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ARTICLE

Two-color Emission in Dy^{3+}-activated $CaZnP_2O_7$ Pyrophosphate for White LED

R. L. Kohale[a], **A. N.Yerpude**[b] and **S. J. Dhoble**[c]

[a] *Department of Physics, Sant Gadge Maharaj Mahavidyalaya, Hingna, Dist-Nagpur, MH, India.441110*

[b] *Department of Physics,N.H.College,Bramhapuri - 441206, MH, India.*

[b] *Department of Physics, R.T.M. Nagpur University, Nagpur-440033, India.*

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Abstract: $CaZnP_2O_7$ pyrophosphate phosphor doped with Dy^{3+} ions was synthesized by modified solid-state reaction. The crystalline phases were recognized using X-ray diffraction. Surface morphology was studied by scanning electron microscopy. Furthermore, the chromaticity coordinates' values were estimated from the emission spectra of $CaZnP_2O_7$:Dy^{3+}. The phosphor photoluminescence emission spectra were found to have an excitation at around 353 nm showing two distinguishing bands centered at about 482 nm (Blue) and 575 nm (Yellow) corresponding to $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transitions of Dy^{3+}, respectively. These phosphors have strong absorption in the near-UV region. The intact study reveals that the present phosphors are suitable for color converter using UV light as the primary light source, which can be used as a blue/yellow phosphor excited by the n-UV LED chip and mixed with other color emission phosphors to obtain white light.

Keywords: Chemical synthesis, Luminescence, X-ray diffraction, Optical properties.

Introduction

Luminescent materials doped with Dy^{3+} have drawn much interest for their white emission (WLED), since they can produce white emission by adjusting the yellow to blue intensity ratio value [1,2] and can be used as one of the components in tricolor fluorescent lamps as well as potential white phosphors [3]. Several researchers are engaged in studying the luminescent properties of Dy^{3+} doped with different compositions. Recently, Shinde et al. [4] reported some Dy^{3+}-activated phosphate-based phosphors $X_6AlP_5O_{20}$ (where X= Sr, Ba, Ca and Mg) and Kim et al. [5] studied the photoluminescence properties of $BaMgP_2O_7$ doped with different rare earth metals as a potential phosphor for white emission. However, it is challenging to fabricate persistent phosphors RGB/YB [6] which have similar emission ratios to ensure white-light-emitting phosphors all the time. Dy^{3+} ions, which have a luminescence appearance in the 470–500 nm region due to $^4F_{9/2}$–$^6H_{15/2}$ transition and in the 570–600 nm region due to $^4F_{9/2}$–$^6H_{13/2}$ [7-9], consequently Dy^{3+} ions with emission lines in the visible (400–600 nm) region, have attracted much attention because of their white-light emissions [10-13]. Dy^{3+} has emissions due to the self-atomic energy levels and due to the acceptor levels of defect sites formed by Dy^{3+}.

The objective of this work is to carry out a detailed investigation of structural, morphological and photoluminescence properties of the newly synthesized $CaZnP_2O_7$:Dy^{3+} pyrophosphate phosphor to examine its

Corresponding Author: R. L. Kohale **Email**: riteshkohale@gmail.com

suitability as a potential candidate for phosphor-converted n-UV white-LEDs and solid-state lighting. A modified solid-state diffusion reaction prepared entitled phosphors. Significantly, $CaZnP_2O_7:Dy^{3+}$ phosphors were intensely studied for the effect of doping of rare earth ions Dy^{3+} to obtain various phosphors for w-UV LEDs. A detailed study was carried out on the luminescence properties and the concentration quenching mechanism of Dy^{3+}. The investigations on surface morphology were carried out by scanning electron microscopy (SEM). Furthermore, the color coordinates were calculated using color chromaticity diagrams. The entire study reveals that this phosphor system could be considered an alternative approach for white-light emission and solid-state lighting due to its excellent luminescent properties, more straightforward manufacturing procedure, lower production cost, and mercury-free excitation nonhygroscopic and environmental-friendly characteristics.

