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Dy^{3+} activated $Na_2Zn_5(PO_4)_4$ novel phosphor for white LED

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This paper describes the synthesis and photoluminescence (PL) characteristics of $Na_2Zn_5(PO_4)_4:Dy^{3+}$ phosphor . A novel Dy^{3+} activated $Na_2Zn_5(PO_4)_4$ phosphors was synthesized by conventional solid state diffusion techniques and confirmed by X-ray diffraction (XRD). In the photoluminescence spectra, the $Na_2Zn_5(PO_4)_4:Dy^{3+}$ phosphor emits two distinctive colors: a blue band centered at 433 nm and a yellow band at 573 nm originating from Dy^{3+} under the 387 nm excitation. The 300–400 nm is Hg-free excitation (Hg excitation is 85% 254 nm wavelength of light and 15% other wavelengths), which is characteristic of solid state lighting phosphors. Surface morphology also has been studied by scanning electron microscope (SEM). The phosphor showed intense blue and yellow emission with good Commission International (CIE) chromaticity coordinates, which can efficiently excited at 387 nm and emit blue-yellow light. Therefore, $Na_2Zn_5(PO_4)_4:Dy^{3+}$ may find application for near UV chip-based white LEDs.

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*Keywords:*Phosphor, White LED, $Na_2Zn_5,(PO_4)_4$

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1. Introduction

The useful applications of rare earth element compounds, especially lanthanide phosphate doped inorganic materials, have been touched upon broadly. The need for mercury-free fluorescent lamps for general lighting has become an important subject for light source manufacturers, due to avoiding environmentally harmful materials in the lamp. As the most demanding and challenging application, to become substitute of conventional fluorescent lamp due to light-emitting diodes (LED) have been in the higher demands for the solid-state lighting technology in recent years. LED technology has flourished for the past few decades. High efficiency, reliability, rugged construction, low power consumption and durability are among the key factors for the rapid development of the solid-state lighting based on high-brightness visible LEDs [1]. Recently, we have reported some phosphate based phosphor for LED applications [2-7]. Dy^{3+} ions, which have the luminescence lines in the 470–700 nm region due to $^4F_{9/2}\rightarrow{}^6H_{15/2,13/2,11/2}$ transition, which has attracted much attention because of its white light emission. In this context, a host that can be activated by different ions emitting in different regions of the visible spectrum is a challenge for the solid material synthesis. It is important to get different regions of the visible spectrum in a matrix, whose different activation ions can be structurally substituted for cation sites. In 2007 Ji *et al.*, reported the new phosphate with a crystal structure of $Na_2Zn_5(PO_4)_4$ which has a good thermal stability during the heating process [8]. Moreover, very recently we reported Ce and Eu activated $Na_2Zn_5(PO_4)_4$ red-green-blue (RGB) phosphor for solid state lighting application [9]. Here, we concentrate to prepare same phosphate based system by conventional solid state diffusion a technique, which has advantages over the other methods. There are currently insufficient references on the use of Dy^{3+} phosphors as white LED illumination sources. Therefore, it is crucial to study phosphors for white light emitting materials. At present, more and more researchers devote them to this work with interest. Phosphate has become an important luminescent material used for LED because of their excellent thermal stability and charge stabilization. In this study, we have reported the luminescence properties of a new phosphate phosphor i.e., Dy^{3+}-doped $Na_2Zn_5(PO_4)_4$.

2. Experimental

The Dy -doped $Na_2Zn_5(PO_4)_4$ phosphate based phosphor synthesize by convetional solid state reaction. The raw materials were pure analytical grade materials ZnO, Na_2CO_3 and $NH_4H_2PO_4$ used as starting materials. These materials were weighed in the proper molar ratio then introduce the Dy_2O_3 as a dopant. Mixed and ground homogeneously in an agate mortar. The mixture was heated to 500^0C in a silica crucible and kept at this temperature for 2 hrs, this will to allow ammonia, water, and nitrogen oxides vapors to evaporate. Then again after grinding the powder were heated at 800 °C for 24 hrs, thereby obtaining the white phosphor powder. The chemical reaction is as follows:

$$10\ ZnO+2\ Na_2CO_3 + 8NH_4H_2PO_4 \rightarrow$$
$$2\ Na_2Zn_5(PO_4)_4+12\ H_2O+ 2\ CO_2+6\ NH_4+N_2$$

