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RESEARCH ARTICLE

Peculiar synthesis and photoluminescence characterization of series of $(Ca_{2-X})PO_4Cl:xEu^{2+}$ phosphor

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Abstract This work describe the synthesis of a series of Europium ion (Eu^{2+}) activated calcium chlorophosphate $Ca_{2-X}PO_4Cl:xEu^{2+}$, $x = 0.01$, 0.015, 0.02, 0.05 and 0.10) phosphors annealed at various temperature. This phosphor is synthesized by wet chemical synthesis. This synthesis method is more efficient than conventional solid state synthesis. The formation of crystalline structure of Ca_2PO_4Cl of the synthesized phosphor is confirmed by X-ray diffraction analysis. The photoluminescence characterization is carried out and optimal Eu^{2+} concentration is determined as 2 mol.%. The excitation spectra of $Ca_2PO_4Cl:Eu^{2+}$ phosphor shows prominent excitation band around 380 nm. Upon excitation at 385 nm, the phosphor emits light in the range 400 nm to 520 nm peaking at 452 nm. The Commission Internationale de I'Eclairage (CIE) chromaticity coordinates of the phosphor are calculated to be $Cx = 0.154$ and $Cy = 0.022$. The PL emission of the prepared phosphor is more intense than commercial $BaMgAl_{10}O_{17}:Eu^{2+}$ BAM phosphor. This phosphor may be a candidate for the application in solid state lighting as blue emitting component.

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Introduction

New age lighting technology, i.e., Solid State Lighting (SSL) has evolved over the years. This technology has been replacing conventional lighting technology due to high energy efficiency, longer lifetime, compactness and cost effectiveness as compared to conventional lighting [1, 2]. It is based on semiconductor LEDs (light emitting diodes), OLED (organic light emitting diodes) for getting white light. Initially, LEDs found applications in simple displays and indicators but by the development of InGaN material system by Amano in the late 1980s [3], LEDs have been used to produce white lighting.

White light can be produced by the combination of red, green and blue phosphors which are coupled to near ultraviolet (n-UV) LED (360–420 nm). The commercially available blue phosphor for near-UV LEDs is $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) that has been intensively studied [4, 5]. However, thermal degradation as well as UV damage are two major problems with BAM:Eu^{2+} which lead to wavelength shift and loss of intensity [6, 7].

Efficiency of red and green phosphors is good but the development of highly efficient blue phosphors for their various applications is still needed. Divalent europium (Eu^{2+}) activated phosphate, halo-phosphate and silicate based compounds are the most promising blue emitting phosphors. Greenblatt et al. [8] reported calcium chlorophosphate Ca_2PO_4Cl (CAP) for the first time. In the 1990s, Blasse et al. reported the photoluminescence (PL) at 4.2 K and thermoluminescence properties of $Ca_2PO_4Cl:Eu^{2+}$ [9]. The luminescence properties, thermal stability and applications

in n-UV LED of blue-emitting $Ca_2PO_4Cl:Eu^{2+}$ ($CAP:Eu^{2+}$) phosphor is reported by Yi-Chen Chiu et al. [10]. Till now, many Eu^{2+} activated phosphate and halo-phosphate phosphors are reported [9–25]. Almost all halo-phosphates have been synthesized by solid state reaction route which requires very high temperature and longer time. This discrepancy prompted the authors 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 method. Recently, $M_5(PO_4)_3Cl$ (M = Ca, Sr, Ba) phosphors were synthesized by a simple wet chemical method are reported [26, 27].

In the present work, we synthesized a series of $(Ca_{2-X})PO_4Cl:xEu^{2+}$ phosphors using wet chemical method and their luminescent properties are discussed in detail. In the context of the excitation band, excellent luminescent properties and cost effective manufacturing, $Ca_2PO_4Cl:Eu^{2+}$ phosphor is a potential candidate for application in n-UV white LEDs.

