

Photoluminescence Properties Of Eu^{3+} and Ce^{3+} Activated Calcium Chlorophosphate Via Combustion Synthesis Method

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ABSTRACT

Calcium chlorophosphate ($\text{Ca}_2\text{PO}_4\text{Cl}$) phosphors, activated by rare earth ions Eu^{3+} and Ce^{3+} were prepared by urea assisted combustion synthesis technique and their characterization and luminescent properties were studied. The synthesized phosphors were investigated by powdered XRD, SEM and Photoluminescence characterization (PL) methods. PL excitation spectra of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{3+}/\text{Ce}^{3+}$ phosphor exhibit narrow bands in the near ultra violet (n-UV) range, and the PL emission spectra of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{3+}/\text{Ce}^{3+}$ phosphor shows sharp narrow bands typical of rare earth ions. The bands observed in the PL emission and excitation spectra of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{3+}/\text{Ce}^{3+}$ phosphors can be ascribed to the electronic transitions within 4f configurations of rare earth ions. The excitation peaks for $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{3+}$ is in n-UV range. The obtained results suggest that these phosphors may be favorable for lamp industry.

Key-words: Urea Assisted Combustion Synthesis Method, Sem, Xrd Method, N-Uv Range.

INTRODUCTION

Phosphor converted white light emitting diodes (Pc-wLEDs) has attained more significance in current times for their various applications such as flashlights, indicator lights, display backlighting and architectural lighting.^{1,2} It is believed that nUV-LED+RGB luminescent materials can be considered as one of the best methods to produce highly efficient white light.^{3,4}

$\text{Ca}_2\text{PO}_4\text{Cl}$, known as Calcium Chloro phosphate was first investigated by Martha Greenblatt⁵ *et-al.,,,,,,* for its crystal structure. A. Meijerink and G. Blasse have reported the photoluminescence and thermoluminescence

properties of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{2+}$.⁶ Yi-Chen Chiu⁷ has reported the application of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{2+}$ as a guaranteed blue phosphor for white light emission diodes by exciting with near ultra violet light and prepared by solid state reaction. Panlai Li *et al.*, reported $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{2+}$, Mn^{2+} as a novel, warm light emitting phosphor for white LEDs.⁸

The photoluminescence of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Yb}^{2+}$ has been investigated and compared with that of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{2+}$, and the application of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Yb}^{2+}$ for white LED has been evaluated by Di-Yin Wang *et al.*,⁹ A series of Ce^{3+} , Eu^{2+} and $\text{Ce}^{3+}/\text{Eu}^{2+}$ doped $\text{Ca}_2\text{PO}_4\text{Cl}$ phosphors, prepared by a high temperature solid-state method were investigated by Panlai Li *et al.*, and found an increase in the

emission intensity of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{2+}$ without affecting the spectral profile.¹⁰

Hence we are motivated to study $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}$ phosphor, but via a different synthesis route. Combustion synthesis (CS) is another wet chemical method for synthesizing powdered materials.¹¹ Combustion synthesis processes have typical characteristics like high-temperatures, fast heating rates and small reaction times. These characteristics make this a striking method for the creation of technologically functional materials at cheap rates compared to other usual processes.

Therefore we are reporting the luminescence properties of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}$ and Ce phosphors, prepared by urea assisted combustion synthesis method.

Experimental

The chloride based Eu^{3+} and Ce^{3+} activated $\text{Ca}_2\text{PO}_4\text{Cl}$ halophosphor material were prepared by combustion synthesis method. Chemically homogenous, well and untainted powders are prepared by this method. The ingredients used to synthesize this halosulphate phosphor were of AR grade Calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), Ammonium Chloride (NH_4Cl), Ammonium di-hydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), ammonium Cerium nitrate [$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$], Europium oxide (Eu_2O_3) and Urea [$\text{NH}_2\text{-CO-NH}_2$]. The initial materials in the stoichiometric proportion were combined together along with Urea in agate mortar by grinding. The solution of dopant in the nitrate form was then added to homogenous mixture to form a semiliquid paste. The stoichiometric composition of all the components were calculated using the total oxidizing and reducing valencies of the chemicals which serve as the numerical coefficients so that the equivalence ratio is unity. The paste formed is moved to silica crucible and kept inside a muffle furnace operating

