National Conference on Recent Trends in Synthesis and Characterization of Futuristic Material in Science for the Development of Society (NCRDAMDS-2018)
In association with
International Journal of Scientific Research in Science and Technology

The Luminescence Properties of Eu^{2+} Doped $Ca_{10}(PO_4)_6Cl_2$ Phosphor

Ashish Akojwar[1], P. K. Naktode[1], K. N. Shinde*[1], N. S. Kokode[2]
[1]N.S. Science and Arts College, Bhadrawati, Chandrapur, Maharashtra, India
[2]N.H. College, Bramhapuri, Chandrapur, Maharashtra, India

ABSTRACT

The blue-emitting phosphors of Eu2+ doped Ca10(PO4)6Cl2 were prepared by combustion synthesis, characterized by X-ray powder diffraction measurement, SEM (Scanning electron microscopy) and Photoluminescence (PL) techniques, has been reported. The luminescence properties were investigated by photoluminescence excitation and emission spectra. The phosphor exhibited the blue luminescence due to the 4f6 5d1 → 4f7 transition of Eu2+ ions under the excitation of near UV light. PL emission spectrum of Eu2+ ion under 353 nm excitation gives PL emission at 456 nm (Blue) due to 4f6 5d transitions. The concentration quenching of Eu2+ ions in the Ca10(PO4)6Cl2 host is determined to be 0.5 mole % , demonstrating CIE chromaticity coordinates of (0.149,0.023). The above results suggest that the Ca10(PO4)6Cl2:Eu2+ phosphor is a promising blue-emitting phosphor for application in near-UV white light-emitting diodes.
Keywords: Combustion synthesis, Luminescence, X-ray diffraction, LED & HaloPhosphate

I. INTRODUCTION

Recent years, rare-earth (RE) activated inorganic compounds have been developed to be efficient luminescence materials in fabricating the white light sources using InGaN based LEDs devices. Nowadays, more and more interest has been focused on the synthesis and luminescence of RE-doped compounds [1-3]. Eu^{2+} activated aluminates, silicates, and phosphates, have been intensively studied for their potential application as white light-emitting diodes (W-LEDs) phosphors [4-8]. White light-emitting diodes (w-LEDs) have great significant attention owing to their satisfactory advantages of energy saving properties, long lifetime, high efficiency as well as high material stability [9, 10]. Because of this, w-LEDs are considered to be potential candidates for the replacement of conventional incandescent and fluorescent lamps and treated as the next-generation solid-state lighting [11-13]. Eu^{2+} activated phosphates were known as a highly efficient blue emitting phosphor for near UV LED excitation [14, 15]. The emission and absorption spectra of Eu^{2+} usually consist of broad band due to transitions between the $^8S_{7/2}$ ($^4f_7$) ground state and the crystal field components of the $4f^65d$ excited-state configuration. Since the 5d orbital involved is external, the position of the energy level and consequently the wavelengths of excitation and emission bands strongly depend on the host crystal [16]. Thus, the host is critical for the luminescence properties of Eu^{2+} ions. Moreover, the Eu^{2+} ion can emit light from UV to infrared with a broad band emitting luminescence on different host matrices since the involved 5d orbital of the Eu^{2+} ion is external and strongly influenced by the crystal field [17]. Due to these excellent properties, Eu^{2+} ion-doped phosphors have been widely studied in LED applications [18-21].

In this present work, the crystal structure, reflectance spectra, and quantum efficiency of blue-emitting $Ca_{10}(PO_4)_6Cl_2:Eu^{2+}$ phosphor is reported, as well as its application in near-UV white light-emitting diodes have been investigated. The white LEDs were fabricated by using an InGaN-based near-UV LED chip (353 nm).

The blue-emitting phosphors of Eu^{2+} doped $Ca_{10}(PO_4)_6Cl_2$ were prepared by Combustion synthesis.

The excitation and emission spectra, the dependence of luminescence on the doping concentration and the temperature were investigated.

