



# REVIEW ON THE PHOTOLUMINESCENCE PROPERTIES OF RARE-EARTH ACTIVATED PHOSPHORS FOR LED APPLICATIONS

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## ABSTRACT

A vast majority of the host materials activated by rare-earth ions were found to be potential candidates as phosphors for light emitting diodes (LEDs). Many of these phosphors were able to tune the emission color by varying the concentration of the dopant rare-earth ions in them. This paper gives a review on the photoluminescence properties of some rare-earth activated phosphors that are suitable for LED applications.

**Keywords:** LED, phosphor, rare-earths, photoluminescence.

## I. INTRODUCTION

Recently, white light emitting sources based on LEDs have gained huge commercial interest owing to their numerous benefits such as high energy efficiency coupled with lower energy consumption, longer operating lifetime and environment-friendly usage [1,2]. Consequently, the research on novel materials for LEDs has also gained momentum.

Several inorganic phosphor materials based on phosphates, borates, nitrides, silicates, garnets and aluminates have been researched for their usability in LED devices. Of them, YAG:Ce phosphors are the most commercially used yellow-emitting phosphors that produce white light when coupled with blue-emitting LED chip [3–5]. Several approaches have been made to fabricate white light emitting diodes (WLEDs) [6]. One method is to blend the light emitted by red, green and blue LEDs (RGB LEDs) or use RGB phosphors pumped by NUV LEDs. Another way is to use a blue LED to pump a yellow phosphor, as in case of YAG:Ce. The third approach is to produce a single-phase white-light emitting phosphor that can be

pumped by a NUV LED. Phosphors have become a key element in LED technology and researchers are currently trying to develop novel materials that could meet the requirements of an LED device. In this review, we shall discuss the luminescence properties of some novel LED phosphors that are activated with rare earth ions.

## II. SOME NOVEL MATERIALS

### A. $M_2Si_5N_8:Eu^{2+}$ (M = Eu, Sr, Ba) phosphor

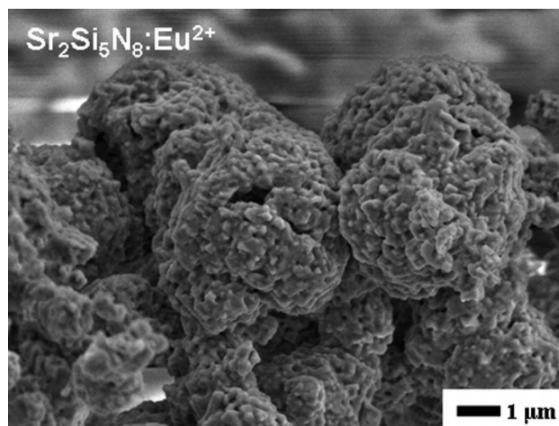


Figure 1: SEM image of  $Sr_2Si_5N_8:Eu^{2+}$  (Reproduced with permission from Ref. [7], copyright 2008, American Chemical Society).

Zeuner *et al.* [7] employed a novel synthesis method wherein metal amides  $M(NH_2)_2$  were employed to synthesize highly efficient nitridosilicate  $M_2Si_5N_8:Eu^{2+}$  (M = Eu, Sr, Ba) phosphors at low temperatures. The metal ions were dissolved in supercritical ammonia at 150 °C and 300 bar to produce precursors for the synthesis. The high reactivity and thermal decomposition feasibility of amides have contributed largely in the synthesis of these nitridosilicates. This has also enabled the

lowering of synthesis temperature to about 570 K and tailoring of the crystal morphology. The use of dopant europium in the form of amides has led to the formation of smooth spherical particles, thus, leading to higher light extraction efficiency. Figure 1 shows the SEM image of  $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ . Further, these nitridosilicates bear covalently bound nitrogen that coordinates with the  $\text{Eu}^{2+}$  ions and alkaline earth ions. The strong nephelauxetic effect is produced by such an arrangement result in low energy emission and excitation bands for these compounds.