at 550°C . Combustion synthesis is a reaction which takes place with the evolution of heat and light. This high temperature plays a vital role in the formation and crystallization of required phosphor material. The mixture when heated rapidly at 550°C started boiling and generating combustible gases. The thin chips of white colored powder in the crucible were then mashed to powdered form. The synthesized host material was characterized for their phase purity and crystalline nature by XRD using PAN-analytical diffractometer. The PL measurement of excitation and emission were recorded on Shimadzu RF-5301PC Spectrofluorophotometer.

Characterization

Structure of compound was established by taking the XRD pattern. The Photoluminescence excitation and emission spectra of the samples were recorded using fluorescence spectrometer RF-5301PC, using a spectral slit width of 1.5nm. The surface morphology was studied by taking scanning electron microscopy photographs.

The XRD pattern of $\text{Ca}_2\text{PO}_4\text{Cl}$ is in agreement with that of JCPDS file No. 72-0010. Calcium chlorophosphate, as reported by Greenblatt⁵ *et al.*, crystallizes in the orthorhombic system with a space group of $Pbcm$,⁷ with four molecules per unit cell. The dimensions of the unit cell are $a = 6.1850 \text{ \AA}$, $b = 6.983 \text{ \AA}$, and $c = 10.816 \text{ \AA}$.⁷ The ionic radii of Ca^{2+} and $\text{Eu}^{3+}/\text{Ce}^{3+}$ are approximately same. Therefore $\text{Eu}^{3+}/\text{Ce}^{3+}$ ions may prefer to occupy Ca^{2+} sites in $\text{Ca}_2\text{PO}_4\text{Cl}$ host lattice.

SEM characterization

The Fig.2 shows SEM images of $\text{Ca}_2\text{PO}_4\text{Cl}$ phosphor. It is clear that the surface morphology is inhomogeneous. The particles are rod like of irregular sizes. The particle size varies from $5\mu\text{m}$ to $10\mu\text{m}$.

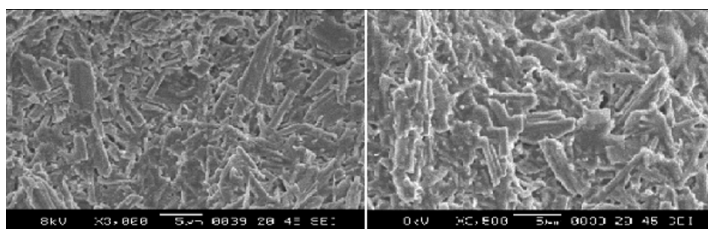


Fig.1: SEM photo graphs of $\text{Ca}_2\text{PO}_4\text{Cl}$ phosphor

RESULT AND DISCUSSION

a. $\text{Ca}_2\text{PO}_4\text{Cl:Eu}^{3+}$

Rare earth ions are identified to be present in a variety of valence states although the trivalent state is the most common.^{7,12} Among rare earth ions, Eu, particularly is known to be steady in both trivalent and divalent states. The excitation spectra for $\text{Ca}_2\text{PO}_4\text{Cl:Eu}^{3+}$ is shown in Fig. 2. The excitation spectra, watched at 620 nm emission wavelength

illustrates a maximum at 396nm which is ascribed to ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition of Eu^{3+} . The sharp excitation bands in the 315 - 450nm region belongs to the intraconfigurational 4f-4f transitions of Eu^{3+} . Two low intensity broad bands peaking at 328nm and 345nm are also seen, which may be due to $4f^7 - 4f^65d$ transitions of the Eu^{2+} ions.¹³ The ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ at 396nm is the strongest absorption. Thus we find that Eu ions dwell in two different sites in the host $\text{Ca}_2\text{PO}_4\text{Cl}$ network.