Experimental

In the present study samples are prepared by wet chemical method. Starting materials used for the preparation of samples are $CaCO_3$, $CaHPO_4$, Eu_2O_3 and HCl. Merk manufactured AR grade materials are used for the synthesis. The samples were prepared by dissolving stoichiometric amount of starting materials in concentrated HCl having molarity 11.32 M (35% assay) for different concentration of Eu. This solution was then heated on magnetic stirrer to boil off excess amount of acid and to get dry compound. This whole process was carried out in a glass distillation assembly which consists of a glass flask placed on hot plate with magnetic stirrer. One neck of the flask is connected to condenser unit, so that the evaporated acid can be cooled and collected in a receiving vessel at the lower end.

The resulting compound was crushed to get fine powder which is further dried at 475 K for 2 h in air, and again crushed to get fine powder. The resulting powder then annealed for 1 h at five different temperatures i.e. 723 K, 773 K, 1023 K, 1073 K and 1173 K under reducing atmosphere provided by burning activated charcoal as described by Gahane et al. [27, 28]. We found highest PL intensity at 1073 K. This process reduced the activator to divalent state. This treatment was found sufficient to yield bright phosphor exhibiting intense Eu^{2+} emission. In this process no nitrogen/H_2 circulation was needed.

These heat-treated samples were quickly sandwiched between quartz plates and transferred to photoluminescence (PL) cell for characterization. The photoluminescence spectra are recorded in the range of 220–700 nm on a Hitachi F-4000 Spectro-fluorimeter under resolution of 1.5 nm.

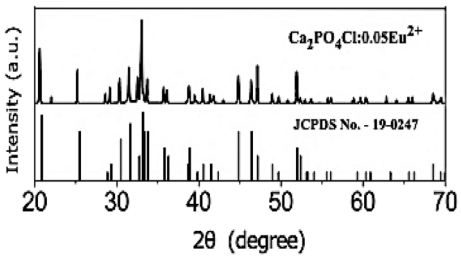

Fig. 1 XRD-pattern of Ca_2PO_4Cl phosphor

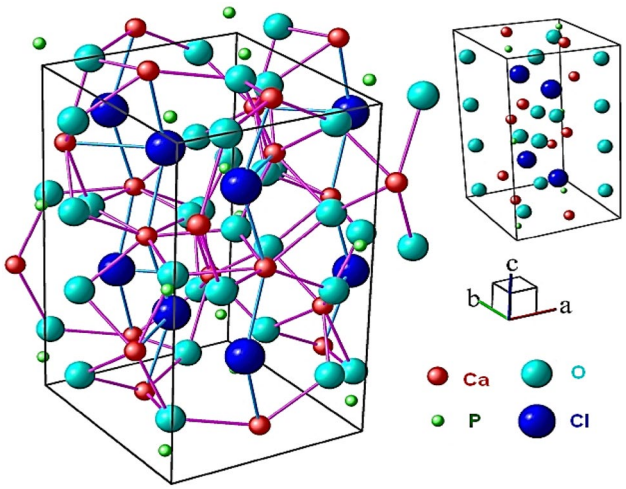

Fig. 2 Unit Cell of Ca_2PO_4Cl with coordination of O–Ca–Cl atoms

The phase purity of the samples was confirmed by powder X-ray diffraction (XRD) analysis with Philips PAN analytical X'pert Pro X-ray diffractometer.

Results and discussion

The XRD pattern of $Ca_2PO_4Cl:0.05Eu^{2+}$ is shown in Fig. 1. The typical XRD pattern obtained is consistent with JCPDS file no 19-0247 that suggests the formation of a crystalline Ca_2PO_4Cl matrix. These results indicate that doping of Eu^{2+} does not generate any impurity phase. Ca_2PO_4Cl has orthorhombic crystal structure with space group of *Pbcm*. It has four formula units per unit cell. The dimensions of the unit cell are $a = 6.1850$ A°, $b = 6.983$ A°, and $c = 10.816$ A° [10]. Ca_2PO_4Cl has the spodiosite structure [8, 29]. In this structure two different crystallographic sites are available for the divalent cation, one with site symmetry C_2 and another with site symmetry C_s. On both sites the cation is coordinated by six oxygen ions and two chlorine ions (Fig. 2). The difference between the two sites is their size. For the larger C_s site the average Ca–O distance is 2.50 A° and the

