



SYNTHESIS AND PHOTOLUMINESCENCE PROPERTIES OF WHITE EMITTING NaCaPO_4 PHOSPHOR DOPED WITH Dy^{3+} FOR SOLID STATE LIGHTING

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ABSTRACT: We have synthesized NaCaPO_4 white emitting phosphors by modified solid state diffusion method doped with different concentration of 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 Dy^{3+} at 481 nm (blue) and 575 nm (yellow) in visible spectrum resulting into white light emission with FWHM of these bands is around 20 nm. The XRD pattern of prepared phosphor well matches with JCPDS Card No.76-1456. Synthesized phosphor particles are of different sizes, with smooth surfaces, from less than 1 micron to few microns. CIE coordinates are (0.278, 0.298) at 351 nm (λ_{ex}) falls in white region of CIE diagram in the close vicinity of standard white point C. 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.

Key words: - Solid State Lighting; solid state diffusion method; white phosphor; photoluminescence.

INTRODUCTION :

In the past 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 coming generation, used in display lighting sources and illuminating systems for domestic as well industrial applications. In present situation, white light-emitting diodes (w-LEDs), as the next 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 an important role. For example, the most common

and simple wLED source is combined of a blue-emitting InGaN chip and a Ce^{3+} doped yttrium aluminium garnets ($\text{YAG}:\text{Ce}^{3+}$) yellow phosphor [3], which is very stable and exhibits high luminescence efficiency. However, in some respects $\text{YAG}:\text{Ce}^{3+}$ 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 reduce some of this variability, which relies critically on the phosphor properties. In recent years, numerous efforts have been made to develop single-phase white-light-emitting phosphors for near-ultraviolet and / or blue excitation to solve the above challenges with certain achievements. As

the Dy³⁺ 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 suitably adjusting the yellow-to-blue intensity ratio. We obtained white light emission in a single-phase orthophosphate phosphor NaCaPO₄ as host with single Dy³⁺ dopant.

EXPERIMENTAL:

MATERIAL AND METHOD:

White emitting NaCaPO₄:Dy³⁺ orthophosphate phosphors with different dopant concentrations were synthesized by Modified Solid State Diffusion (MSSD) method. For synthesis of Dy³⁺ activated orthophosphate phosphors stoichiometric amount of the analytical grade nitrate precursors and Dy₂O₃ converted to Dy(NO₃)₃ were taken in a china clay basin and dried in a desiccator. (NH₄)H₂PO₄ was separately dried in another china basin and mixed together with above dried precursors. The dried precursors were then finely ground 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 Dy³⁺ doped orthophosphate phosphors.

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).

RESULTS AND DISCUSSION:

XRD analysis:

The XRD patterns of as synthesized NaCaPO₄:Dy³⁺ phosphor is shown in **Figure 1 (a)** compared with **Joint Committee on Powder Diffraction Standards (JCPDS)** card 76-1456. All the peaks in diffractions spectra are in well agreement with the standard card, meaning that prepared sample is of single pure phase. This indicates that calcium sodium orthophosphate phosphor, α-NaCaPO₄ crystallizes in the orthorhombic system, space group Pn21a (33), with lattice parameters $a = 20.3970 \text{ \AA}$, $b = 5.4120 \text{ \AA}$, $c = 9.1610 \text{ \AA}$, $V = 1011.27 \text{ \AA}^3$ and $Z = 12$ [4].

When the concentrations of Dy³⁺ ions were varied from 0.001 to 0.02 mole there was no change found in the XRD pattern. This indicates that the sites of Ca have been successfully replaced by dopant cation Dy³⁺ in the phosphors without affecting the crystal structure of the host materials. Charge neutrality in the phosphor material is maintained by lattice defects (vacancies- generally created in place of divalent cations) formed during the process of crystal formation because the added impurity is very small. The schematic crystal structure of as synthesized NaCaPO₄ phosphor host is shown in **Figure 1 (b)** [5].

EDS spectrum:

The energy dispersive spectrum [Figure 2 (a)] shows that all the element in composition of prepared phosphor i.e. Na, Ca, P, O and Dy are in an appropriate atomic ratio with some minor peaks of Platinum (Pt)

which are due to Platinum used for coating during sample preparation for scanning electron microscopy.

Morphology study:

Figure 2 (b) exhibits the SEM image of the as synthesized $\text{NaCaPO}_4:\text{Dy}^{3+}$ orthophosphate phosphor. The image show agglomerated particles that consist of mixture of different particle sizes. The approximate particle size of the prepared phosphor can be estimated from resolution scale ranges from less than 1 micron to few microns which is a suitable size for fabrication of SSL devices [6]. From literature, it is evident that the crystalline powder with micrometer particle dimensions will find more applications as it can exhibit high luminescent intensities [7].