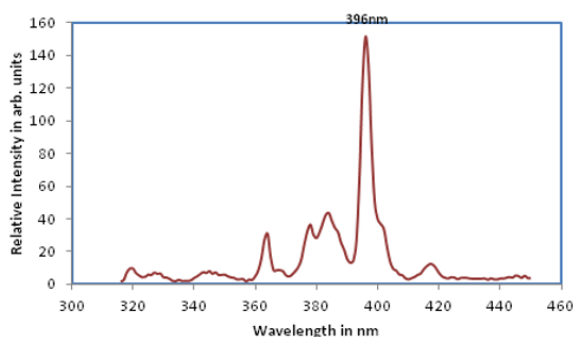


Fig.2: PL Excitation spectra of $\text{Ca}_2\text{PO}_4\text{Cl:Eu}^{3+}$ monitored at 620 nm emission wavelength

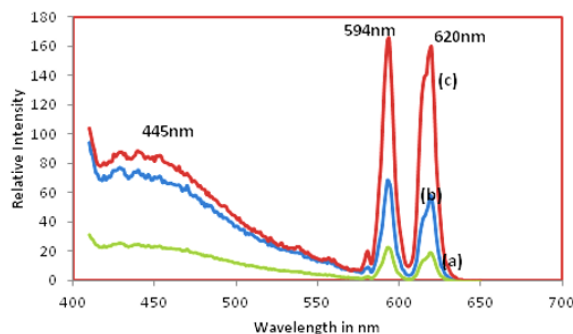


Fig.3: PL emission spectra of $\text{Ca}_2\text{PO}_4\text{Cl:Eu}^{3+}$ monitored at 396nm excitation wavelength. (a) 0.2mol%, (b) 0.5mol%, (c) 1mol%

Upon excitation with 396nm radiation, the emission spectra (Fig.3) consists of two types of transitions one is the broad emission at 440 nm lying in the blue region of visible spectrum, which can be ascribed to the transition from $4f^65d$ excited state to the $4f^7$ ground state of a Eu^{2+} ion. And the second is the sharp intense emissions at 594nm and 620nm which are due to ${}^5\text{D}_0 \rightarrow {}^5\text{F}_J$ ($J=1-4$) of the $4f_6$ configuration of Eu^{3+} . The bands obtained can be represented as: ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (593nm) and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (620 nm). Thus along with Eu^{3+} emission, a

broad emission at around 440 nm attributable to Eu^{2+} emission could be seen in the emission spectra, pointing that the reduction of Eu^{3+} to Eu^{2+} ions is possible to be achieved in this host $\text{Ca}_2\text{PO}_4\text{Cl}$ material. The rare earth ion Eu^{2+} emission is a consequence of two forms of transitions. Commonly the transition is due to $4f_6^5d_1 \rightarrow 4f_7$ (${}^6\text{S}_{7/2}$). As the position of the band corresponding to $4f_65d$ configuration is strongly affected by the host, the emission can stretch out anywhere between 365 nm to 650 nm.¹⁴

The intensity of emission line 594nm assigned to the magnetic dipole ${}^5D_0 \rightarrow {}^7F_1$ (MD) transition of the Eu^{3+} ions is slightly greater than the intensity of emission peak at 620 nm corresponding to the forced (ED) electric dipole ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} . The electric dipole transition $D_0 \rightarrow {}^7F_2$ with $\Delta J=2$ is hypersensitive, and the intensity can vary by the order of magnitude, depending on the neighboring environment.¹⁵ It is recognized that when the Eu^{3+} ions are embedded in a site with inversion symmetry, ${}^5D_0 \rightarrow {}^7F_1$ MD transition of Eu^{3+} is directed, whereas without inversion symmetry the ${}^5D_0 \rightarrow {}^7F_2$ ED transition is the strongest among the ${}^5D_0 \rightarrow {}^7F_J$ ($J=1,2,3,4$) transitions.¹⁶

The result of Eu^{3+} ions concentration on the emission intensity of $\text{Ca}_2\text{PO}_4\text{Cl}$ is studied. The variation of emission intensities of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{3+}$

with different doping concentration of Eu ions can be seen from Fig. 3. The form of the emission curve was same for all the concentrations, but the emission intensity was found to increase with the increase in the Eu doping content. The maximum intensity was for 1mol% concentration of the activator Eu^{3+} ions. No concentration quenching was observed for europium activator ions up to 1mol%.