II. METHODS AND MATERIAL

The Eu^{2+} activated $Ca_{10}(PO_4)_6Cl_2$ phosphors were prepared via combustion synthesis. The starting AR grade materials (99.99% purity) were taken where Calcium nitrate $(CaNO_3)_2$, Ammonium di-hydrogen phosphate $NH_4H_2(PO_4)$, Europium oxide (Eu_2O_3), Ammonium chloride (NH_4Cl) and urea used as fuel. In the present investigation, materials were prepared according to the chemical formula $Ca_{10-x}(PO_4)_6Cl_2{:}Eu_x$ $(0.1 \leq x \leq 1.0)$. Eu^{2+} ions were introduced as $Eu(NO_3)_3$ solutions by dissolving Eu_2O_3 into dil. HNO_3 solution for the preparation of $Ca_{10-x}(PO_4)_6Cl_2{:}Eu_x$ $(0.1 \leq x \leq 1.0)$ phosphor. After mixing all reagents for about 15 min, mixture was transferred to a furnace preheated at 650^0C and the porous products were obtained. The photoluminescence measurement of excitation and emission were recorded on the Shimadzu RF5301PC spectrofluorophotometer. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. The prepared host lattice was characterized for its phase purity and crystallinity by X-ray powder diffraction (XRD), using a PAN-analytical diffractometer (Cu-Kα radiation).

III. RESULTS AND DISCUSSION

XRD analysis of $Ca_{10}(PO_4)_6Cl_2{:}Eu^{2+}$ phosphor
X-ray diffraction (XRD)

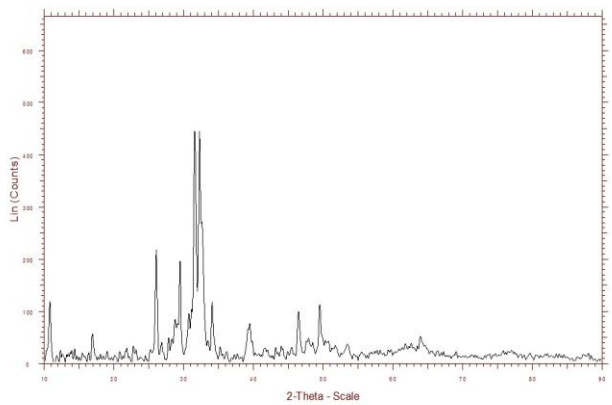

Figure 1. X-ray diffraction (XRD) patterns $Ca_{10}(PO_4)_6Cl_2$ phosphor powder.

The XRD pattern of the powder was recorded on an X-ray diffractometer using Cu-Kα radiation (1.54060 nm) and at a scanning scan step time of 10.3377 s. Figure 1. Show the XRD pattern of $Ca_{10}(PO_4)_6Cl_2$ prepared at 650 °C combustion synthesis. However, the obtained diffraction peaks of these compounds did not match any data in the JCPDS base after careful comparison with the reported compounds, considering that the starting materials were weighed according to the given chemical compositions of the $Ca_{10}(PO_4)_6Cl_2$ matrix, they are thereby named as $Ca_{10-x}(PO_4)_6Cl_2{:}Eu_x$ $(0.1 \leq x \leq 1.0)$ phosphor in this paper. The XRD pattern did not indicate presence of the constituents like, $(CaNO_3)_2$, NH_4H_2 (PO_4), (NH_4Cl_2), Eu_2O_3 and other likely phases, for the obtained phase, it was carefully observed that there were no peaks of raw materials. It was found that the main phase did not agree with any JCPDS data available. These results indicate that the final product was formed in crystalline and homogeneous form. Prepared compounds XRDs data are not available in the standard JCPDs file. However, some new diffraction peaks also emerged, which were characteristic diffraction peaks for the prepared samples but could not be attributed to any known compounds.

