



# Synthesis and Photoluminescence properties of White Emitting $\text{LiSrPO}_4$ Phosphor doped with $\text{Dy}^{3+}$ for Solid State Lighting

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## Abstract

We have synthesized  $\text{LiSrPO}_4$  white emitting phosphors by modified solid state diffusion method doped with different concentration of  $\text{Dy}^{3+}$ . Crystal structure, surface morphology, photoluminescence properties, concentration quenching, color co-ordinates and other characteristics of these phosphors with reference to SSL are studied. These phosphors exhibit number of excitation peaks in nUV region. Emission spectra have two characteristic narrow bands of  $\text{Dy}^{3+}$  at 483 nm (blue) and 574 nm (yellow) in visible spectrum resulting into white light emission with FWHM of these bands is around 20 nm. The XRD pattern of prepared  $\text{LiSrPO}_4$  phosphor is well matched with the JCPDS file with Card Number 14-0202. Synthesized phosphor particles are of different sizes ranging from less than 1 micron to few microns. The chromaticity coordinate measured as (0.298, 0.342) falls in white region of CIE diagram. This point is in the close vicinity of standard white point D. These results indicates that the synthesized phosphors are promising material for a color converter using nUV LED as the primary light (pumping) source in phosphor converted white LED for solid state lighting.

**Keywords:** Solid State Lighting; solid state diffusion method; white phosphor; photoluminescence

## 1. Introduction

In the last few decades energy-efficient solid-state lighting and less power consuming white light emitting diodes (w-LEDs), which are regarded as the source of light in current generation, used in display lighting sources and illuminating systems for domestic, commercial and industrial applications. In present situation, white light-emitting diodes (w-LEDs), as the current generation of solid-state lighting, have attracted much attention due to

their special advantages, such as high efficiency, long lifetimes, weak environmental impact, absence of mercury, short response times, applicability in final products of various sizes, and so on [1, 2]. In the case of the phosphor converted white light LEDs (pc wLED), the phosphor materials play a significant role. For example, the most common and simple wLED source is combined of a blue-emitting InGaN chip and a Ce<sup>3+</sup> doped yttrium aluminium garnets (YAG:Ce<sup>3+</sup>) yellow phosphor [3], which is very stable and exhibits high luminescence efficiency. However, in some respects YAG:Ce<sup>3+</sup> based dichromatic systems often suffer from reduced thermal stability and exhibit a poor color-rendering index (CRI) caused by the color deficiency in the red and blue-green of the phosphor. In principle, using a single white phosphor instead of phosphor blends could help to lessen some of this variability, which relies critically on the phosphor properties. In latest years, numerous efforts have been made to improve single-phase white-light-emitting phosphors for near-ultraviolet and / or blue excitation to solve the above challenges with certain accomplishments. As the Dy<sup>3+</sup> ion has two dominant emission bands, one in the blue region (450–500 nm) and other in the yellow region (550–600 nm), it is possible to obtain a phosphor with near-white-light emission by appropriately adjusting the yellow-to-blue intensity ratio. We obtained white light emission in a single-phase orthophosphate phosphor LiSrPO<sub>4</sub> as host with single Dy<sup>3+</sup> dopant.

## 2. Experimental

### 2.1. Materials and method

White emitting LiSrPO<sub>4</sub>:Dy<sup>3+</sup> orthophosphate phosphors with different dopant concentrations were produced by Modified Solid State Diffusion (MSSD) method. For production of Dy<sup>3+</sup> activated orthophosphate phosphors stoichiometric amount of the analytical grade nitrate precursors and Dy<sub>2</sub>O<sub>3</sub> converted to Dy(NO<sub>3</sub>)<sub>3</sub> were taken in a china clay basin and dried in a desiccator. (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> was separately dried in another china basin and mixed together with above dried precursors. The dried pre-cursors were then finely crushed with small amount of acetone. This homogeneous mixture was dried with heating on heating mantle at 150°C for around 1 h. On drying the mixture was again crushed into mortar with pestle. The mixture was placed in an alumina crucible and sintered in an resistive electric furnace by a three-step heating process at 300°C for 2 h, 600°C for 1 h, and 950°C for 3 h with intermittent crushing and grinding to obtain Dy<sup>3+</sup> doped orthophosphate phosphors.