Experimental Details

Synthesis of $CaZnP_2O_7:Dy^{3+}$ Phosphor

The Dy^{3+}-activated $CaZnP_2O_7$ phosphor was prepared by chemical synthesis *via* modified solid-state diffusion. The starting AR grade materials (99.99% purity) were taken as follows:

Calcium Carbonate $CaCO_3$ (Merck, 99.999%), Zinc Carbonate $ZnCO_3$ (Merck, 99.990%), Ammonium dihydrogen phosphate $NH_4H_2PO_4$. (Merck 99.99% pure). The molar ratio of rare earth dysprosium oxide Dy_2O_3 (Aldrich, 99.999%) varied from 0.3 mol% to 1 mol% in $CaZnP_2O_7$ phosphor relative to Ca ions. The mixture of reagents was ground together to obtain a homogeneous powder and Dy^{3+} ions were introduced as Dy_2O_3 in solid-powder form. After being ground thoroughly in stoichiometric ratios using an agate mortar, the powder was transferred to silica crucible and then heated in a muffle furnace to ensure the best homogeneity and reactivity at 350 °C for 1 hr to decompose $NH_4H_2PO_4$. Afterward, the mixture was reground and heated in a furnace at 700 °C for 12 hrs. The temperature was cooled to 500°C and air-quenched to room temperature. All samples were found out to be purely white. Several complementary methods were used to characterize the prepared phosphors. The prepared host lattice was characterized for phase purity and crystallinity by X-ray powder diffraction (XRD) using a PAN-analytical diffractometer (Cu-Ka radiation). The photoluminescence measurements of excitation and emission were recorded on the Shimadzu RF5301PC spectrofluorophotometer. The same amount of sample (2 g) was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. The morphological studies were examined by scanning electron microscopy (SEM, JEOL 6380A)

The basic chemical reactions for $CaZnP_2O_7$ can be described as follows:

$$Ca\ (CO_3) + Zn\ (CO_3) + 2(NH_4H_2PO_4) \rightarrow CaZnP_2O_7 + 2NH_3 + 3H_2O + 2CO_2.$$

Results and Discussion

XRD Patterns of $CaZnP_2O_7$ Pure and $CaZnP_2O_7:Dy^{3+}$ Phosphor

In the present work, polycrystalline samples of $CaZnP_2O_7$ phosphor were obtained as described above in the experimental section. The phase purities of all the samples were checked by powder X-ray diffraction using PAN-analytical diffractometer (Cu-Kα radiation) at a scanning step of 0.010, with a continue time of 20s, in the 2θ range from 10^0 to 60^0. The XRD pattern for $CaZnP_2O_7$ pure samples is presented in Fig. 1. The sample XRD pattern is in good agreement with the standard PDF 50-0361, indicating that $CaZnP_2O_7$ powder was formed with no impurity phases. It gives the complete formation of the homogeneous product. The XRD patterns of these samples described above did not indicate constituents like Ca (CO_3), Zn (CO_3) or $NH_4H_2PO_4$, which forms a direct evidence for the formation of the desired compound.

Surface Morphology of $CaZnP_2O_7:Dy^{3+}$

In order to obtain insight information about the surface morphology of $CaZnP_2O_7$ phosphor, SEM analysis was performed. The particle morphology of the synthesized sample was observed by (SEM, JEOL 6380A) and the typical morphological images for $CaZnP_2O_7$ are represented in Fig.2.