Scanning electron microscopy (SEM):-

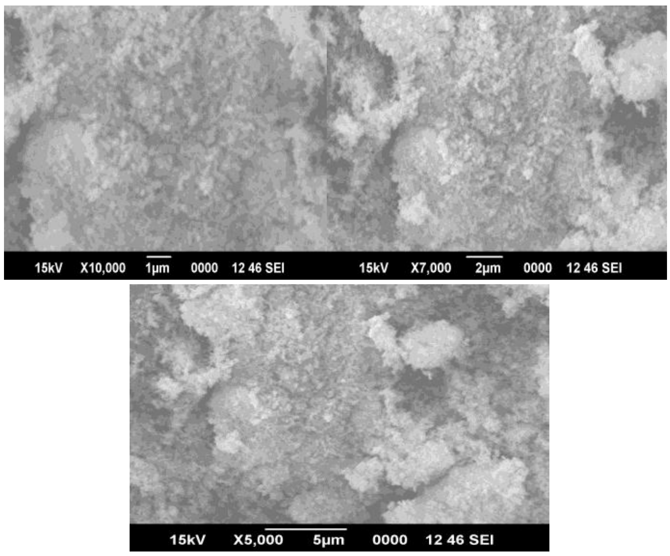

Figure 2. SEM patterns of $Ca_{10}(PO_4)_6Cl_2$: Eu^{2+} phosphor powder.

The particle size distribution of the phosphor is an important factor for its application in WLEDs. SEM photographs of $Ca_{10}(PO_4)_6Cl_2$: Eu^{2+} phosphors clearly shows that the grains are irregular shaped particles with a size 1-5 µm. This shows that the combustion reactions of the mixtures took place well. The typical morphological images are represented in Figure 2**.** The particles possess foamy like morphology formed from highly agglomerated crystallites. An average crystallite size is in sub-micrometer range of $Ca_{10}(PO_4)_6Cl_2:Eu^{2+}$ phosphors. The size distribution is about 1-5 μm with some agglomeration. This is a suitable size for fabrication of solid-state lighting devices.

Photoluminescent properties of $Ca_{10-x}(PO_4)_6Cl_2$: Eu_x^{2+} ($0.1 \le x \le 1.0$)

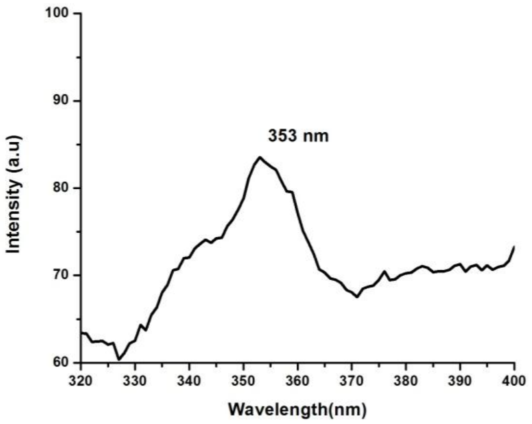

Figure 3. Excitation spectrum $Ca_{10}(PO_4)_6Cl_2$: Eu^{2+} phosphor monitored at 456 nm