As the phosphor $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}$, shows three distinct colors due to Eu^{2+} and Eu^{3+} emissions, at 445nm (blue), 544nm (yellow) and 620nm (red), we have calculated the CIE color coordinates to find out the resultant emission color from the spectral distribution of intensity. The CIE color coordinates are found to be (0.310, 0.217) which lies in the white region of the visible spectrum as shown in Fig.4.

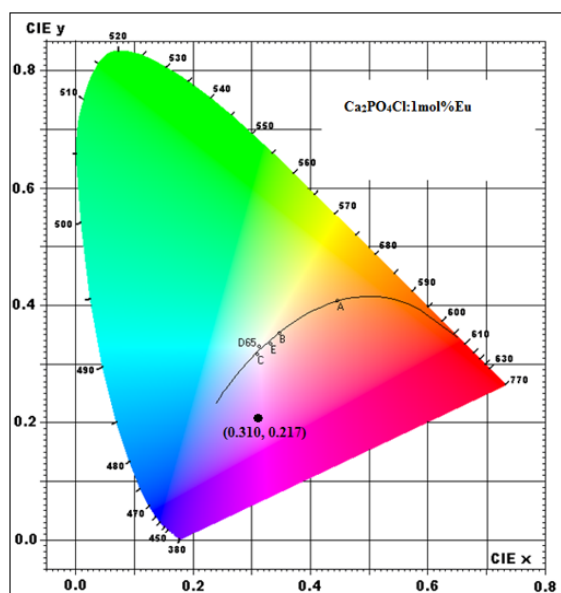


Fig.4: CIE color coordinates of 1mol% Eu^{3+} doped $\text{Ca}_2\text{PO}_4\text{Cl}$ phosphor at 396nm excitation wavelength

b. $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Ce}^{3+}$

Fig. 5 illustrates the photoluminescence excitation (PLE) of Ce^{3+} doped $\text{Ca}_2\text{PO}_4\text{Cl}$ phosphor. As shown in the figure, the excitation spectrum monitored at 360 nm emission wavelength, shows two broad bands centered at 267nm and 316nm, which can be attributed to the crystal field splitting of 5d states of Ce^{3+} .¹⁷

The excitation at 316nm of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Ce}^{3+}$ agrees well with the emission of nUV chips. Fig. 6 shows the emission spectrum at 316 nm excitation wavelength. The emission spectrum shows a broad band which extends between 335 to 400 nm peaking at 360 nm, which can be attributed to characteristic 5d -4f emission of Ce^{3+} . This emission could be utilized in scintillators and photo-therapy. Also it could

act as a good sensitizer in energy transfer process for phosphors. From the emission spectrum we find

that the intensity of emission at 360 nm increases with increase in dopant concentration.

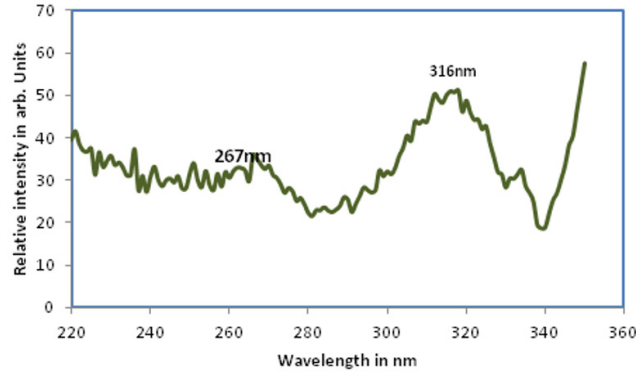


Fig.5: Photoluminescence Excitation spectra of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Ce}^{3+}$ watched at 360 nm emission wavelength

