On the preparation and photoluminescence of Eu\(^{2+}\)-doped alkaline-earth apatites \(M_5(PO_4)_3Cl\) (\(M = \text{Ca, Sr, Ba}\))

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Abstract

Divalent europium (Eu\(^{2+}\))-doped alkaline-earth apatites \(M_5(PO_4)_3Cl\) (\(M = \text{Ca, Sr, Ba}\)) are prepared by wet chemical synthesis method. Formation of \(Ca_5(PO_4)_3Cl\) and \(Sr_5(PO_4)_3Cl\) is confirmed by X-ray diffraction. Prepared phosphors are analyzed for photoluminescence spectrum. Photoluminescence emission spectrum for \(Ca_{4.95}(PO_4)_3Cl:0.05\text{Eu}^{2+}\) and for \(Sr_{4.95}(PO_4)_3Cl:0.05\text{Eu}^{2+}\) shows bands centered at 449 nm and 446 nm respectively, whereas, the emission peak for \(Ba_{4.95}(PO_4)_3Cl:0.05\text{Eu}^{2+}\) is centered at 437 nm. This shows that emission peak is red-shifted in the order of Ba, Sr and Ca from 437 to 449 nm. All the phosphors showed efficient response in near-UV region. This shows these phosphors can be used as blue phosphor in pLED for solid-state lighting.

Keywords

Photoluminescence · Phosphor · Apatite · LED

Introduction

Alkaline-earth metal halophosphates are generally known as apatites having common formula \(M_5(PO_4)_3X\) (\(M = \text{Ca, Sr, Ba}; X = \text{F, Cl, Br, OH}\)) [1, 2]. McKeag and Ranby discovered alkaline-earth halophosphates as efficient ultraviolet stimulable luminescent materials in 1942 [3]. Apatites are naturally occurring materials which have found applications in imaging, lighting, display, etc., fields. Naturally occurring apatite has hexagonal crystal structure with \(P6_3/m\) space group \((a = b = 9.37\AA, \ c = 6.88\AA\) and \(z = 2\)). Each chloride ion is surrounded by three Ca atoms, and CaO columns are linked with the \(PO_4\) group forming hexagon [4, 5]. Stoichiometric synthetic chlorapatite exhibits the pseudohexagonal structure with monoclinic space group \(P2_1/b\) \((z = 4)\) [6].

Many alkaline-earth halophosphates like \(Sr_5(PO_4)_3Cl\), \(Ba_5(PO_4)_3Cl\), \(Ca_5(PO_4)_3Cl\) are known, prepared by solid state synthesis method [7]. Many of these Eu\(^{2+}\)-doped alkaline-earth halophosphates are used in various applications like fluorescent lamps, projection television tubes, X-ray imaging. Welker et al. [2] reported the use of Eu\(^{2+}\)-doped strontium chlorophosphate (\(Sr_5PO_4)_3Cl\) as a blue phosphor in compact fluorescent lamp. \(Ba_5(PO_4)_3Cl:Eu^{2+}\) can be used for X-ray imaging [8], Zhang et al. [9] synthesized \(Ca_5(PO_4)_3Cl:Eu^{2+}\) using solid-state reaction with excess chloride which showed intense blue emission under nUV excitation. They also fabricated blue and white LEDs with \(Ca_5(PO_4)_3Cl:Eu^{2+}\) phosphor and 395 nm emitting InGaN chips, indicating that the phosphor is a promising blue component for nUV-based white LED. Recently, \(Ca_5(PO_4)_3Cl:Eu^{2+}\) was synthesized by Game et al. [10] by novel Pechini (citrate gel) method and Mungmode et al. [11] by wet chemical method using \((NH_4)_2HPO_4\).