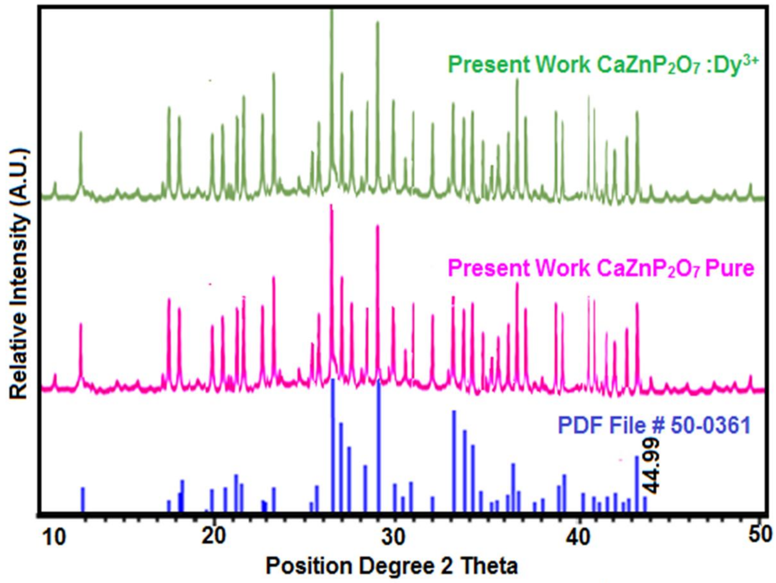

FIG. 1. XRD pattern of $CaZnP_2O_7$ and $CaZnP_2O_7:Dy^{3+}$ materials.

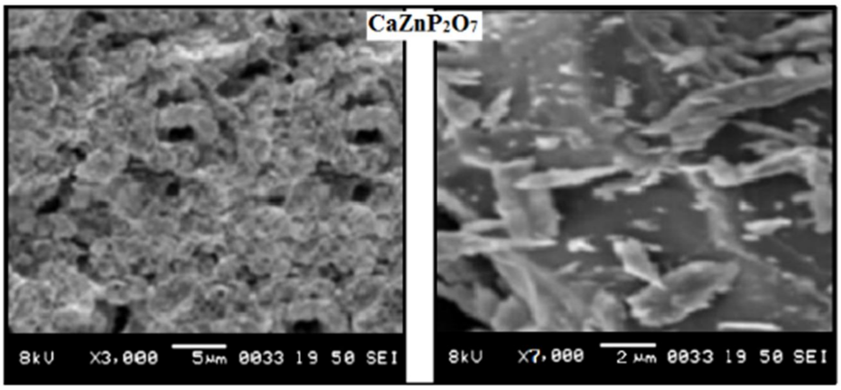

FIG. 2. SEM images of $CAZnP_2O_7$ phosphor.

SEM micrographs of the compound (Fig. 2) confirmed the polycrystalline nature of the material. Highly distinctive, nearly uniform and compact grain distributions are the unique features of the micrograph. Rod-shape and needle-shape morphologies could be visibly observed in the SEM micrographs. The sample size was moderately uniform and estimated in the micrometer range of 2-5 µm as seen in the SEM images. The size of the particles for $CaZnP_2O_7$ is around 1-4 µm (Fig.2). This shows that the solid-state reactions of the mixtures took place well. The sample $CaZnP_2O_7$ revealed a fine structure formed from highly agglomerated crystallites. Most particles showed a rod-shaped structure and sizes of a few micrometers. The sample revealed sintered structures in which individual particles could hardly be distinguished. These characteristics are advantageous when considering their application as phosphor powders to fabricate white LED and solid-state lighting [14].

Photoluminescence Spectra of Dy^{3+}-activated $CaZnP_2O_7$

Measurement of excitation and emission spectra was made by monitoring the peak wavelength of the Dy^{3+} emission of blue and yellow bands, respectively. The excitation spectra of the $CaZnP_2O_7:Dy^{3+}$ phosphor monitored at around 575nm are shown in Fig. 3. The excitation spectrum monitored at yellow emission from Dy^{3+} ions indicates several bands in the wavelength region of 200 - 400 nm, which are due to excitation of the f–f shell transitions of Dy^{3+} [15]. The several peaks at 290 nm and 353 nm correspond to the transitions from the ground state $^6H_{15/2}$ to the excited states; $^4P_{7/2}$; $^4P_{3/2}$ and $^4F_{7/2}$, respectively. Maximum PL intensity for the excitation wavelength is located at 353 nm, which is a characteristic of solid-state lighting and hence, it has been selected for further photoluminescence investigation [16].