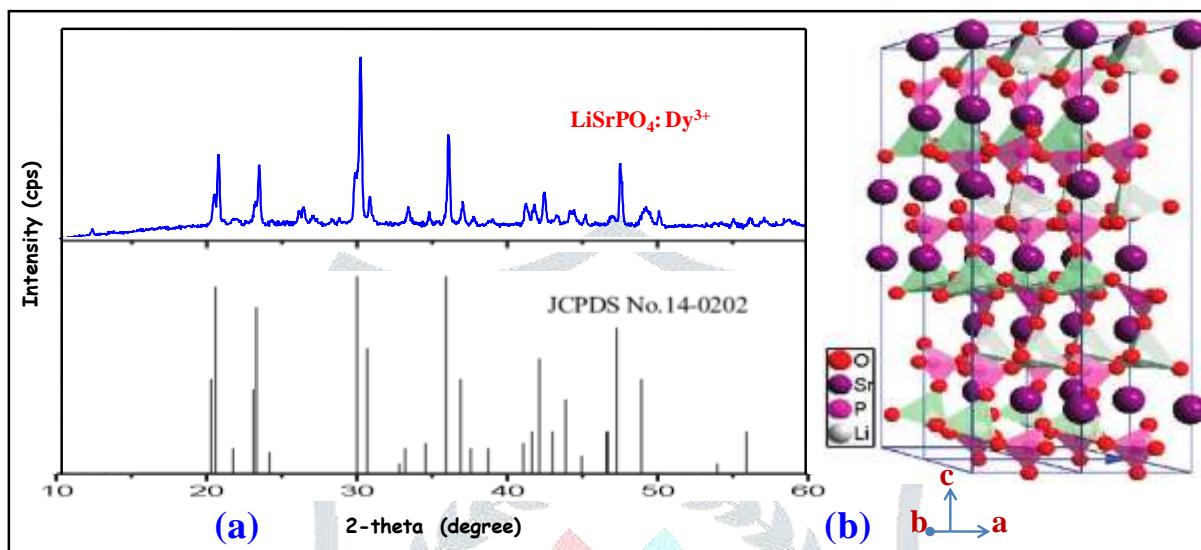
### 2.2. Characterization

The prepared materials were characterized by powder XRD. Powder X-ray diffraction measurements were taken on Rigaku Miniflex II X-ray Diffractometer and compared with the JCPDS card. The Surface morphology of the annealed particles was performed on Hitachi Field Emission Scanning Electron Microscope model S-4800. It is equipped with energy-dispersive X-ray spectroscopy (EDS) system that enables sample element analysis. The photoluminescence (PL) and PL excitation (PLE) spectra were measured on Hitachi F-7000 fluorescence spectrophotometer at room temperature. The parameters such as spectral resolution, width of the monochromatic slits (1.0 nm), photomultiplier tube (PMT) detector voltage and scan speed were kept constant throughout the analysis of samples. The color chromaticity coordinates were obtained according to Commission International de l'Eclairage (CIE).

### 3. Results and Discussion

#### 3.1. XRD analysis

Figure 1 (a) represented the XRD pattern of the  $\text{LiSrPO}_4$  doped with different concentration of  $\text{Dy}^{3+}$  synthesized by modified solid state diffusion method. The XRD pattern of prepared  $\text{LiSrPO}_4$  phosphor is well matched with the JCPDS file with card number 14-0202. The XRD results are well agreed with the reported data of  $\text{LiSrPO}_4$  [4].



**Figure 1: (a) X-ray diffraction patterns of as produced  $\text{LiSrPO}_4:\text{Dy}^{3+}$  phosphor and (b) Schematic crystal structures of  $\text{LiSrPO}_4$  host revealing a well ordered array of Li, Sr, P, and O atoms in a hexagonal structure**