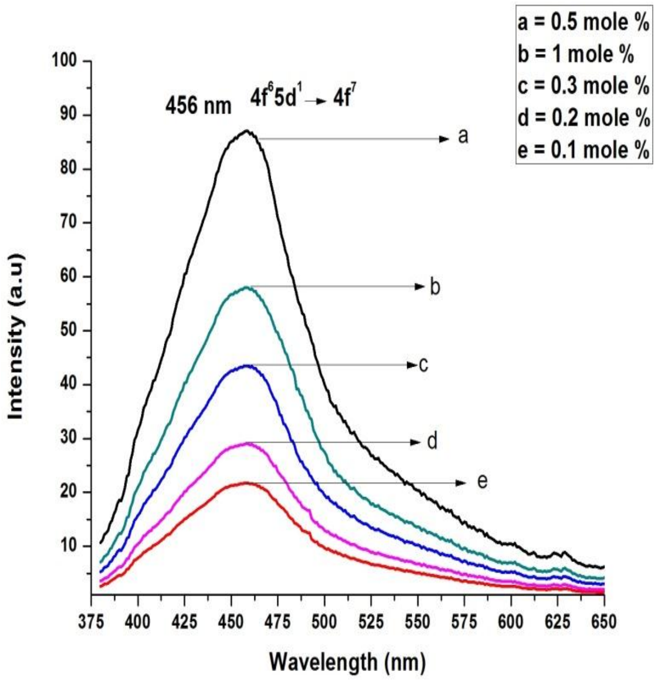

Figure 4. Emission spectra of $Ca_{10-x}(PO_4)_6Cl_2$: Eu_x^{2+} phosphor
($0.1 \le x \le 1.0$) (excited at 353 nm).

PL measurements were performed at room temperature, using a Shimadzu RF5301PC Spectrofluorimeter equipped with a 450 W xenon lamp, in the range from 200 to 700 nm, with spectral width of 1.5 nm. Prepared phosphors for W-LED meet the basic requirement that exhibits a bright emission under the excitation of near-UV light. Thus, the excitation and emission spectra of the prepared phosphors $Ca_{10}(PO_4)_6Cl_2:Eu^{2+}$ were studied in order to assess their potential to be used for near-UVLED based W-LEDs. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of phosphor prepared are shown in Figure 3. The broad bands in the PLE (λem = 456 nm) spectra of phosphors, which are due to the transition from $^8S_{7/2}$ ($4f^{\ 7}$) ground state of Eu^{2+} to the $4f^65d^1$ excited state [22]. The band is located at around 353 nm, which matches well with the emission of commercially available near- UV LED chips. The bright blue emission band with peak at about 456 nm is observed in the PL (λex = 353 nm) spectra of this phosphors, which could be attributed to the typical $4f^65d^1$ ($t2g$) → 4f 7 ($^8S7_{/2}$) transition of Eu^{2+} [23] .

The concentration of activator has an impact on the performance of a phosphor. Therefore, it is important to determine the composition of the $Ca_{10}(PO_4)_6Cl_2:Eu^{2+}$ phosphor with optimal PL emission intensity. A series of $Ca_{10-x}(PO_4)_6Cl_2$: Eu_x^{2+} ($0.1 \le x \le 1.0$) phosphors with various Eu^{2+} content x was prepared and studied for the effect of activator concentration. The emission spectra of $Ca_{10}(PO_4)_6Cl_2:Eu^{2+}$ phosphor (λex =353 nm) with different activator concentration are shown in Figure 4 .

No obvious changes were observed for all the samples in our experimental wavelength range, except the fact that the emission intensity of phosphor increases with the increase in Eu^{2+} concentration and reaches the maximum at 0.5 mole % then concentration quenching occurs as the concentration of Eu^{2+} shown in Figure 5. This type of quenching may be attributed to the fact that energy transfer between two identical ions occurs because the average distance between the activator ions becomes short enough for the energy to migrate [24]. The excitation spectrum is at 353 nm and it is properties of LED lighting and gives the emission in blue region and this phosphor may be good candidates for white LED lighting.

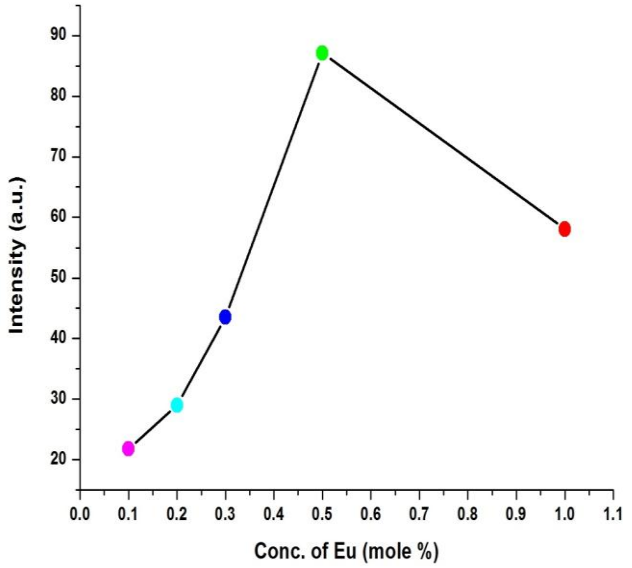

Figure 5. Variation in the PL intensity due to Eu^{2+} ion concentrations

Chromatic properties:

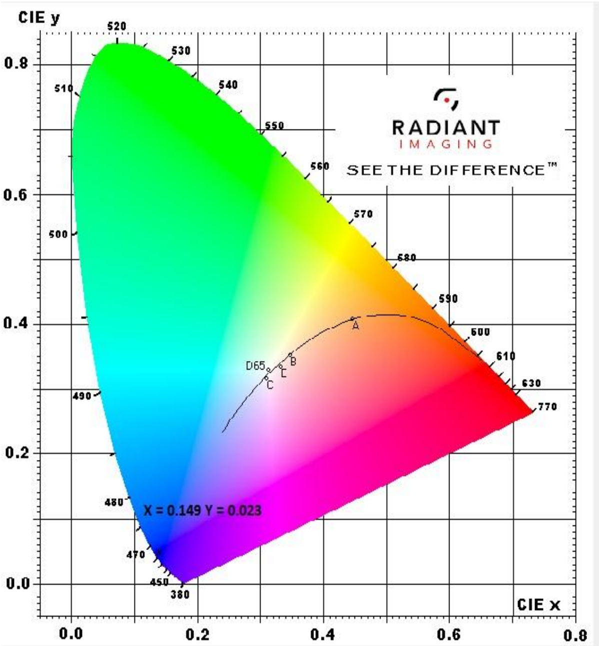

Figure 6. CIE chromatic diagram showing the coordinates $Ca_{10}(PO_4)_6Cl_2:Eu^{2+}$ phosphor

By using 1931 CIE chromatic colour coordinates are specified lighting that recognize human visual system uses three colours red, green and blue [25,26]. In this system the light sources are represented by (X, Y) coordinates and coloured are compared with 1931 CIE diagram. The colour purity was compared to the 1931 CIE Standard Source C (illuminant Cs (0.3101, 0.3162)). The chromatic coordinates (x, y), was calculated using the colour calculator program radiant imaging [27]. In this article the coordinates of Eu^{2+} are doped $Ca_{10}(PO_4)_6Cl_2$ Phosphor are located (X = 0.149,Y = 0.023) as shown in Figure 6 indicates that the colour properties of the phosphor powder prepared by combustion method is approaching those required for field emission displays. The dominant wavelength is the single monochromatic wavelength that appears to have the same colour as the light source. This result indicates that high colour purity of this $Ca_{10}(PO_4)_6Cl_2:Eu^{2+}$ halophosphate phosphors because it is slightly near to the edge of the CIE diagram. Hence, such material may be an efficient photoluminescent material for solid-state lighting phosphors as a blue component, and helpful in generating white light with a particular ratio of this phosphor.

IV. CONCLUSION

In conclusion, a series of Eu^{2+} doped $Ca_{10}(PO_4)_6Cl_2$ blue emitting phosphors was synthesized by combustion method. Photoluminescence measurements showed that Eu^{2+} doped $Ca_{10}(PO_4)_6Cl_2$ synthesized by this method exhibits intensive blue wide band emission with maximum intensity at 456 nm under near-UV excitation. Both blue and white LEDs can be fabricated by pre-coating the above synthesized phosphors onto 353 nm emitting In-GaN chips. Moreover, the strong absorption of phosphor in the range of 300 nm to 410 nm makes this Eu^{2+} activated chlorapatite phosphor a potential candidate as a blue component (one of the three primary color components) for fabrication near-UV based phosphor is good candidate for white light LED application.

V. REFERENCES

[1]. X. Zhang, J.S. Kim, Appl. Phys. A: Mater. Sci. Process.97, (2009) 549.