average Ca–Cl distance is 2.89 A°. For the smaller C_2 site these distances are 2.46 A° and 2.81 A°, respectively [9]. The ionic radius of Eu^{2+} ($r = 1.25$ A° when coordination no = 8) is close to that of Ca^{2+} ($r = 1.120$ A° when coordination no = 8). Since the four-coordinated P^{5+} ($r = 0.17$ A°) site is too small for Eu^{2+} to occupy, the Eu^{2+} was supposed to occupy the Ca^{2+} sites due to size considerations [10, 30].

Eu^{2+} emission and excitation arises from the transition between $4f^6 5d^1$ configuration and the $^8S_{7/2}$ state of the $4f^7$ configuration. 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 the allowed nature of the transition, d–f emission is intense. In some cases, especially in certain fluorides, the position of the band corresponding to the f–d transition lies above f–f levels. The line emission corresponding to the $^6P_j \rightarrow {}^8S_{7/2}$ transitions of the $4f^7$ configuration is then observed [31–34].

The photoluminescence spectra of $Ca_2PO_4Cl:Eu^{2+}$ annealed at different temperatures ranging between 723 and 1073 K were studied and maximum emission intensity was observed at 1073 K as shown in Figs. 3 and 4.

Figures 5 and 6 shows PL intensities of $(Ca_{1-x}Eu_x)_2PO_4Cl$ as a function of doped Eu^{2+} content annealed at 1073 K. Maximum and very intense emission peak was observed for 2 mol.% concentration. The PL intensity was found to decline when the concentration of Eu^{2+} exceeds 2 mol.% showing concentration quenching. For 2 mol.% of Eu^{2+} annealed at 1073 K, the excitation spectrum consists of several overlapping bands near the UV region 350–410 nm; the one around 360 nm being the most prominent. The variation of emission intensity with Eu^{2+} concentration in host material is shown in Fig. 7.

Very intense emission is observed with a maximum around 452 nm under 385 nm excitation. The emission

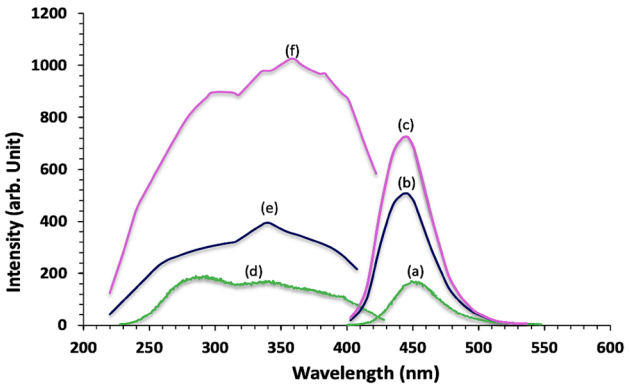

Fig. 3 PL spectra for $Ca_2PO_4Cl:Eu^{2+}$(1 mol.%) **a–c** emission in $Ca_2PO_4Cl:Eu^{2+}$for 380 nm excitation at various reducing temperature. Temperature in °K: **a** 723, **b** 1173, **c** 1073 and **d**, **e** and **f** excitation for 450 nm emission at various reducing temperature 723 °K, 1173 °K and 1073 °K, respectively