The sharp and narrow diffraction peaks show that the phosphor powder was crystalline in nature and is in single phase with hexagonal crystal structure having the cell parameter  $a = b = 5.004 \text{ \AA}$  and  $c = 24.632 \text{ \AA}$ ,  $V=534.15(5) \text{ \AA}^3$ , and  $Z=6$  in the space group  $P6_5$ . The incorporation of dopant does not influence the structure of host of phosphor because of their relatively low concentrations. The schematic crystal structure of  $\text{LiSrPO}_4$  unit cell is shown in **Figure 1 (b)**. In  $\text{LiSrPO}_4$  lattice the ionic radius of  $\text{Sr}^{2+}$  is 1.18 nm, the ionic radius of  $\text{Li}^+$  is 0.59 nm, the ionic radius of  $\text{Dy}^{3+}$  is 0.94 nm. Based on the effective ionic radii of cations with coordination number, it is assumed that  $\text{Dy}^{3+}$  ions are preferable to replace the  $\text{Sr}^{2+}$  ions in the prepared phosphor material. Generally, when a metal cation is substituted for an ion with a different valence in the host lattice, the charge compensator, such as  $\text{Li}^+$ ,  $\text{Na}^+$  or  $\text{K}^+$ , is employed to keep the charge balance. The charge compensation in the above mentioned structure is most likely to be described by charge compensation by a strontium vacancy ( $3\text{Sr}^{2+} = 2\text{Dy}^{3+} + \text{V}_{\text{Sr}}$ ).

#### 3.2.EDS spectrum

The EDS spectrum of the synthesized  $\text{LiSrPO}_4:\text{Dy}^{3+}$  phosphor is shown in **Figure 2 (a)** shows that the elementary composition of the sample consists of major peaks corresponding to Sr, P, and O except Li being low energy element does not appear in EDS spectrum. Some small peaks of dopant element Dy and element Pt also appear in the spectrum, element Pt used for sample preparation. Inset table in the figure clearly shows the content of the elements in the phosphor. All the results indicated that the prepared samples were phosphates and the content

of constituent elements was excellently matched with the stoichiometric ratio of  $\text{LiSrPO}_4$  except Li being low energy element does not appear in EDS spectrum.

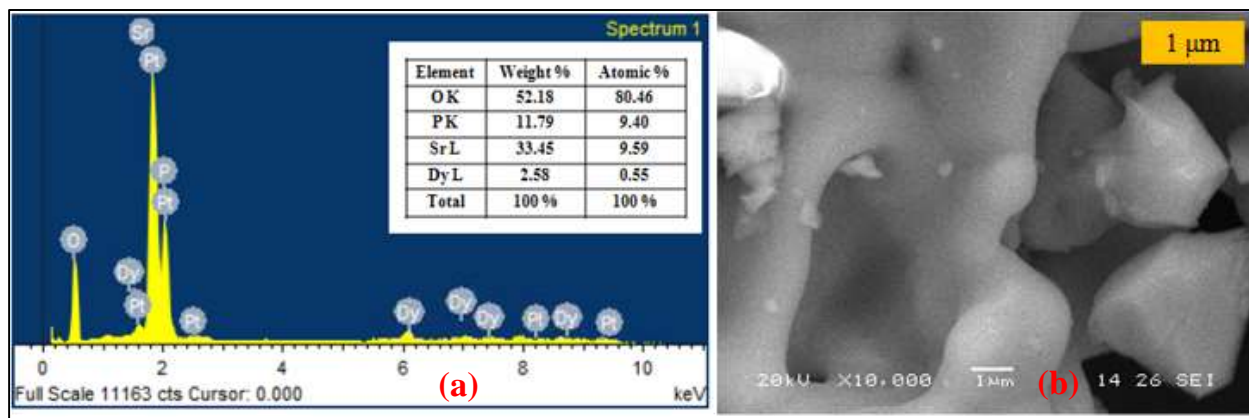


Figure 2: (a) EDS pattern and elemental composition of as synthesized  $\text{LiSrPO}_4: \text{Dy}^{3+}$   
(b) SEM image of as synthesized  $\text{LiSrPO}_4: \text{Dy}^{3+}$  phosphor