In the present work, we have synthesized a series of Eu\(^{2+}\)-doped \(M_5(PO_4)_3Cl\) (\(M = \text{Ca, Sr, Ba}\)) phosphors using wet chemical method which proved to be efficient than conventional high-temperature solid-state reaction method and their luminescent properties are discussed in detail.
Experimental details

$\text{Eu}^{2+}$-activated $\text{M}_5(\text{PO}_4)_3\text{Cl}$ (M = Ca, Sr, Ba) samples are prepared by wet chemical method dissolving stoichiometric amount of metal carbonates ($\text{CaCO}_3$, $\text{SrCO}_3$, $\text{BaCO}_3$), $\text{CaHPO}_4/\text{SrHPO}_4/\text{BaHPO}_4$ and $\text{Eu}_2\text{O}_3$ in HCl. Excess acid was then boiled off, and the solutions are evaporated to dryness. All starting materials used are AR grade manufactured by Merk. The resulting product was dried at 473 K for 2 h in the air; after this, it is crushed to fine powder. An alumina crucible containing the powder was placed in steel container. The annular space between crucible and container was filled with activated charcoal. A tight fitting lid covered the container. This container was then placed in furnace and samples were annealed for 1 h at temperatures 973 K, 1023 K and 1123 K in a reducing atmosphere provided by burning charcoal so as to reduce the activator to $\text{Eu}^{2+}$ state. This treatment is found sufficient to yield bright phosphor exhibiting intense $\text{Eu}^{2+}$ emission. The heat-treated samples were quickly sandwiched between the fused quartz plates and shifted to the photoluminescence (PL) cell for characterization. The photoluminescence spectra are recorded in the range of 220–700 nm on a Hitachi F-4000 spectrofluorimeter under the spectral resolution of 1.5 nm.

Results and discussion

$\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$

Crystal structure of calcium chlorapatite is pseudohexagonal, with monoclinic space group $P2_1/c$ ($z = 4$, $a = 9.643$ Å, $b = 6.7641$ Å, $c = 2a$, $\alpha = 90^\circ$, $\beta = 120.003^\circ$, $\gamma = 90^\circ$) [12]. The most significant feature of the monoclinic structure is that an ordered arrangement of the Cl atoms above and below $z = \frac{1}{2}$ on the pseudohexagonal axis.

We prepared first sample by using $(\text{NH}_4)_2\text{HPO}_4$ and second sample using $\text{CaHPO}_4$ in place of $(\text{NH}_4)_2\text{HPO}_4$ and studied their photoluminescence comparatively. The XRD pattern of the obtained $\text{Eu}^{2+}$ (1 mol%)-doped $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ (prepared using $\text{CaHPO}_4$) 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 $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ prepared using $\text{CaHPO}_4$ are included in Fig. 2. Maximum intensity is observed for the sample containing 1 mol% $\text{Eu}^{2+}$ and quenched from 1023 K. Upon 385 nm excitation, intense blue emission is observed with a maximum around 449 nm having FWHM equal to 50 nm. The excitation curve contains peaks around 341 nm and 297 nm having shoulder around 386 nm.

Figure 3 presents PL emission and excitation spectra of $\text{Eu}^{2+}$-activated $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ (1.5 mol.% $\text{Eu}^{2+}$) prepared using CaHPO$_4$. a Emission in $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ for 337 nm excitation. b Excitation for 449 nm emission of $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$.
around 295 nm being the most prominent. A shoulder is also observed around 350 nm.

Highly intense PL emission is observed for the phosphor prepared using CaHPO₄ compared to that prepared using (NH₄)₂HPO₄. This may be due to increased crystallinity. Moreover, emission peak is slightly red-shifted to 451 nm when phosphor is prepared using CaHPO₄ as compared to 449 nm when prepared using (NH₄)₂HPO₄. FWHM is also reduced to 43.7 from 50 nm.

Sr₅(PO₄)₃Cl:Eu²⁺

Pentastrontium chloridephosphate Sr₅(PO₄)₃Cl was reported by Sudarsanan et al [14]. They reported that it crystallizes in the hexagonal crystal system with the space group P6₃/m. The lattice parameters are \(a = 9.9641\) (1) Å, \(c = 7.2070\) (1) Å, \(z = \beta = 90^\circ\), \(z = 2\) (Fig. 4) [15]. The Sr²⁺ ions are situated at two crystallographically different sites, the 4f and the 6h positions. At 4f position, Sr²⁺ ions are surrounded by nine oxygen ions, whereas at the 6h position, Sr²⁺ ions have the coordination number 8 (six oxygen and two chlorine ions). The oxygen ions occupy the three Wyckoff positions 6h, 6h, 12i; there is only one position each for P (6h) and for Cl (2b) [14, 16]. XRD pattern for Sr₄.925(PO₄)₃Cl:0.075Eu²⁺ is presented in Fig. 5. It matches with JCPDS file no. 16–0666 confirming the formation and phase purity of the phosphor.