Photoluminescence:

Combined Excitation and Emission spectra of $\text{NaCaPO}_4:\text{Dy}^{3+}$:

The combined excitation and emission spectrum measured for 1 mole% Dy^{3+} doped NaCaPO_4 phosphor is given in Figure 3 (a). Excitation spectra in the wavelength range from 250–400 nm are consists of number of excitation bands. These are ascribed to transition from the ground state of $^6\text{H}_{15/2}$ to the various excited states of $4f^9$ electronic configurations of the Dy^{3+} ions [Figure 3 (b)]. Among all the excitation bands, the band located at 351 nm ($^6\text{H}_{15/2} \rightarrow ^4\text{I}_{11/2}$) has the maximum intensity. Therefore, the emission spectra were measured by exciting the different doping concentrations of Dy^{3+} in NaCaPO_4 samples at 351 nm in order to determine the optimized Dy^{3+} concentration. The 351 nm radiation excites the Dy^{3+} ions to the $^6\text{P}_{5/2}$ ($^4\text{I}_{11/2}$) level and then quickly relaxes non-radiatively to populate the $^4\text{F}_{9/2}$ level. The emission spectra

exhibit two sharp peaks at 481 nm (blue) and 575 nm (yellow), corresponding to the $^4\text{F}_{9/2}$ to $^6\text{H}_{15/2}$ and $^6\text{H}_{13/2}$ transition, respectively.

Two different emission bands originated from the same excited level. The $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ is a hypersensitive transition ($\Delta L = \Delta J = 2$), which is strongly influenced by the surrounding environment around the Dy^{3+} ion. In general, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transition is prominent when Dy^{3+} ions are located at low-symmetry sites with no inversion center, whereas the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ transition is stronger when Dy^{3+} is located at high symmetry with an inversion center [8]. The blue emission ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$) at 481 nm is stronger than the yellow emission, which indicates that the Dy^{3+} ions occupy a high-symmetry local site with inversion symmetry in the host matrix.

Effect of dopant concentrations on emission spectra of $\text{NaCaPO}_4:\text{Dy}^{3+}$:

Figure 4 (a) clearly shows that the intensities of yellow and blue emission bands increase with the increase of the activator (Dy^{3+}) concentration become maximum at 1 mole% and then decreases due to concentration quenching, when the concentration is more than 1 mole%. Inset figure illustrates the integrated emission intensity as a function of Dy^{3+} concentration.

It can be clearly observed that the integrated emission intensities of $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ (465–500 nm) and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ (553–602 nm) transitions increase until Dy^{3+} concentration reaches the maximum value of 1 mol%, and then decrease due to concentration quenching. Such behavior indicates that the optimum Dy^{3+} concentration is around 1mol% for the NaCaPO_4 host. The most reasonable explanation for this concentration quenching is due to the cross relaxation among Dy^{3+} pairs between the intermediate Dy^{3+} ($^6\text{F}_{3/2}$) and Dy^{3+} ($^6\text{H}_{9/2}$) energy levels [Figure 3 (b)], where the ions decay non-radiatively. This cross relaxation may be mainly due to the quenching transitions in the form of

${}^4F_{9/2}+{}^6H_{15/2}\rightarrow{}^6F_{3/2}+{}^6H_{9/2}$. The ratio (B/Y) of luminous intensities of blue (481 nm) and yellow (575 nm) emission bands for different Dy^{3+} concentration is constant (1.59). The inset shows relative luminescence intensity at 483 nm (${}^4F_{9/2}\rightarrow{}^6H_{15/2}$) and 574 nm (${}^4F_{9/2}\rightarrow{}^6H_{13/2}$) as a function of Dy^{3+} concentrations.

Effect of excitation wavelength on emission spectra of $NaCaPO_4:Dy^{3+}$:

The emission spectra recorded for the optimized 1mol% doped $NaCaPO_4$ phosphors upon different excitations are measured and shown in **Figure 4 (b)**. There are no observed differences in the emission band shape and position under different excitation wavelengths ($\lambda_{ex} = 326, 351, 365, 388$ nm) except emission intensity. Moreover, the Y/B integral intensity ratio is not much affected by exciting the samples at different wavelengths. The value of B/Y ratio is around at 1.59 for different excitation wavelengths, which implies that Dy^{3+} ions occupy only one kind of site in the $NaCaPO_4$ and gives rise to a single emission center. Furthermore, the relative intensity ratio of the electric dipole allowed (${}^4F_{9/2}-{}^6H_{13/2}$) to the magnetic dipole allowed (${}^4F_{9/2}-{}^6H_{15/2}$) transition is known as an asymmetric ratio [9]. This is a measure of the structural distortion around Dy^{3+} ions. In the present paper, the asymmetric ratio is constant for different UV excitations, which indicates that the Dy^{3+} ions are located in the crystal lattice without any distortion.