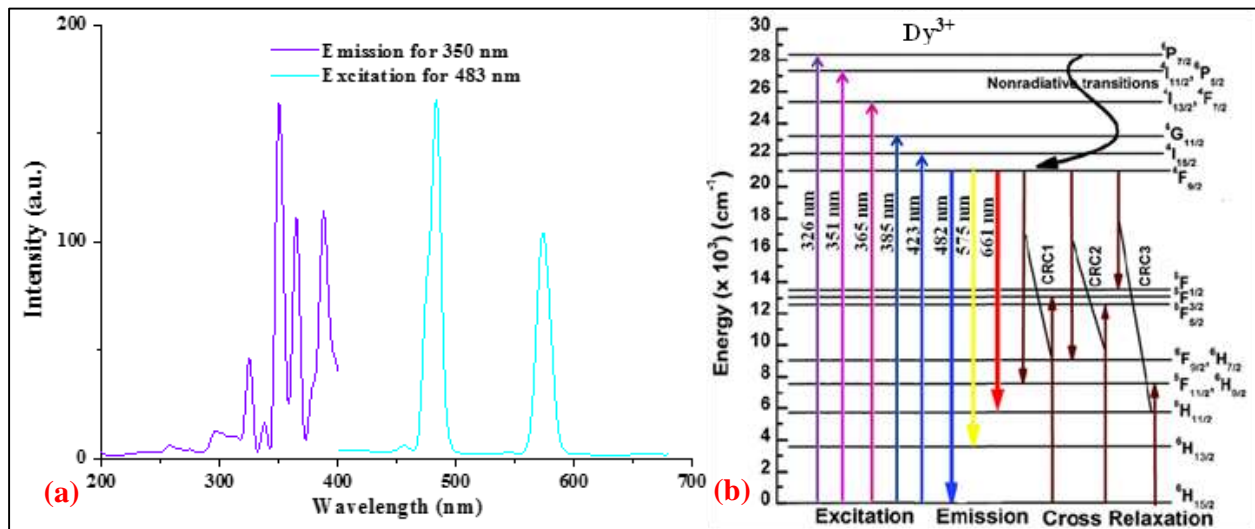
### 3.3. Morphology study

Figure 2 (b) exhibits the SEM image of the  $\text{LiSrPO}_4: \text{Dy}^{3+}$ . The image shows network like structure of non-homogeneous particles that contains voids or empty spaces with particle size which extends to few microns. In addition, an aggregation of irregular lumps that consisted of irregular particles was also observed.

### 3.4. Photoluminescence

#### 3.4.1. Combined Excitation and Emission spectra of $\text{LiSrPO}_4: \text{Dy}^{3+}$

Figure 3 (a) presents combined excitation and emission spectrum of  $\text{LiSrPO}_4: 0.01\text{Dy}^{3+}$ . When excitation spectra of phosphor monitored by 484 nm, which comes from the transition of  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$  of  $\text{Dy}^{3+}$ , it can be seen from it that the present phosphor has effective energy absorption mainly in the region of 250–400 nm, and the excitation bands consist of number of peaks of these main peaks, which are located at 325, 338, 350, 365 and 388 nm respectively. These excitation bands are attributed to the electronic transitions of  $^6\text{H}_{15/2} \rightarrow ^4\text{K}_{15/2}$ ,  $^6\text{H}_{15/2} \rightarrow ^4\text{F}_{5/2}$ ,  $^6\text{H}_{15/2} \rightarrow ^4\text{M}_{15/2}$ ,  $^6\text{H}_{15/2} \rightarrow ^4\text{P}_{3/2}$  and  $^6\text{H}_{15/2} \rightarrow ^4\text{M}_{21/2}$  respectively. Figure 3 (b), which are all due to the typical f–f transitions of  $\text{Dy}^{3+}$  [5] with maximum intensity band peaked at 350 nm. The emission spectrum monitor upon an excitation at 350 nm exhibits two characteristic emission bands peaking at 483 nm (blue) and 574 nm (yellow), respectively, which can be attributed to  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$  and  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ , respectively.