[2]. Gan, Y. Huang, L. Shi, X. Qiao, H.J. Seo, Mater. Lett.63, (2009) 2160.

[3]. H.S. Jang, Y.H. Won, S. Vaidyanathan, D.H. Kim, D.Y.Jeon, J. Electrochem. Soc. 156, (2009) J138.

[4]. J.S. Kim, P.E. Jeon, J.C. Choi, H.L. Park, S.I. Mho, G.C.Kim, Appl. Phys. Lett. 84, (2004) 2931.

[5]. W.J. Park, Y.H. Song, J.W. Moon, D.S. Jang, D.H. Yoon,J. Electrochem.Soc. 156, (2009) J148.

[6]. J.K. Park, M.A. Lim, C.H. Kim, H.D. Park, J.T. Park,S.Y. Choi, Appl. Phys. Lett. 82, (2003) 683.

[7]. X. Zhang, B. Park, J. Kim, J. Lee, J. Choi, J. Lumin. 130,(2010) 117.

[8]. X. Zhang,W. Li, H.J. Seo, Phys. Lett. A 373, (2009) 3486.

[9]. W. R. Liu, C. H. Huang, C. P. Wu, Y. C. Chiu, Y. T. Yeh and T. M. Chen, J. Mater. Chem.21, (2011) 6869.

[10]. X. Li, J. D. Budai, F. Liu, J. Y. Howe, J. Zhang, X.-J.Wang and Z. Pan, Light: Sci. Appl.2, (2013) 50.

[11]. N. Zhang, C. Guo, J. Zheng, X. Su and J. Zhao, J.Mater.Chem.C 2, (2014) 3988.

[12]. K. Li, J. Xu, X. Cai, J. Fan, Y. Zhang, M. Shang, H. Lianand J. Lin, J. Mater. Chem.C 3, (2015) 6341.

[13]. Y. Li, J. Wang, W. Zhou, G. Zhang, Y. Chen and Q. Su,Appl. Phys. Express, 6, (2013) 082301.

[14]. Z.C. Wu, J.X. Shi ,J. Wang , M.L Gong, Q.J Su, SolidState Chem 179, (2006) 2356.

[15]. Y.S.Tang, S.F. Hu, C.C. Lin, N.C. Bagkar, R.S. Liu.Appl Phys Lett 90,(2007) 151108.

[16]. P. Dorenbos, J. Lumin. 104, (2003) 239.

[17]. X. Lan, Q. Wei, Y. Chen and W. Tang, Opt. Mater.34,(2012) 1330

[18]. P. Pust, V. Weiler, C. Hecht, A. Tucks, D. Wiechert, C.Scheu, P. J. Schmidt & W. Schnick, Nat. Mater.13,(2014) 891.

[19]. Z. C. Wu, H. H. Fu, J. Liu, S. P. Kuang, M.-M. Wu, J. G.Xuand X. J. Kuang, RSC Adv.5, (2015) 42714.

[20]. S. Yu, Z. Xia, M. S. Molokeev, H. Miao and V. V. Atuchin,ECS J. Solid State Sci. Technol.3, (2014) R159.

[21]. J. Zheng, L. Ying, Q. Cheng, Z. Guo, L. Cai, Y. Lu and C. Chen, Mater. Res. Bull.64, (2015) 51.

[22]. S. J. Gwak, P. Arunkumar and W. B. Im, J. Phys. Chem. C, 118 (2014) 2686

[23]. J. Yu , C. Guo , Z. Ren , J. Bai , Opt. Laser Technol. 43,(2011) 762.

[24]. G. Blasse , B. Grabmaier , Springer, Berlin, 1994.

[25]. Stringfellow GB, Craford MG. Academic Press;(1997) 48.

[26]. Shionoya S, Yen WM. Phosphor handbook. Phosphor Research Society, CRC Press; (1998) 459.

[27]. Color Calculator version 2, software from Radiant Imaging Inc; 2007.