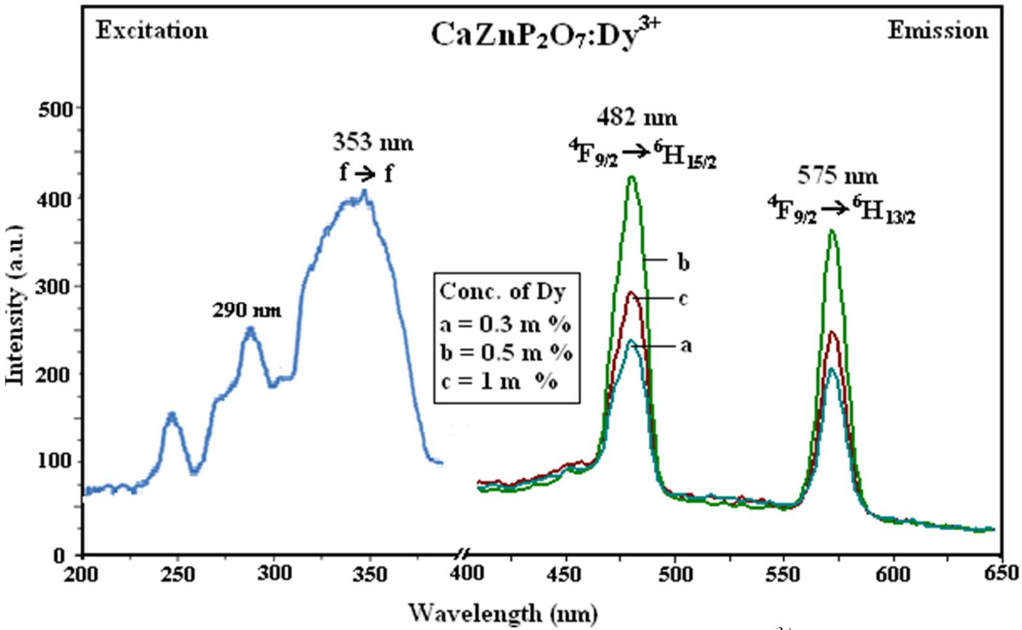

FIG. 3. PL excitation and emission spectra of $CaZnP_2O_7:Dy^{3+}$ phosphor.

Furthermore, Fig. 3 shows the emission spectra of the $CaZnP_2O_7:Dy^{3+}$ phosphors with around 353-nm excitation. The emission spectra were measured between 400–700 nm. Two emission bands peaked at 482 nm and 575 nm are observed. The blue emission at 482 nm is related to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ magnetic dipole transition, while the yellow emission at 575 nm is ascribed to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ electric dipole transition [17, 18]. Within these emission transitions, the yellow and the blue band is the predominant transition. The $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition is hypersensitive (ΔL-2; ΔJ-2) and it can be influenced by its microscopic environment, so its intensity strongly depends on the host. As a result, the entire characteristic indicates that Dy^{3+}-doped $CaZnP_2O_7$ phosphor is a good candidate for solid-state lighting devices (mercury-free excited lamp phosphor) and is suitable as a color converter using UV light as the primary light source.

Chromatic Properties of $CaZnP_2O_7:Dy^{3+}$

The CIE diagram of chromaticity for $CaZnP_2O_7:Dy^3$ is presented in Fig. 4. In the CIE diagram, every natural color could be identified by (x, y) coordinates disposed inside the 'chromatic shoe' representing the saturated colors [19]. Luminescence colors of dysprosium-activated $CaZnP_2O_7:Dy^{3+}$ phosphor are placed in the blue and yellow corners. The location of the color coordinates for $CaZnP_2O_7:Dy^{3+}$ phosphate-based phosphor on the CIE chromaticity diagram presented in Fig.4 indicates that the color properties of the phosphor powder prepared by the solid-state diffusion method are approaching those required for emission displays. The dominant wavelength can be determined by drawing a straight line from one of the CIE white illuminants (*C*s (0.3101, 0.3162)), through the (*x*, *y*) coordinates to be measured, until the line intersects the outer locus of points in Fig. 4. The CIE chromatic diagram shows the chromatic coordinates along the spectral edge of the 1931 CIE chromatic diagram.