Several complementary methods were used to characterize the prepared phosphors. The prepared host lattice was characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer (Cu-Ká radiation) at a scanning step of 0.01^0, continue time 20s, in the 2θ range from 10^0 to 100^0 ; the average crystallite size was calculated from the broadening of the X-ray line (311) using Scherer's equation. The photoluminescence measurement of excitation and emission were recorded on the Shimadzu RF5301PC spectrofluorophotometer. The same amount of sample 2g was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. The morphology of the products were examined by scanning electron microscopy (SEM, JEOL 6380A).

3. Results and discussion

3.1 XRD and morphology of $Na_2Zn_5(PO_4)_4$

The structure was solved and reported by Ji et al.[8] in 2007. Fig. 1 shows the XRD pattern of prepared $Na_2Zn_5(PO_4)_4$ materials . The XRD pattern did not indicate presence of the constituents like, ZnO, $NaCO_3$ or $NH_4H_2PO_4$ and other likely phases which are an indirect evidence for the formation of the desired compound. These results indicate that the final product was formed in crystalline and homogeneous form. The $Na_2Zn_5(PO_4)_4$ phosphor is prepared first time; therefore the XRD standard data is not available in JCPDs files. For the obtained phase, it is carefully observed that there are no peaks of raw materials. It is found that the main phase does not agree to any JCPDS available. These results imply that the prepared samples are not simple physical mixtures of ZnO, Na_2CO_3 and $NH_4H_2PO_4$, but a new single host $Na_2Zn_5(PO_4)_4$ materials. Different temperatures do not result in new other phase except the unknown main phase. Consequently, we speculate that the obtained unknown phase is likely to be a new phase. With respect to this point, a further study is still being carried on.

