

Project Report on

# Lanthanide based Phosphor materials for White LEDs

By  
Onkar Kumar Das

Under the guidance of

**DR. V. SIVAKUMAR**

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**DEPARTMENT OF CHEMISTRY**  
**NATIONAL INSTITUTE OF TECHNOLOGY**  
**ROURKELA – 769008**  
**ODISHA**

**Abstract:** Semiconductor based white light-emitting diodes (WLEDs) are considered as a new class of lighting sources due to their excellent properties over the incandescent lightings. Currently the major challenges in WLEDs research are to achieve high luminous efficacy, high chromatic stability, brilliant color-rendering properties, and price cheapness against fluorescent lamps, which rely critically on the phosphor properties. In recent years, several efforts have been made to develop single-phase white-light-emitting phosphors for near-ultraviolet or ultraviolet excitation to solve the above challenges with certain achievements. There are several methods available to achieve the same, however here efforts have been made to understand the white light emission in a single-phase host by doping a single rare earth ion ( $\text{Eu}^{3+}$  or  $\text{Eu}^{2+}$ ) into appropriate single-phase host.

**Key words:** Luminescence, Phosphor, LED.

### **Introduction:**

Generally the light emitting diodes are monochromatic by nature, generating white light from LEDs can be realized by several general approaches, (i.e) (1): mixing individual red-green-blue (RGB) LED combinations to generate white light; and (2): a single InGaN-based blue ( $\sim 465$  nm) or near-UV (NUV: 370 ó 410 nm) LED chip coated with one (i.e. yellow emitting) or more (i.e. green-red and blue-green-red emitting for blue- and NUV-LEDs, respectively) phosphors that down-convert some of the emission to generate white light by mixing.

### **Phosphor:**

A phosphor, most generally, is substances that exhibit the phenomenon of luminescence. The term phosphor means "light bearer". In general, a phosphor is a solid that converts certain types of energy into electromagnetic radiation over and above the thermal radiation. In order to get the desired wavelength (color), phosphors are synthesized doping with transitional ions like Mn, Bi and rare earths like Eu, Tb, Ce etc.

### **Literature review on Phosphor materials for White LEDs:**

Hua Yu, *et al.*, reported the synthesis and luminescent properties of  $\text{Eu}^{2+}$ -activated,  $\text{Ba}_2\text{Ca}(\text{PO}_4)_2$ :  $\text{Eu}^{2+}$  phosphor for solid state lighting by using a conventional solid state reaction [1]. By using

X-ray powder diffraction (XRD) and FT-IR spectroscopic analysis confirmed the phase formation. The Electron paramagnetic resonance (EPR) analysis of the synthesized phosphor indicated that there are three different crystallographic  $\text{Ba}^{2+}$  sites, namely, Ba(1), Ba(2) and Ba(3), occupied by the  $\text{Eu}^{2+}$  ions. The broad excitation spectra observed between 250 and 470 nm, which is attributed to the  $4f^7 \rightarrow 4f^65d^1$  transition of the  $\text{Eu}^{2+}$  ions. The emission spectra show broad emitting band from 400 to 700 nm, which were attributed to the  $4f^65d^1 \rightarrow 4f^7$  transition of the  $\text{Eu}^{2+}$  ions. The decay curve is a single exponential distribution because the radiative time and phonon relaxation rate are identical for all the  $\text{Eu}^{2+}$  ions. With increasing  $\text{Eu}^{2+}$  concentration, the emission peak wavelength red shifted from 457 to 500 nm, and the color hue can be tuned from a greenish blue to a yellowish green. The white LED fabricated by using InGaN chip and synthesized phosphor [2]. The EL spectral bands are located at about 410, 525, and 625 nm with purple, greenish - blue and red bands, respectively. The white LED has CIE color coordinates of (0.3249, 0.3421) at a white light ( $T_c = 6020$  K), an excellent  $R_a$  of 93 and a luminous efficiency of  $31 \text{ lm W}^{-1}$ . D. Kim, *et al.*, reported the synthesis of a blue-emitting  $\text{LaOCl}:\text{Eu}^{2+}$  phosphor by using solid-state reaction [3]. XRD results and PL measurements for synthesized phosphor indicate a preferred orientation along the [001] direction, which results in the blue-emission associated with the spectral characteristics of  $\text{Eu}^{2+}$ . The excitation spectra at 426 nm, consist of broad bands between 250 nm and 420 nm, which may be due to the  $4f^7(^8S_{27}) \rightarrow 4f^65d^1$  transitions of  $\text{Eu}^{2+}$  [466]. The formation of red-emission due to  $\text{Eu}^{3+}$  appears in a non-oriented one. These reveal that  $\text{Eu}^{2+}$  ions are exclusively stabilized into the (00l) oriented  $\text{LaOCl}$  crystal lattice because the excitation and emission spectra of the blue-emitting synthesized phosphor consist of the spectral characteristics of  $\text{Eu}^{2+}$ . The line spectrum with the red emission centered at 617 nm is observed, which is related to the  $^5D_0 \rightarrow ^7F_2$  transition of  $\text{Eu}^{3+}$ . Emission intensity is raised with increasing  $\text{Eu}^{2+}$  concentration until the maximum intensity at  $x = 0.01$  is observed, and then it is decreased due to the concentration quenching. The CIE chromaticity index ( $x = 0.151$ ,  $y = 0.048$ ) with high color saturation indicates that it is a promising candidate as a blue-emitting phosphor for white light UV-LEDs.