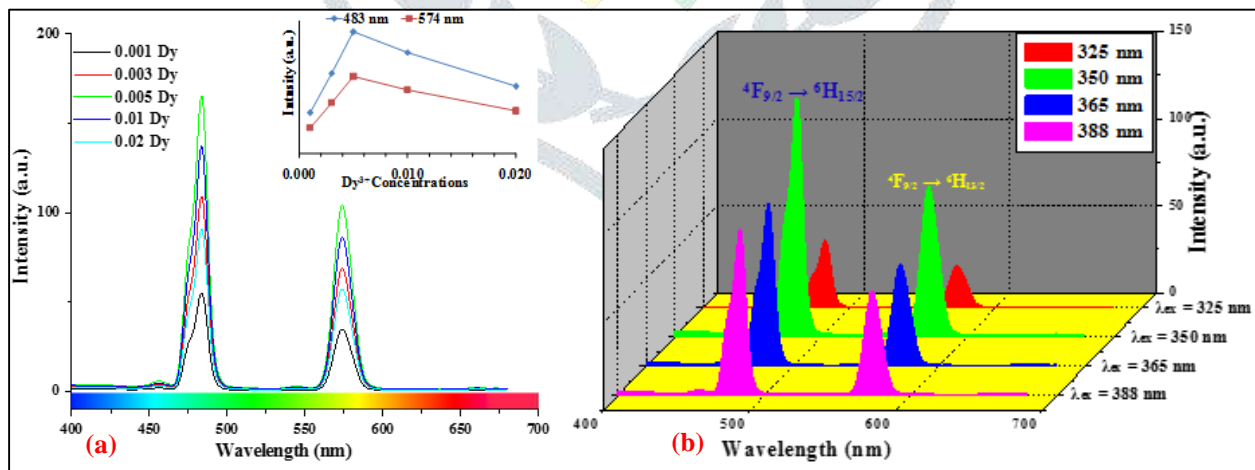


**Figure 3: (a) The excitation and emission spectra of as synthesized LiSrPO<sub>4</sub>:Dy<sup>3+</sup> and (b) Schematic energy level diagrams of Dy<sup>3+</sup> along with possible cross relaxation mechanisms between a pair of adjacent Dy<sup>3+</sup> ions [5]**

Generally speaking, the optical properties of the phosphors are often influenced by the structure of the host matrix, when Dy<sup>3+</sup> is located at a high symmetry site (with an inversion center), the blue emission is dominant, whereas the yellow emission is stronger when Dy<sup>3+</sup> is located at a low symmetry site (without an inversion center) [6], [7]. The observed emission spectrum for LiSrPO<sub>4</sub>:Dy<sup>3+</sup> phosphor in this work suggests that the blue emission at 483 nm is stronger than the yellow emission at 574 nm, which means that Dy<sup>3+</sup> is located at a high symmetry site in LiSrPO<sub>4</sub>.

### 3.4.2. Effect of dopant concentrations on emission intensity of LiSrPO<sub>4</sub>:Dy<sup>3+</sup>

**Figure 4 (a)** shows the emission spectra ( $\lambda_{\text{ex}} = 350$  nm) of LiSrPO<sub>4</sub>:Dy<sup>3+</sup> phosphor with various Dy<sup>3+</sup> concentrations.



**Figure 4: (a) The emission spectra of LiSrPO<sub>4</sub> for different Dy<sup>3+</sup> concentration, the inset shows Dy<sup>3+</sup> concentration of relative luminescence intensity at 483 nm and 574 nm**

**(b) Emission spectra of LiSrPO<sub>4</sub>:Dy<sup>3+</sup> phosphors with different excitations**

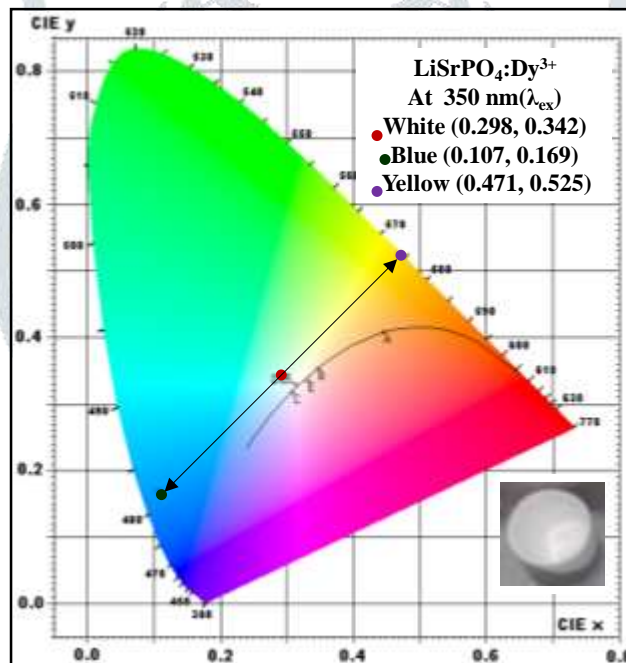
It is observed that the profiles of the emission spectra keep invariable by altering Dy<sup>3+</sup> concentration. However, the emission intensity firstly increases with increasing Dy<sup>3+</sup> concentration, and then reaches the maximum when the Dy<sup>3+</sup> concentration is 0.005, followed by decreasing with further increasing Dy<sup>3+</sup>