### B. Blue-emitting $\text{Ba}_3\text{Si}_5\text{O}_{13}:\text{Eu}^{2+}$ nanophosphor

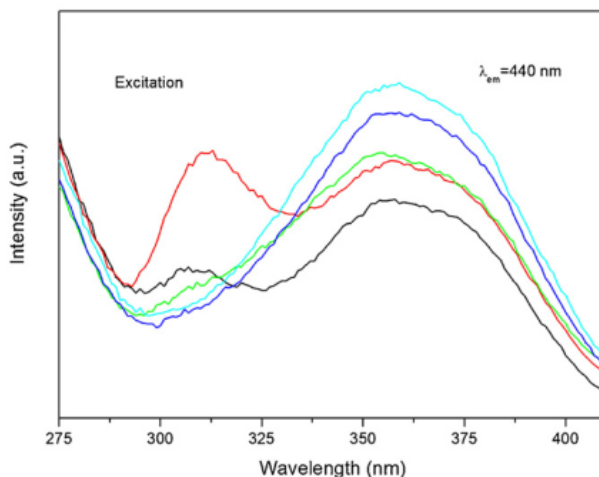


Figure 2 : PL emission spectra of  $\text{Ba}_3\text{Si}_5\text{O}_{13}:\text{Eu}^{2+}$  nanophosphor (Reproduced with permission from Ref. [8], copyright 2012, Elsevier).

$\text{Ba}_3\text{Si}_5\text{O}_{13}:\text{Eu}^{2+}$  nanophosphor was synthesized by Lue *et al.* by employing hydrothermal synthesis method [8]. Tetraethyorthosilicate (TEOS) was used as the precursor for Si. By varying the ratio Ba:Si, the size and morphology of this nanophosphor was tailored. The photoluminescence emission spectra of these nanophosphors show a broad band extending from 400 nm to 625 nm. The emission peak is centered at 440 nm. As shown in Figure 2. An asymmetric nature was observed for the emission spectra and this means that there are two or more peaks in the emission spectra. The  $\text{Ba}_3\text{Si}_5\text{O}_{13}$  structure has three types of Ba sites and  $\text{Eu}^{2+}$  ions can occupy any or all of these Ba sites to form luminescence centers. On monitoring the emission wavelength at 440 nm, the excitation spectra were recorded and it extends from 300 to 400 nm with two distinct peaks at 310 nm and 360 nm.

### C. $\text{BaLu}_6(\text{Si}_2\text{O}_7)_2(\text{Si}_3\text{O}_{10}):\text{Ce}^{3+},\text{Tb}^{3+}$ phosphor

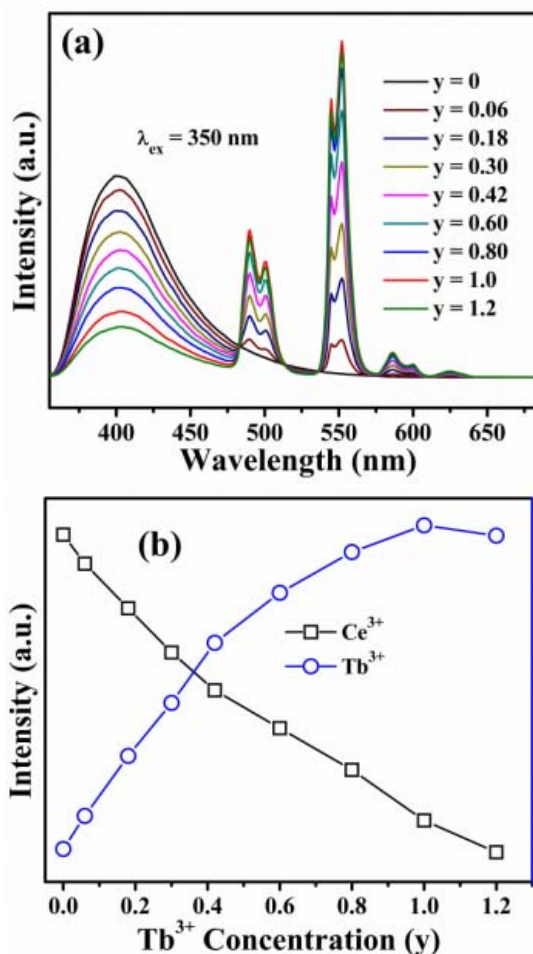


Figure 3: (a) Variations of emission spectra of  $\text{BaLu}_6(\text{Si}_2\text{O}_7)_2(\text{Si}_3\text{O}_{10}):\text{Ce}^{3+},\text{Tb}^{3+}$  phosphors and (b) their corresponding emission intensities (Reproduced with permission from Ref. [9], copyright 2016, Elsevier).