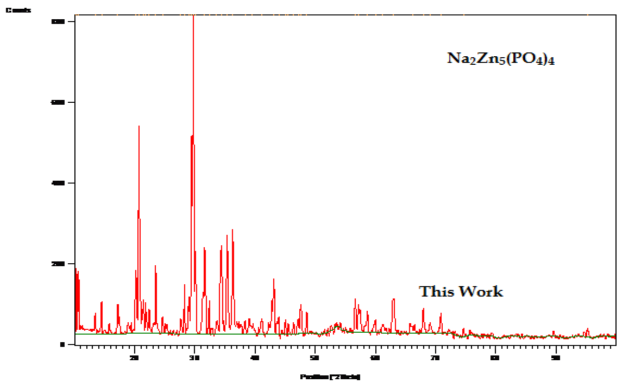

Fig.1 XRD Pattern of $Na_2Zn_5(PO_4)_4$

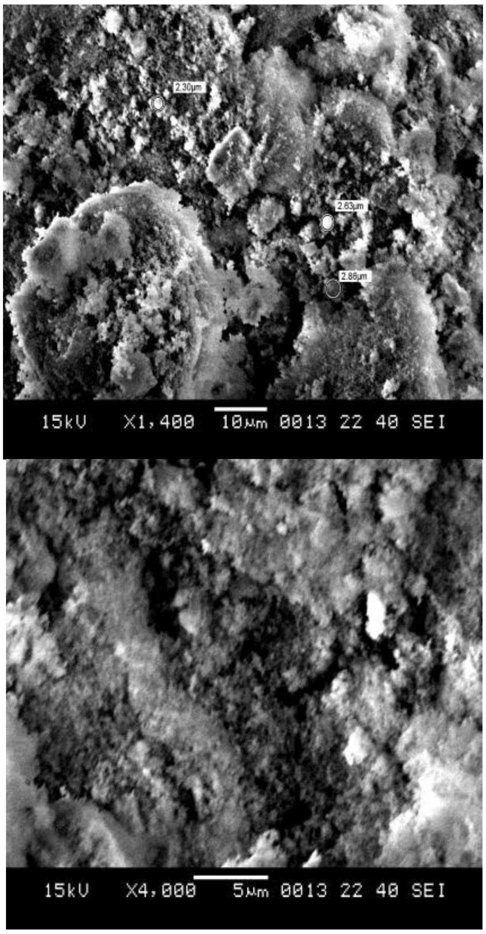

Fig. 2 SEM images of $Na_2Zn_5(PO_4)_4$ phosphor

It is clearly seen that from Fig. 2 the grains have an irregular shape of particles with a size of about 0.5–2 µm. An average crystallite size is in sub-micrometer range seen in SEM images. The size of prepared sample is 0.5–2 µm, which is suitable for the solid state lighting (coating purpose).

3.2 Photoluminescence characterization of $Na_2Zn_5(PO_4)_4:Dy^{3+}$

The photoluminescence excitation spectrum of the prepared Dy activated $Na_2Zn_5(PO_4)_4$ phosphor shown in Fig.3. The excitation peaks are observed at 350 nm, 363 nm and 387 nm due to transition of $^6H_{15/2} \rightarrow {}^6F_{9/2}$ Dy^{3+} ion. Between these three excitation bands we choose 387 nm because it is suitable for solid state lighting. The photoluminescence emission spectra of the prepared Dy activated $Na_2Zn_5(PO_4)_4$ phosphor shown in fig.4. In the photoluminescence emission spectra, the $Na_2Zn_5(PO_4)_4:Dy^{3+}$ phosphor emits two distinctive colors, a blue band centered at 433 nm and yellow band at 573 nm originating from Dy^{3+} ion under the excitation of 387 nm (i.e. excitation of the LED lighting). Thus the combination of colors gives BY (blue–yellow) emissions which can produce white light by Hg-free excitation (Hg excitation is 85% 254 nm wavelength of light and 15% other wavelengths). It is known that Dy^{3+} emission around

433 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) due to magnetic dipole moment and 573 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) due to electric dipole moment. Recently, more research done on the development of new solid state lighting phosphors, while, out of them maximum phosphors shows the only single color visible emission. It is well known that the color of the trivalent dysprosium ($4f^9$ configuration) luminescence is close to white. In $Na_2Zn_5(PO_4)_4:Dy^{3+}$ predominant emission is around 433 nm suggesting that ligand field slightly deviates from its inversion symmetry. A slight marginal shift in the peak position of Dy^{3+} ions is observed in all prepared phosphors. Such behavior is as expected for the emission involving f-f transitions where ligand field changes with the host matrix. The change in the host metal atom, yellow/blue ratio changes due to the change of local site symmetry around Dy^{3+} ion, gives blue-yellow emissions. This excitation, color co-ordinates are such that it is suitable as white-light-emitting phosphor. In this case, the Dy^{3+} ion may enter the host lattice to substitute Zn^{2+} or it may be located on surfaces of the crystals structure. It is clear from the photoluminescence spectra that in the Dy^{3+}-doped phosphor, energy transfer from the host to the Dy^{3+} activator ions occurs. When illuminated by near UV light excitation source, excitation energy is absorbed by the host and creates the self-trapped excitation (the 387 nm broad band) emission; meanwhile, the absorbed energy is transferred to the Dy^{3+} ion and creates the typical emissions of Dy^{3+}. Generally, a small doping gives weak luminescence but surplus doping possibly causes quenching of luminescence. With the increase in concentration of Dy^{3+} ions the peak intensity increases and maximum intensity is observed for 0.5 mol% of Dy^{3+} ion. The increase in the luminescence intensity with the increases in concentration of Dy ion can be explained as follows: The luminescence spectrum of Dy^{3+} ion was slightly influenced by surrounding ligands of the host material, because electronic transitions of Dy^{3+} involve only redistribution of electrons within the inner 4f sub shell [10]. The results show that the phosphor has the highest emission intensity at 0.5 mol% of Dy^{3+}, which should be considered as the quenching concentration. The position of the emission peak is not influenced by the Dy^{3+} concentration.