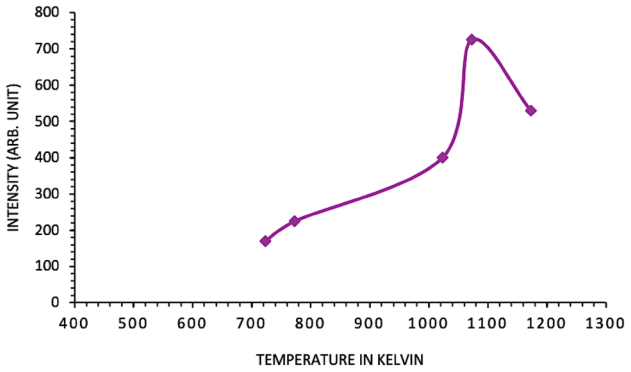

Fig. 4 Variation of PL emission intensity with Annealing Temperature

wavelength of $Ca_2PO_4Cl:Eu^{2+}$ (452 nm) is close to that of $BaMgAl_{10}O_{17}$: Eu^{2+} (BAM) (453 nm) as shown in Fig. 8. However, the emission intensity of $Ca_2PO_4Cl:Eu^{2+}$ was found to be higher than BAM. The full width at half maximum (FWHM) of CAP:Eu^{2+} is about 32.2 nm which is much narrower than BAM (61 nm) reported in the literature [10].

Color quality of the phosphor is described in terms of color rendering index. Figure 9 Shows the Commission Internationale de I'Eclairage (CIE) 1931 chromaticity coordinates of prepared $Ca_2PO_4Cl:2\%Eu^{2+}$ shown by solid red dot. The chromaticity coordinates are $Cx = 0.154$ and $Cy = 0.022$. CIE chromaticity coordinates show that the phosphor emissions is in the blue region. In an earlier work carried out by Chiu et al. [10, 35] studied luminous efficiency and color tunability of the phosphor which is high and excellent for lighting applications. Thus, $Ca_2PO_4Cl:Eu^{2+}$ (2%) prepared in the present study may show high color tunability and luminescence efficiency and may be suitable for applications in solid state white lighting.

Conclusion

A series of $Ca_{2-x}PO_4Cl:xEu^{2+}$ ($x = 0.01$, 0.015, 0.02, 0.05 and 0.10) phosphors is synthesized by wet chemical method. XRD studies confirm the formation of a crystalline Ca_2PO_4Cl matrix. The excitation and emission spectra of the phosphors is broad band due to the $4f^7$–$4f^6 5d^1$ transitions of Eu^{2+}. The $Ca_2PO_4Cl:2\%Eu^{2+}$ phosphor exhibits very intense emission with a maximum around 452 nm under 385 nm excitation. The emission intensity of $Ca_2PO_4Cl:Eu^{2+}$ was found to be higher than commercially available BAM phosphor. CIE 1931 chromaticity coordinates show that the phosphor emissions are in the blue region. It may be used for applications in near-UV phosphor-converted white LED lighting and display devices.