Li *et al.* synthesized a novel blue-green emitting  $\text{BaLu}_6(\text{Si}_2\text{O}_7)_2(\text{Si}_3\text{O}_{10}):\text{Ce}^{3+},\text{Tb}^{3+}$  phosphor via the high-temperature solid-state reaction method [9]. The photoluminescence emission spectra illustrated an asymmetric broad band extending from 365 nm to 550 nm, when the phosphor is excited by 350 nm. This emission spectra is found to overlap with the excitation bands of  $\text{Tb}^{3+}$  singly-doped  $\text{BaLu}_6(\text{Si}_2\text{O}_7)_2(\text{Si}_3\text{O}_{10})$ . The emission bands of  $\text{BaLu}_6(\text{Si}_2\text{O}_7)_2(\text{Si}_3\text{O}_{10}):\text{Tb}^{3+}$  were located in the green region. However, these emission bands showed ten-fold increase in the intensity for the  $\text{Ce}^{3+}$  codoped samples. The energy transfer taking place from  $\text{Ce}^{3+}$  to  $\text{Tb}^{3+}$  ions are held responsible for such an increase. As shown in Figure 3, it is possible to tune the emission color from blue to green by

keeping the concentration constant for  $\text{Ce}^{3+}$  ions and varying for  $\text{Tb}^{3+}$  ions. The thermal stability of  $\text{BaLu}_6(\text{Si}_2\text{O}_7)_2(\text{Si}_3\text{O}_{10})\text{:Ce}^{3+},\text{Tb}^{3+}$  phosphor is satisfactorily good with an activation energy of 0.250 eV.

#### D. $\text{Dy}^{3+}$ - activated $\text{REVTa}_2\text{O}_9$ (RE = Y, La, Gd) phosphor

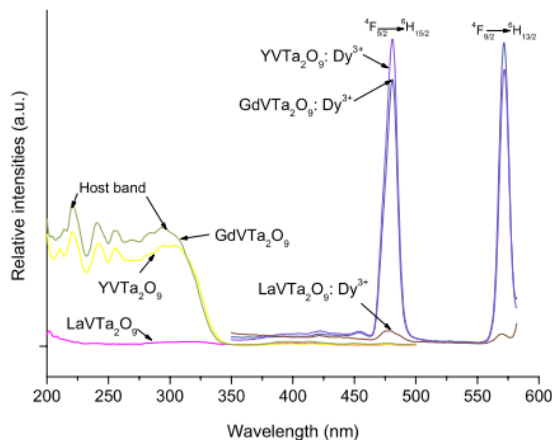


Figure 4: PL excitation and emission spectra of  $\text{Dy}^{3+}$  doped  $\text{REVTa}_2\text{O}_9$  (RE = Y, La, Gd) phosphor (Reproduced with permission from Ref. [10], copyright 2007, Springer-Verlag).

$\text{Dy}^{3+}$  is one of the good activators which exhibits narrow emission bands in blue region (480 nm) and yellow region (580 nm) corresponding to  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_j$  ( $j = 13/2, 15/2$ ) transition.  $\text{Dy}^{3+}$  doped materials can produce white light by tuning the yellow to blue (Y/B) intensity ratio. Thus,  $\text{Dy}^{3+}$  doped luminescent materials play a key role as potential white-emitting phosphors [11,12]. Xiao *et al.* has introduced a novel method for preparing  $\text{Dy}^{3+}$  doped  $\text{REVTa}_2\text{O}_9$  (RE = Y, La, Gd) [10]. In this method, complex aromatic carboxylic acid was used as rare earth species, which coordinates with rare earth and form polymer of infinite chain structures. Such hybrid precursor in chain structure produces material in low temperature which is able to control the morphology of particle and facilitate dispersion of different metals. The PL excitation and emission of  $\text{Dy}^{3+}$  doped  $\text{REVTa}_2\text{O}_9$  (RE = Y, La, Gd) phosphors can be seen in Figure 4. Excitation spectra for  $\text{YVTa}_2\text{O}_9$  and  $\text{GdVTa}_2\text{O}_9$  is nearly the same, except for  $\text{LaVTa}_2\text{O}_9$  that strong absorption band in short ultra violet region but weak luminescence intensity as compared to the former two. The emission spectra consist of narrow bands at 483 nm and 573 nm

corresponding to the  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$  and  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$  transitions, respectively.