Color Quantification (CIE 1931) of $NaCaPO_4:Dy^{3+}$:

The emission color was analyzed and confirmed with the help of CIE chromaticity coordinates. The CIE chromaticity coordinates for 1mole% Dy^{3+} doped $NaCaPO_4$ phosphors at all different excitation wavelengths are nearly located at (0.278, 0.298), as indicated in the CIE diagram as shown in **Figure 5**. It is obvious that these coordinates are very close to the standard point 'C' of white illuminate that exhibits white light

emission in the chromaticity diagram. At the same time this point lies on line joining points (0.117, 0.108) and (0.462, 0.523) corresponding to CIE coordinates of blue and yellow bands respectively in emission spectra of synthesized phosphors.

CONCLUSION :

The blue and yellow double color emitting orthophosphate phosphors $NaCaPO_4:Dy^{3+}$ 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 481 nm and 575 nm respectively corresponding to ${}^4F_{9/2}\rightarrow{}^6H_{15/2}$ and ${}^4F_{9/2}\rightarrow{}^6H_{13/2}$ characteristic transitions of Dy^{3+} ions. The CIE coordinates of as prepared phosphors are (0.278, 0.298). The prominent excitation peak of all these phosphors is located around 351 nm corresponding to ${}^6H_{15/2}\rightarrow{}^4M_{15/2}$ transitions of 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 lacking in red emission therefore will exhibit poor CRI. This shortcoming can be overcome by co-doping them with appropriate red emitting activator along with Dy^{3+} .

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Figure 1: (a) XRD patterns and (b) crystal structure of as synthesized $\text{NaCaPO}_4:\text{Dy}^{3+}$ phosphor

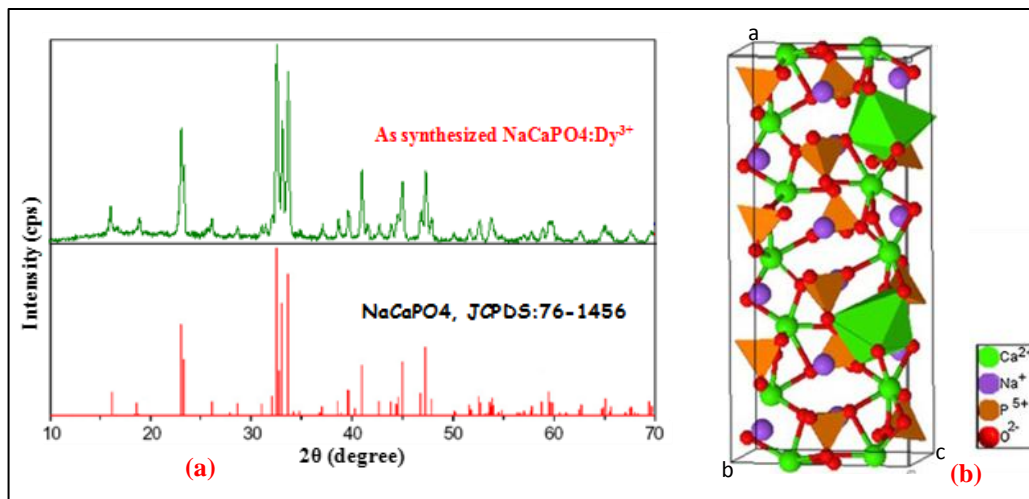


Figure 2: (a) EDS pattern and (b) SEM image of as synthesized $\text{NaCaPO}_4:\text{Dy}^{3+}$ phosphor