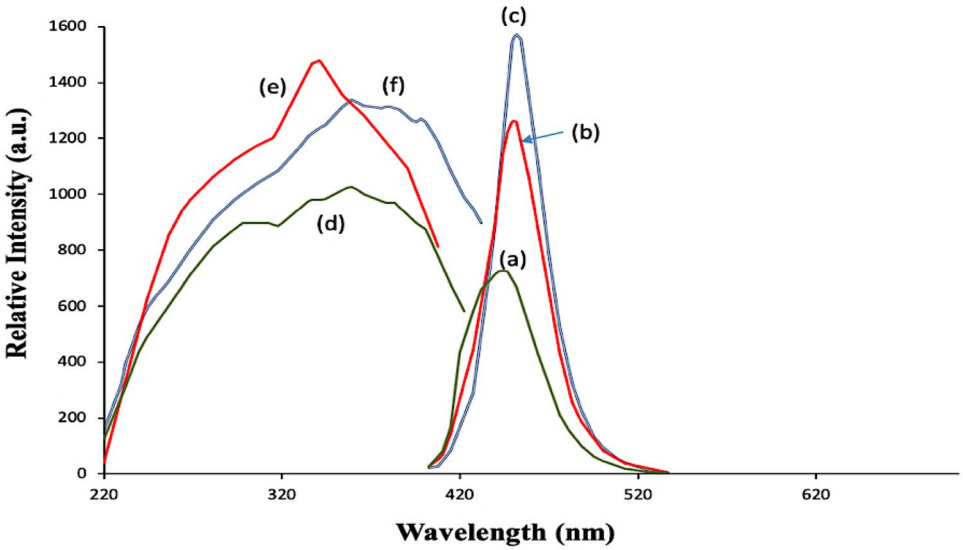

Fig. 5 PL spectra for $Ca_2PO_4Cl:Eu^{2+}$ **a–c** emission in $Ca_2PO_4Cl:Eu^{2+}$for 385 nm excitation for various Eu^{2+} concentrations. Concentrations in mol.%: **a** 1, **b** 1.5, **c** 2 and **d**, **e** and **f** excitation for 450 nm emission for Eu^{2+}concentrations 1, 1.5 and 2 mol.%, respectively

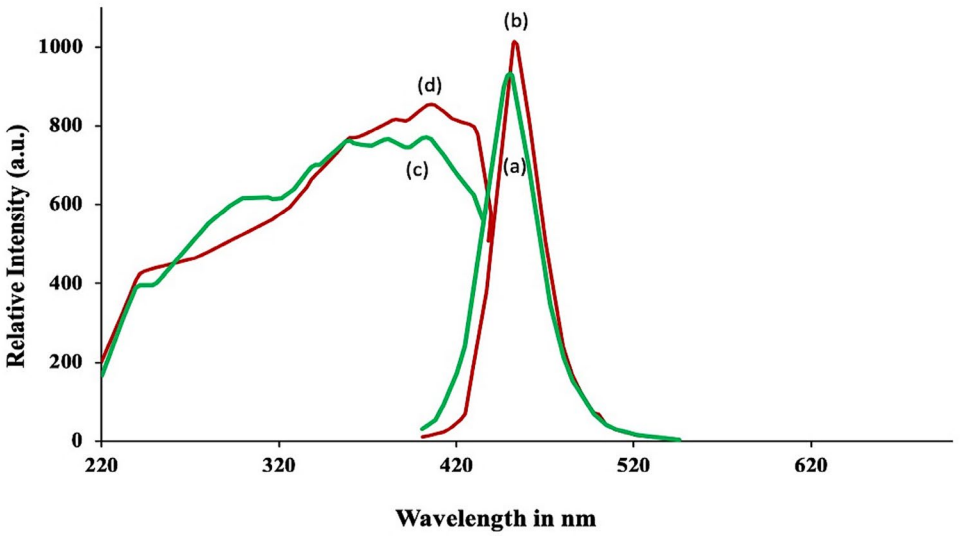

Fig. 6 PL spectra for $Ca_2PO_4Cl:Eu^{2+}$. **a** and **b** emission in $Ca_2PO_4Cl:Eu^{2+}$for 385 nm excitation for 10 and 5 mol.% of Eu^{2+}concentrations, respectively. **c** and **d** excitation for 450 nm and 452 nm emission for Eu^{2+}concentrations 10 and 5 mol.%, respectively