#### E. $\text{Tb}_2(\text{MoO}_4)_3$ nanophosphor

$\text{Tb}_2(\text{MoO}_4)_3$  nanophosphor was synthesized by Mani *et al.* using sol-gel method [13]. In general,  $\text{Tb}^{3+}$  ions are doped in certain host materials to produce green light emission. However, in this case, terbium is itself a part of the host matrix. The energy band gap of  $\text{Tb}_2(\text{MoO}_4)_3$  nanophosphor is found to be 3.4 eV, as derived from the diffuse reflectance spectrum. Its TEM and HRTEM images showed high crystallinity with spherical particles having 30-35 nm size. The PL excitation spectrum shows highly intense peaks at 485 nm and 376 nm. Thus, a NUV- or a blue-LED chip can be used to efficiently excite the  $\text{Tb}_2(\text{MoO}_4)_3$  nanophosphor. The emission spectra, obtained by exciting the phosphor at 376 nm and 485 nm, are shown in Figure 5. The PL emission spectra is found to exhibit a similar profile when the  $\text{Tb}_2(\text{MoO}_4)_3$  nanophosphor is excited by 376 nm and 485 nm. The emission spectra consist of peaks at 490 nm, 545 nm, 600 nm and 619 nm. Among these, the most intense peak is found at 545 nm and it is extremely intense in comparison to other emission peaks.  $\text{Tb}_2(\text{MoO}_4)_3$  nanophosphor gives a stable and efficient green emission with CIE chromaticity coordinates (0.31, 0.55). Thus, it is a potential green-emitting phosphor for WLEDs.

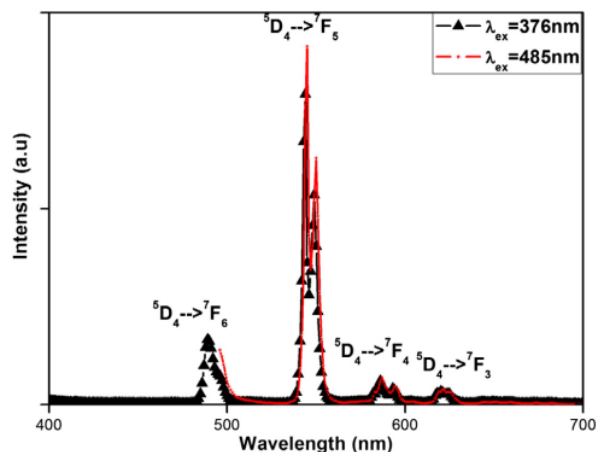


Figure 5: PL emission spectra of  $\text{Tb}_2(\text{MoO}_4)_3$  nanophosphor (Reprinted with permission from Ref. [13], copyright 2015, Elsevier).

### F. Color-tunable $\text{Ba}_5\text{Zn}_4\text{Y}_8\text{O}_{21}:\text{Eu}^{3+}$

Dalal *et al.* synthesized a novel color tunable  $\text{Ba}_5\text{Zn}_4\text{Y}_8\text{O}_{21}:\text{Eu}^{3+}$  nanophosphor by urea-assisted solution combustion method [14]. The combustion-synthesized  $\text{Ba}_5\text{Zn}_4\text{Y}_8\text{O}_{21}:\text{Eu}^{3+}$  nanophosphor crystallized in a pure tetragonal phase. From its SEM image, the particle morphology is found to be semi-spherical and ellipse-shaped. The particle size was determined to be in the range from 60 to 90 nm from the TEM image and this was theoretically confirmed using Scherrer's equation. From the first principle calculations, the density of states and the electronic band structure of  $\text{Ba}_5\text{Zn}_4\text{Y}_8\text{O}_{21}$  host were determined. The band gap ( $E_g$ ) was found to be 2.872 eV and this was found to be suitable for  $\text{Eu}^{3+}$  doping to produce luminescence.  $\text{Ba}_5\text{Zn}_4\text{Y}_8\text{O}_{21}:\text{Eu}^{3+}$  nanophosphor showed a versatile luminescence emission.