Figure 6 presents photoluminescence spectrum for Sr₅(PO₄)₃Cl: Eu²⁺ (1.5 mol.%). The excitation spectrum of Sr₄.925(PO₄)₃Cl:0.075Eu²⁺ (1.5 mol.% ) for 446 nm emission (Fig. 6, curve d) covers several overlapping bands in near-UV region, one around 360 nm being most prominent, whereas excitation spectrum of Sr₄.75(PO₄)₃Cl:0.25Eu²⁺ (5 mol.% ) (Fig. 6, curve e) covers the wavelength range from UV to visible region and phosphor can be excited efficiently in the region 270–400 nm. This shows that phosphor can be efficiently excited by nUV light which is
useful for SSL application. Figure 6(a) presents PL emission spectra of Sr$_{4.95}$(PO$_4$)$_3$Cl:0.05Eu$^{2+}$ annealed at 973 K under 270 nm excitation. The PL spectrum consists of a weak broad band centered around 446 nm attributed to $4f^65d^{10}→4f^7$ transition of Eu$^{2+}$. The emission intensity increases with increasing Eu$^{2+}$ concentrations. Maximum intensity is observed for Sr$_{4.75}$(PO$_4$)$_3$Cl:0.25Eu$^{2+}$ (5 mol.%) annealed at 1023 K (Fig. 6, curve c). Very intense blue emission peaking at 448 nm is observed. The emission peak is in good agreement with reported value in earlier work (448 nm) [13, 17]. Emission width (FWHM) for Sr$_{4.75}$(PO$_4$)$_3$Cl:0.25Eu$^{2+}$ is 29 nm. Emission peak is slightly red-shifted from 446 to 448 nm with increase in Eu$^{2+}$ concentration.

Ba$_5$(PO$_4$)$_3$Cl:Eu$^{2+}$

Pentabarium chloride phosphate, Ba$_5$(PO$_4$)$_3$Cl, was studied by Hata et al. [18], who reported that it crystallizes in the hexagonal crystal system with the space group P6$_3$/m (Z = 2, $a = 10.284$, $c = 7.651$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$) (Fig. 7).

Figure 8 shows the PL spectrum for Ba$_5$(PO$_4$)$_3$Cl:Eu$^{2+}$. The excitation spectrum (Fig. 8, curve b) is characterized by peak around 270 nm and shoulder around 320 nm attributable to Eu$^{2+}$, thus possessing appreciable response throughout the entire nUV region. Figure 8(a) shows the emission spectra for Ba$_5$(PO$_4$)$_3$Cl:Eu$^{2+}$ (1 mol %) reduced at 973 K. Emission spectra show that strong broad band emission peaking at 437 nm under 270 nm excitation corresponding to a $4f^55d→8S$ allowed electric dipole transition of Eu$^{2+}$.

The results presented show that emission peak is red-shifted in the order of Ba, Sr and Ca from 437 to 449 nm, which is attributed to the crystal field effect. As per the crystal field theory, the crystal field strength is inversely proportional to bond length through the replacement of smaller cations $10^{-Dq}/R^5$, where $Dq$ is the crystal field strength and $R$ is the bond length between a center ion and ligand ions [19]. Therefore, red shift of the emission peak for Eu$^{2+}$ transition is caused by an increase in the crystal field strength due to the replacement of Ba$^{2+}$ with Sr$^{2+}$ and Ca$^{2+}$. Moreover, the emission intensity is also found to increase.

**Conclusion**

Eu$^{2+}$-activated chlorophosphates, viz. Ca$_5$(PO$_4$)$_3$Cl, Sr$_5$(PO$_4$)$_3$Cl and Ba$_5$(PO$_4$)$_3$Cl, are prepared by wet chemical method which is a simple, time-efficient and low-cost synthesis method. Under near-UV excitation, the emission spectra consist of a single blue emitting broad band (437–452 nm). Highest emission intensity is observed for Ca$_5$(PO$_4$)$_3$Cl:Eu$^{2+}$ (1.5 mol% of Eu$^{2+}$). The emission peaks are red-shifted in the order of Ba, Sr and Ca from 437 to 452 nm, which is attributed to the crystal field effect. The phosphors can be efficiently excited by nUV light. Therefore, these phosphors are promising candidates as a blue component for solid-state lighting.

**References**