concentrations because of the concentration quenching effect. The ratio (B/Y) of luminous intensities of blue (483 nm) and yellow (574 nm) emission bands for different  $\text{Dy}^{3+}$  concentration is constant (1.58). The inset shows relative luminescence intensity at 483 nm ( ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ ) and 574 nm ( ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ ) as a function of  $\text{Dy}^{3+}$  concentrations.

### 3.4.3. Effect of excitation wavelength on emission spectra of $\text{LiSrPO}_4:\text{Dy}^{3+}$

The emission spectra recorded for the optimized dopant concentration in  $\text{LiSrPO}_4$  phosphors upon different excitations are shown in **Figure 4 (b)**. The emission band shape and position under different excitation wavelengths ( $\lambda_{\text{ex}} = 325, 350, 365, 388 \text{ nm}$ ) remains unchanged except emission intensity. At the same time B/Y emission intensity ratio is also not much affected. The value of B/Y ratio is around 1.58 for different excitation wavelengths, which implies that  $\text{Dy}^{3+}$  ions occupy only one kind of site in the  $\text{LiSrPO}_4$  and gives rise to a single emission center. Furthermore, the integral intensity ratio of the electric dipole ( ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ ) to the magnetic dipole ( ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ ) allowed transitions are known as an asymmetric ratio [8]. This is a measure of the structural distortion around  $\text{Dy}^{3+}$  ions. In the present case, the asymmetric ratio is constant for different UV excitations, which indicates that the  $\text{Dy}^{3+}$  ions are located in the crystal lattice without any distortion.

### 3.4.4. Color Quantification (CIE 1931) of $\text{LiSrPO}_4:\text{Dy}^{3+}$



**Figure 5:** Color coordinates and in the inset image of as synthesized  $\text{LiSrPO}_4:\text{Dy}^{3+}$

Figure 5 displays the CIE chromaticity diagram of  $\text{LiSrPO}_4:0.005\text{Dy}^{3+}$ . The chromaticity coordinate (x, y) is measured as (0.298, 0.342) falls in white region of CIE diagram. This point is in the vicinity of standard white point D. At the same time this point lies on line joining points (0.298, 0.342) and (0.471, 0.525) corresponding to CIE coordinates of blue and yellow bands respectively in emission spectra of synthesized phosphors. This result indicates that synthesized phosphor would be a kind of phosphor converted materials used in w-LEDs.

#### 4. Conclusion

The blue and yellow double color emitting orthophosphate phosphors  $\text{LiSrPO}_4: \text{Dy}^{3+}$  is successfully synthesized by modified solid state diffusion method. Photoluminescence of as synthesized phosphors exhibits two bright blue and yellow emission narrow bands in the wavelength range 450 nm to 600 nm with maximum intensity centered around 483 nm and 574 nm respectively corresponding to  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$  and  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$  characteristic transitions of  $\text{Dy}^{3+}$  ions. The CIE coordinates of as prepared phosphors are (0.298, 0.342). The prominent excitation peak of all these phosphors is located around 350 nm corresponding to  $^6\text{H}_{15/2} \rightarrow ^4\text{M}_{15/2}$  transitions of  $\text{Dy}^{3+}$  ions, which indicates that these phosphors are very suitable for a color converter using nUV LED as the primary light source in pc wLED. As it is evident from the emission spectra of these phosphors, they are deficient in red emission therefore will exhibit poor CRI. This deficiency can be overcome by co-doping them with appropriate red emitting activator along with  $\text{Dy}^{3+}$ .

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