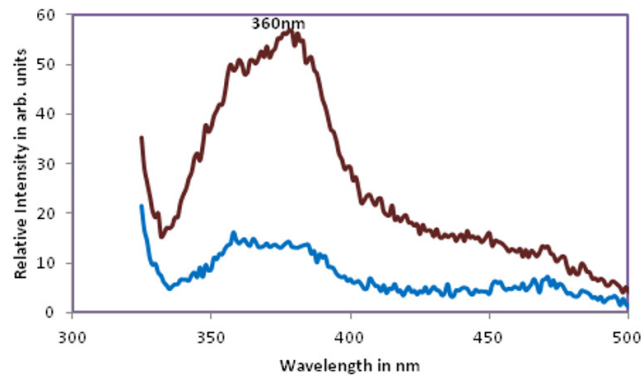


Fig.6: Photoluminescence Emission spectra of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Ce}^{3+}$ monitored at 316 nm excitation wavelength

CONCLUSION

Phosphor $\text{Ca}_2\text{PO}_4\text{Cl}$ activated by rare earth ions Eu^{3+} and Ce^{3+} were synthesized by Urea assisted combustion synthesis procedure. The powdered phosphors were described by XRD and SEM procedures. Phase purity of phosphors was confirmed by XRD. The prepared micro phosphors display good luminescence properties. The $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{3+}$ phosphor exhibit emission in

the white region of the visible spectrum due to three prominent emissions peaking at 445nm, 594nm and 620nm, upon excitation at 396nm wavelength. The CIE color coordinates of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{1mol\%Eu}$ was calculated to be (0.310, 0.217). By changing the dopant concentration, the phosphor $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}$ can be further investigated for its potential application as a white light emitting phosphor for Lamp industry.

REFERENCES

1. Zukauskas A. Kauskas V. *Appl. Phys. Lett.* 2008, 93: 051115
2. Allen S.C, *et al.*, *Appl. Phys. Lett* 2008;
3. Thornton W.A. *J.opt.soc.Am.*61(1971)1155
4. Koedam M., Opstelten J. J., *Lighting Res.* 92:143309

- Technology* .3(1971)205
5. Greenblatt M., Banks E., Post B., *Acta Cryst.* (1967)23,166.
 6. Meijerink A. and Blasse G., *J. Phys. Condens matter* 1990 , 2,3169.
 7. Chiu Y.C., Liu W., Chang C.K, Liao C.C., Yeh Y.T., Janga S.M., Chen T-M, *Journal of material chemistry*, 20(2010) 1755
 8. Panlai Li, Wang Z. , Yang Z., and Qinglin G., *J. Mater. Chem. C*, 2014,2, 7823
 9. Wang D.Y., Chiu Y.C., Huang C. H. , Wu Y. C., Chen T. M., *J. Luminescence* (04) 2014; 148
 10. Panlai Li, Wang Z. , Yang Z., and Qinglin G. *RSC Adv.*, 2014,4, 27708
 11. Patil K.C., Aruna S.T., Mimani T., *Current Opinion in Solid State and Materials Science* 6 (2002) 507
 12. Singh V, Haque MD. M., Kim D.K., *Bull. Korean chem. Soc.* 28(12)(2007)2477
 13. Nguyen H.D., Yeo T.H., Mho S.I., *ECS Trans*, 28(2010) 167
 14. Singh R., Dhoble S.J. *Bull. Mater. Sci.* Vol. 34.No.3(2011) 557
 15. S. Shionaya, *Phosphor Handbook*, CRC Press, Boca 303(1999)110.
 16. Blasse G. Grab Maier B.C. *Luminescent materials*. Berlin:Springer-Verlay 1994
 17. Kodama N, Sasaki N, Yamaga M, Masui Y, *J.Lumin*, 94 (2001) 19