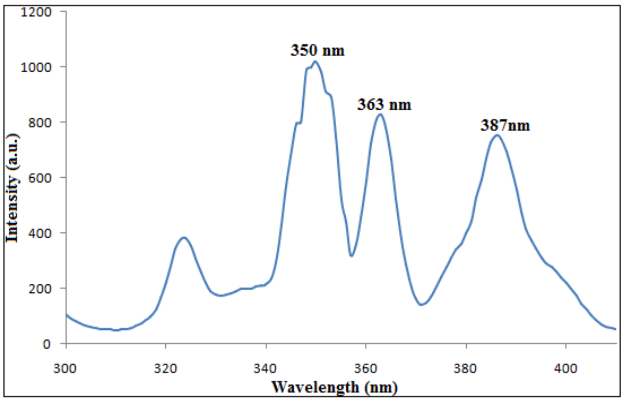

Fig. 3 Excitation spectrum of $Na_2Zn_5(PO_4)_4:Dy^{3+}$ monitored at 433 nm.

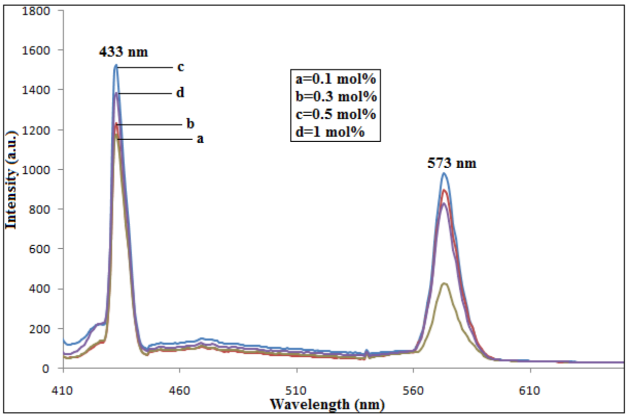

Fig. 4 Emission spectrum of $Na_2Zn_5(PO_4)_4:Dy^{3+}$ when excited at 387 nm.

A series of $Na_2Zn_{5-x}(PO_4)_4:Dy_x^{3+}$ phosphors with various Dy^{3+} concentrations (x=0.1–1 mol%) were prepared and the effect of doped Dy^{3+} concentration on the emission intensity was investigated. It is known that Dy^{3+} shows intense peaks at 433 nm due to fluorescent transitions of $^4F_{9/2} \rightarrow {}^6H_{15/2}$ that is due to magnetic dipole and 573 nm due to fluorescent transitions of $^4F_{9/2} \rightarrow {}^6H_{13/2}$ that is due to electric dipole moment, when Dy^{3+} ions are located at low-symmetry sites with no inversion centers. Thus, the yellow and blue ratio known as the asymmetry ratio of Dy^{3+} ion varies while locating in different host lattices. Fig. 5 shows schematic energy-level diagram of $Na_2Zn_5(PO_4)_4:Dy^{3+}$.