Le Zhang, *et al.*, reported the synthesis and photoluminescence of  $\text{Eu}^{3+}$ -activated double perovskite  $\text{NaGdMg}(\text{W}, \text{Mo})\text{O}_6$  for a potential red phosphor for solid state lighting [7]. The host material has high efficiency absorption, high doping concentration for many rare earth ions and

intense emission with different colors. The white LEDs require red phosphors excited by blue or near ultraviolet (NUV) LED chips [8]. The double perovskite structure host  $A_2BMO_6$  ( $A = Sr, Ba$ ;  $B = Ca, Mg$ ;  $M = W, Mo$ ) could effectively transfer energy to the activator ions ( $Eu^{3+}$ ) and then generate intense red emission [9]. However, the principal transition of  $Eu^{3+}$  ions in this lattice is  ${}^5D_0 \rightarrow {}^7F_1$  (594 nm). A novel double perovskite  $NaGdMgWO_6$  was first selected as the host to obtain the electric dipole transition (615 nm) of  $Eu^{3+}$  due to the lower symmetry of A-site. A great luminescence enhancement of  $Eu^{3+}$  will occur if CTB shifted to the NUV region.  $MoO_6$  is used to substitute  $WO_6$  to tune the CTB of the tungstate host because of the isomorphism effect. In XRD, the appearance of (001) and (111) peaks confirmed the layered ordering of A-site cations [10]. The diffuse reflection spectra of synthesized phosphor and excitation spectra monitored the  ${}^5D_0 \rightarrow {}^7F_2$  transition (615 nm). With the increase of Mo content, the CTB gradually shifted to the long wavelength and reached 386 nm at  $x = 0.5$  but then shifted back when  $x > 0.5$  due to the damage of perovskite. The luminescence intensity of  ${}^5D_0 \rightarrow {}^7F_2$  reached the maximum when  $x = 0.5$ . The replacement of W with Mo increases the distance between  $WO_6$  and increases the electron delocalization of  $WO_6$  [11]. The charge transfer from O to W/Mo easily occurs due to the decrease of energy gap. A lower excitation energy will lead to the charge transfer occur. Therefore, the red shift of CTB was observed. The quantum yield was about 58.4%.

Zhi Zhou, *et al.*, reported the synthesis of  $Ba_3LiMgV_3O_{12}: Eu^{3+}$  phosphor for white LED using solid state reaction method [12]. The XRD (015) peak shift from  $27.38^\circ$  for the sample sintered at  $700^\circ C$  to  $27.16^\circ$  for the sample sintered at  $800^\circ C$  was observed. The peak shift indicates there is an increase in lattice spacing as sintering temperature was increased. At  $800^\circ C$  the synthesized phosphor obtained single phase, the same crystal structure with  $Ba_3V_2O_8$ . The excitation and emission spectra exhibit that the excitation band distributes between 260 nm and 395 nm and peaks at 343 nm, emission band covers from 400 nm to 600 nm and centers at 500 nm, respectively. The emission band peaks at 613 nm originated from charge transfer transitions from  $Ba_3LiMgV_3O_{12}$  host to doped  $Eu^{3+}$  ions can be observed when the  $Eu^{3+}$  ions doped into the host. The PL intensity of synthesized phosphor varied with  $Eu^{3+}$  doping concentration and the optimized PL intensity was obtained when  $x=0.05$ . It was also found that the peak emission intensity of the samples varied with sintering temperature. The combination of intrinsic  $VO_4^{3-}$  emission and  $Eu^{3+}$  emission sensitized by  $VO_4^{3-}$  gives a white emission spectrum with

reasonable color temperatures and good CRI for general lighting. White light can be obtained with coordinate of (0.312, 0.321) from the fabricated light emitting diodes (LEDs) with the doped content of  $\text{Eu}^{3+}$  ions at 5.0 mol%. These indicate that this phosphor is a good candidate as a single-phase white light phosphor in fabrication of phosphor-converted W-LEDs.

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