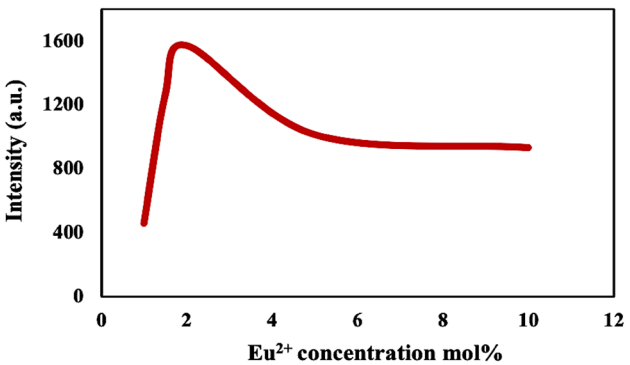

Fig. 7 Variation of the emission intensity with Eu^{2+}concentration

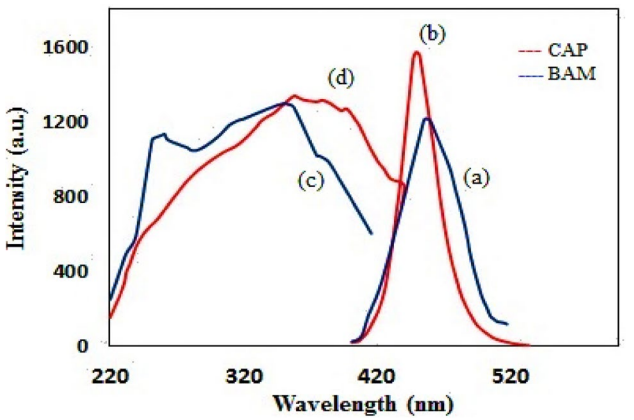

Fig. 8 PL spectra of $Ca_2PO_4Cl:2\%Eu^{2+}$compared with those of the commercial phosphor BAM

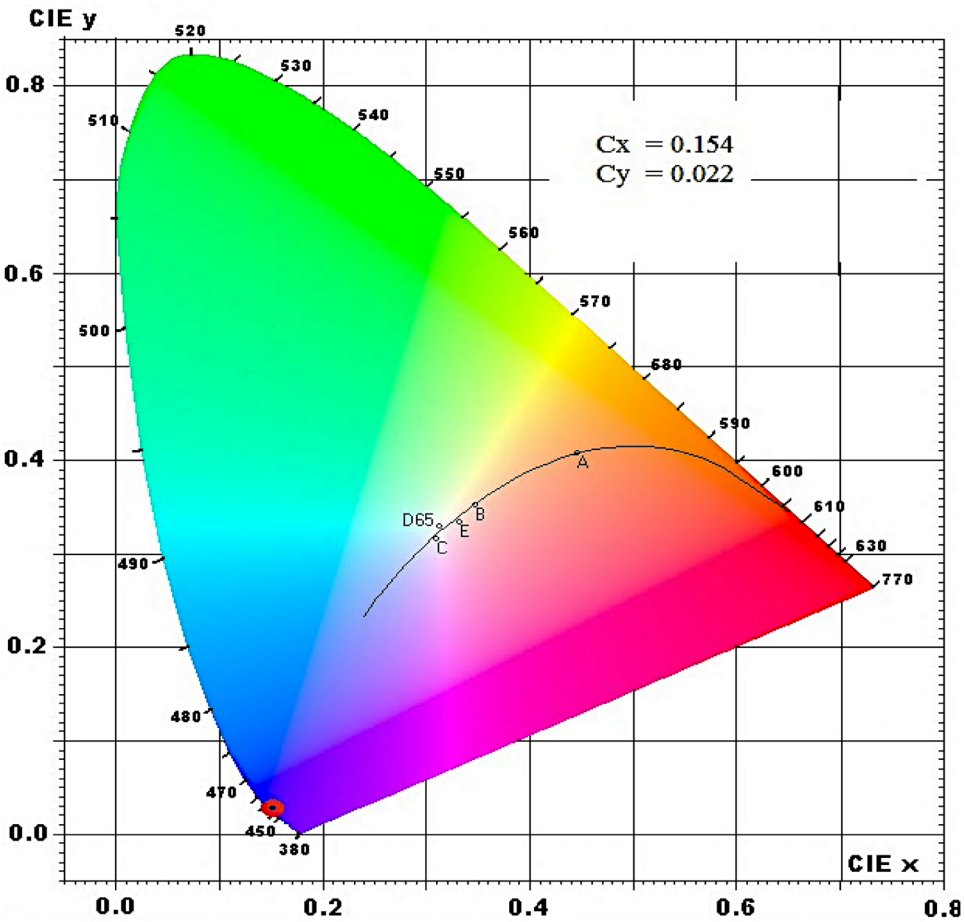

Fig. 9 CIE chromatic coordinates of Eu^{2+}activated Ca_2PO_4Cl

Declarations

Conflict of interest The present work is not funded by any funding agency.

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