more crystal field splitting than the  $4f^7$  levels due to the increased spatial extent of the  $5d$  orbitals and often are the metastable state, or the lowest excited state, when the  $\text{Eu}^{2+}$  ion is incorporated in a crystalline host. The effect of the crystal field of octahedral symmetry on the  $5d$  electron is to split the  $5d$  orbitals into two components  $t_{2g}$  and  $e_g$ . For lesser symmetries, the splitting can be as much as fivefold. The isotropic part of the exchange interaction between  $5d$  and  $4f$  electrons results in an exchange splitting into states with total spins of  $S = 7/2$  and  $5/2$ . Thus for the absorption spectra of  $\text{Eu}^{2+}$  in the solids, the lowest energy band arises from the state described by the notation  $|4f^6(^7F_0)e_g, S = 7/2 > ^{[5]}$ . The lowest energy configuration corresponds to the situation where  $^7F_1(4f^6)$  state couples to the  $5d e_g$  orbital such that all spins are parallel. Spectral positions of these bands vary a great deal from lattice to lattice  $^{[6]}$ . The most commonly observed emission is the dipole and spin allowed  $d-f$  emission starting from the relaxed  $4f^6(^7F_0) 5d^1$  level. Due to allowed nature of the transition,  $d-f$  emission is intense.

Crystal structure of chlorapatite is pseudohexagonal, with monoclinic space group  $P2_1/b$  ( $z = 4$ ,  $a = 9.628(5)\text{ \AA}$ ,  $b = 2a$ ,  $c = 6.764(5)\text{ \AA}$ ,  $\gamma = 120^\circ$ )  $^{[7]}$ . The most significant feature of the monoclinic structure being an ordered arrangement of the Cl atoms above and below  $z = \frac{1}{2}$  on the pseudohexagonal axis.

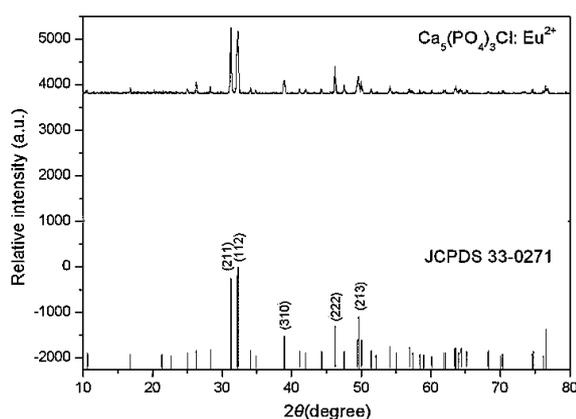


Fig. 1: XRD pattern of  $\text{Eu}^{2+}$  doped  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$

The XRD pattern of the obtained  $\text{Eu}^{2+}$ -doped PL  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$  is shown in Fig. 1. The patterns of calcium apatite suggest the formation of a crystalline  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$  matrix (JCPDS33-0271). PL data of  $\text{Eu}^{2+}$  activated  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$  is included in Fig. 2. Maximum intensity was observed for the sample containing 1mol%  $\text{Eu}^{2+}$ , and quenched from 975 K. For 385 nm excitation, intense

emission is observed with a maximum around 449 nm containing half intensity wavelengths at 428 nm and 478 nm. The excitation curve contains peaks around 341 nm and 297 nm having shoulders around 386 nm.

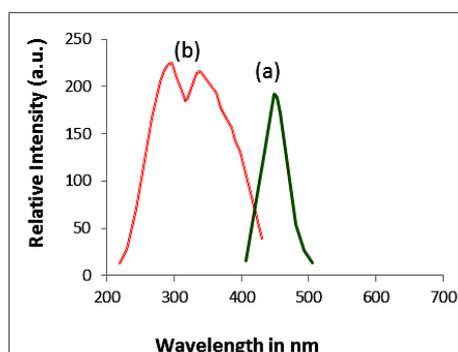


Fig. 2: PL spectra for  $\text{Eu}^{2+}$  activated  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$   
(a) Emission in  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$  for 385 nm excitation;  
(b) Excitation for 449 nm emission of  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$

#### 4. CONCLUSIONS

A simple procedure to prepare  $\text{Eu}^{2+}$  activated chlorapatite phosphor  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$  is described. Phosphates are generally prepared by high temperature Solid State Reaction method which is time consuming and requires very high temperature. In the present work simple Wet Chemical method is used which is time saving and low temperature method. Prepared phosphor gives bright blue emission when excited by near UV radiations. The developed phosphor could provide one of the three primary colour components in phosphor converted LED producing white light.

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