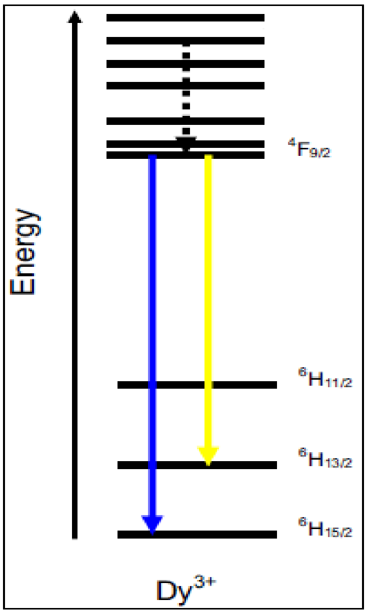

Fig. 5. Schematic energy-level diagram of $Na_2Zn_5(PO_4)_4:Dy^{3+}$

3.3 Chromatic properties

Most lighting specifications refer to colour in terms of the 1931 CIE chromatic colour coordinates which recognizes that the human visual system uses three primary colours: red, green, and blue [11,12]. In general, the colour of any light source can be represented on the (*x*, *y*) coordinate in this colour space. Three properties, the chromatic coordinates, dominant wavelength and color purity for $Na_2Zn_5(PO_4)_4:Dy^{3+}$ (0.5 mol%) phosphor are determined from the spectrum in Fig.4. The colour purity was compared to the 1931 CIE Standard Source C (illuminant *C*s (0.3101, 0.3162)). The chromatic coordinates (*x*, *y*), was calculated using the colour calculator program radiant imaging [13].The coordinates of the blue $Na_2Zn_5(PO_4)_4:Dy^{3+}$ (0.5 mol%) ($x \approx 0.1677$, $y \approx 0.0078$) and yellow ($x \approx 0.4649$, $y \approx 0.5339$) phosphor is shows in Fig .6 by solid circle. The location of the colour coordinates of the triple phosphate powder on the CIE chromaticity diagram presented in Fig.6 indicates that the colour properties of the phosphor powder prepared by solid state diffusion technique are approaching those required for field emission displays. The dominant wavelength is defined as the single monochromatic wavelength that appears to have the same colour as the light source. 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 along the spectral edge of the 1931 CIE chromatic diagram.

All the results calculated from the spectra in Fig. 4 are plotted in the Commission International de l'E´clairage (CIE) 1931 chromaticity diagram, as shown in Fig. 6. It indicates that Dy^{3+} doped $Na_2Zn_5(PO_4)_4$ are close to the edge of CIE diagram, which indicates the high color purity of this phosphor. By connecting these two points in the form of a triangle (included white light point (0.31, 0.32)) the intermediate compositions can generate white light with a particular ratio of this phosphor.

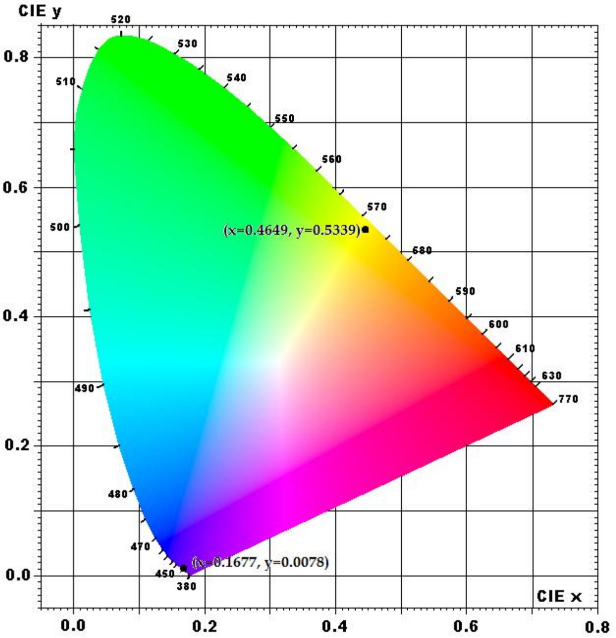

Fig.6 CIE chromatic diagram showing the chromatic coordinates for $Na_2Zn_5(PO_4)_4:Dy^{3+}$

4. Conclusions

$Na_2Zn_5(PO_4)_4:Dy^{3+}$ phosphor prepared by conventional solid state diffusion techniques and confirmed by X-ray diffraction pattern. Photoluminescence characteristics of prepared phosphor shows the two emission peaks at 433 nm(blue) and 573 nm(yellow) due to Dy^{3+} ion under the 387 nm excitation of solid state lighting. Scanning electron microscope results shows the grains have an irregular shape of particles with a size of about 0.5–2 μmand it is suitable for lamp industry. The $Na_2Zn_5(PO_4)_4:Dy^{3+}$ phosphor showed intense blue and yellow emission with good Commission International chromaticity coordinates, which can efficiently excited at 387 nm and emit blue-yellow light. Therefore, $Na_2Zn_5(PO_4)_4:Dy^{3+}$ may be useful for near UV chip-based white LEDs lighting.

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