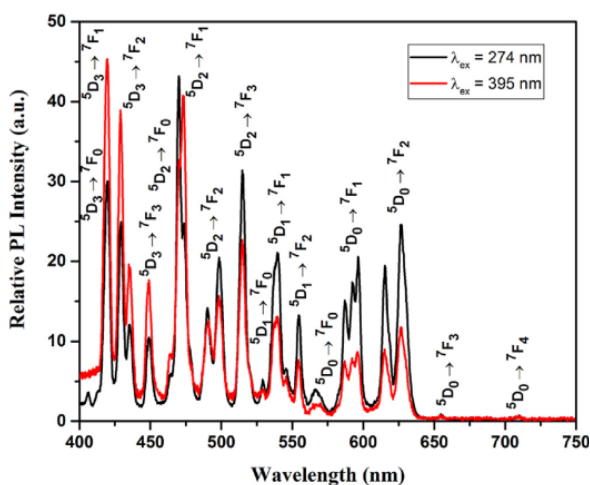


Figure 6: Emission profile of  $\text{Ba}_5\text{Zn}_4\text{Y}_{7.92}\text{Eu}_{0.08}\text{O}_{21}$  nanophosphor for excitation wavelengths 274 nm and 395 nm (Reproduced with permission from Ref. [14], copyright 2016, Elsevier).

Generally,  $\text{Eu}^{3+}$  doped phosphors show luminescence emission at 596 nm and 614 nm with sharp narrow band [15]. However,  $\text{Ba}_5\text{Zn}_4\text{Y}_8\text{O}_{21}:\text{Eu}^{3+}$  produced luminescence in a wide range of the visible light spectrum. On exciting the nanophosphor by 395 nm, several sharp peaks were noticed between 400 and 650 nm. On exciting the nanophosphor by 274 nm, a similar emission profile was observed. Figure 2 shows the emission spectra of  $\text{Ba}_5\text{Zn}_4\text{Y}_8\text{O}_{21}:\text{Eu}^{3+}$  nanophosphor monitored for the excitation wavelengths 395 nm and 274 nm. With the variation of  $\text{Eu}^{3+}$ -concentration, the color emission can be tuned from blue to white

to red. For lower concentrations of  $\text{Eu}^{3+}$  ions, the emission peaks were more dominant in the blue region. With the increasing  $\text{Eu}^{3+}$ -concentration, the peaks in the red region also start to emerge dominantly. For the highest concentrations of  $\text{Eu}^{3+}$ , the peaks in the blue and green region diminish and the peaks in the red region dominate. Thus, it is possible to tune the emission color from blue to white to red by varying the concentration of  $\text{Eu}^{3+}$  ions in  $\text{Ba}_5\text{Zn}_4\text{Y}_8\text{O}_{21}$ .

### III. CONCLUSION

In summary, we have reviewed several phosphors based on different families of host materials. We conclude that  $\text{Eu}^{2+}$  and  $\text{Ce}^{3+}$  doped materials are best suited for LED applications owing to their allowed 4f-5d transitions. For blue-emission, it is advisable to consider phosphors that have phosphates activated with  $\text{Eu}^{2+}$  and silicates doped with  $\text{Ce}^{3+}$ . Green/yellow emission can be obtained with garnets doped with  $\text{Ce}^{3+}$  or some  $\text{Eu}^{2+}$  doped phosphates that experience strong nephelauxetic effect.  $\text{Tb}^{3+}$  ions can also be considered as a suitable dopant ion that can bring green luminescence irrespective of the host in which it is doped. For red luminescence, the best options are available with  $\text{Eu}^{2+}$  doped nitride phosphors.

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