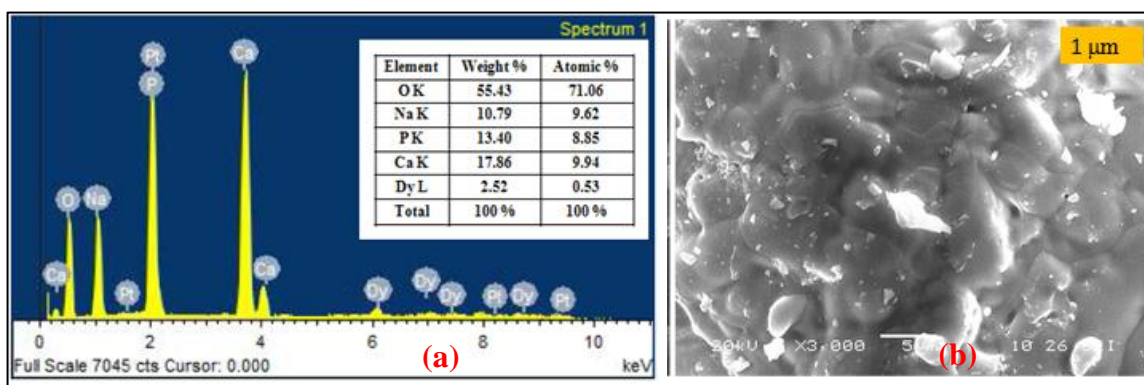


Figure 3: (a) The combined excitation and emission spectra and (b) Schematic energy level diagrams of Dy³⁺ along with possible cross relaxation mechanisms between a pair of adjacent Dy³⁺ ions

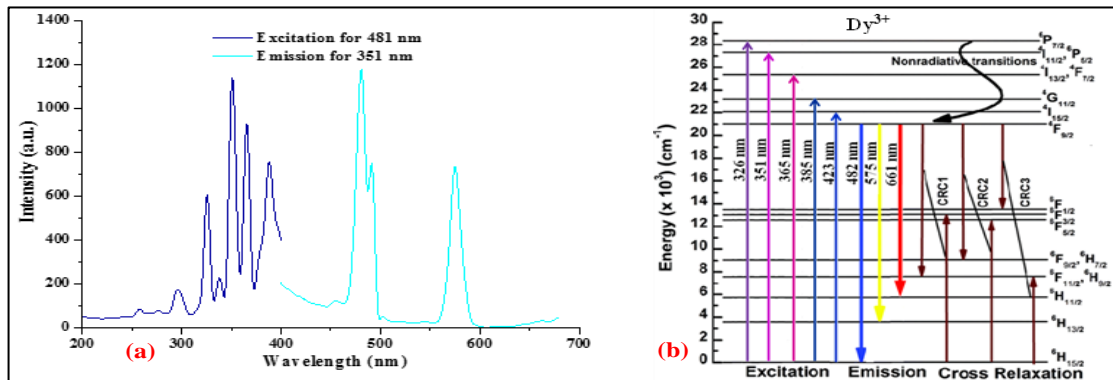


Figure 4: (a) Effect of dopant concentration on emission spectra with relative luminescence intensity at 481 nm and 575 nm; (b) Effect of excitation wavelength on emission spectra of as synthesized phosphor

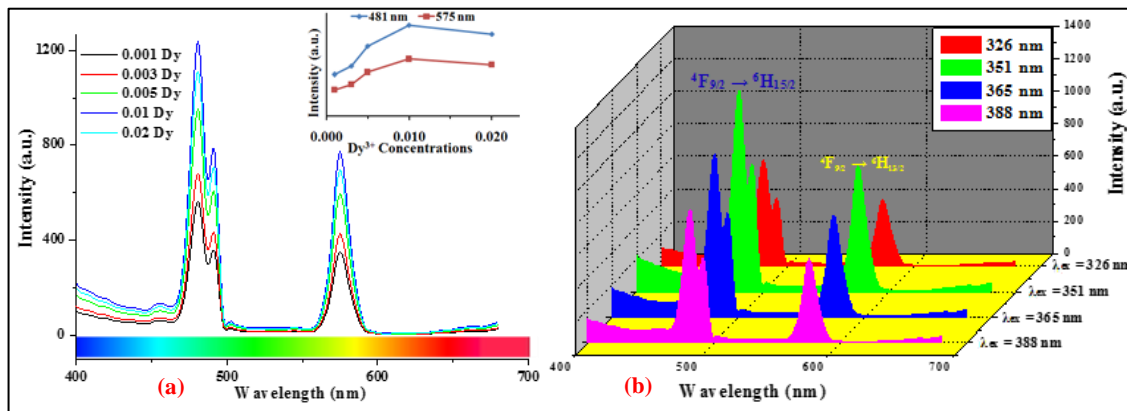


Figure 5: Colour coordinates and in the inset image of as synthesized NaCaPO₄:Dy³⁺ phosphor powder