The color purity was compared to the 1931 CIE Standard Source C (illuminant *C*s (0.3101, 0.3162)). The chromatic coordinates (*x*, *y*) were calculated using the color calculator program radiant imaging [20]. The coordinates of the $CaZnP_2O_7:Dy^{3+}$ phosphor of color range blue ($x \approx 0.085$, $y \approx 0.159$) and yellow ($x \approx 0.475$, $y \approx 0.518$) for 483 and 575 nm emission wavelengths are shown in Fig. 4 by the cross sign (×).

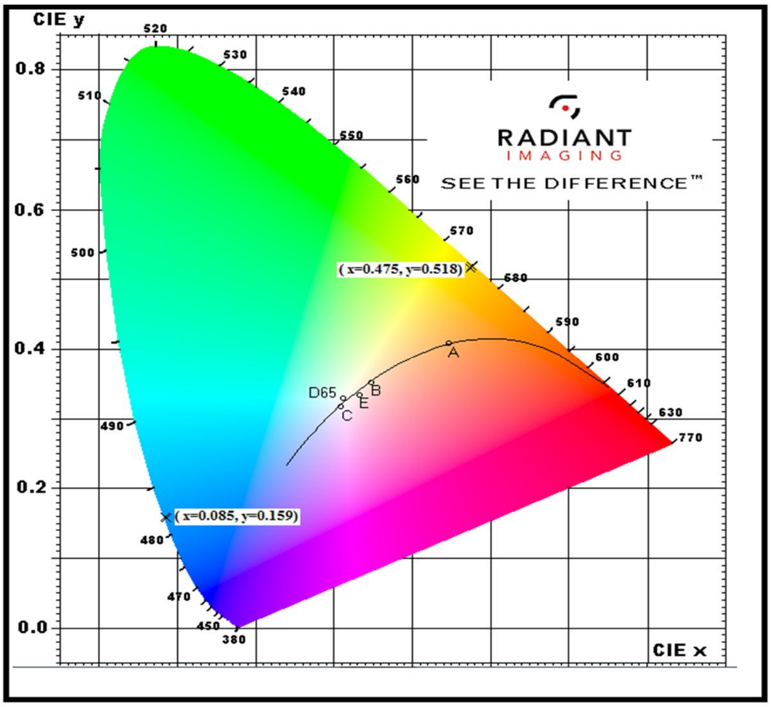

FIG. 4. CIE chromatic diagram showing the chromatic coordinates.

Conclusion

An efficient $CaZnP_2O_7$: Dy^{3+} pyrophosphate phosphor is prepared by modified solid-state diffusion. The XRD pattern for $CaZnP_2O_7$ reasonably agrees with the standard PDF File available. Morphological examination by scanning electron microscope indicates that particles have rod-shape and needle-shape morphologies. The average particle size is in the micrometer range of 2-5 µm and shows uniformity, which is advantageous for fabricating white LEDs (coating purpose). Chromaticity coordinates' values suggest that $CaZnP_2O_7$ pyrophosphate phosphor is suitable for white light-emitting phosphor. In the photoluminescence spectra of present phosphor, under the excitation of 353 nm, only the characteristic transition emissions of Dy^{3+} can be observed, which gives emission at around 482 nm (blue) and 575 nm (yellow). In view of the broad excitation band and excellent luminescent properties, $CAZnP_2O_7$:Dy^{3+} is expected to be a potential candidate for application in n-UV white LEDs and solid-state lighting because of its cost-efficient manufacturing, mercury-free excitation and eco-friendly characteristics.

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