



Investigation of Photoluminescence Properties of Reddish-Orange Emitting $\text{Na}_2\text{ZnP}_2\text{O}_7\text{:Eu}^{3+}$ Phosphor

A.M. Bhake¹, G.D. Zade², Govind B. Nair³ and S.J. Dhoble^{3*}

¹Department of Physics, P.I. E.T., Nagpur, India.

²Department of Physics, J.N College, Nagpur, India.

³Department of Physics, R.T.M. Nagpur University, Nagpur, India.

Abstract— In the present work, a series of Eu^{3+} ions doped sodium zinc diphosphate ($\text{Na}_2\text{ZnP}_2\text{O}_7$) phosphor was synthesized by wet chemical method. Morphological (SEM), spectroscopic (FTIR) and photoluminescence (PL) properties of this phosphor were investigated and well analyzed at room temperature. The excitation spectra indicate that these phosphors can be effectively excited by near-UV (370–410 nm) light. The emission spectra exhibit a strong reddish-orange emission, which is due to the $^5D_0 \rightarrow ^7F_1$ transitions of Eu^{3+} ions. The orange emission arising due to $^5D_0 \rightarrow ^7F_1$ transition is dominant over that of $^5D_0 \rightarrow ^7F_2$. The emission spectra showed maximum intensity for 1mol% concentration of Eu^{3+} . SEM micrographs show that the particles are of quadrate shape with an average diameter of 1–2 μm , which suggests that these phosphors can be used in the fabrication of solid-state lighting devices. An FTIR spectrum of this pyrophosphate phosphor gives information about metal-oxygen vibrations and the internal and external modes of $\text{P}_2\text{O}_7^{4-}$ group.

1. INTRODUCTION

Alkali metal pyrophosphates (AMP_2O_7 or $\text{A}_2\text{MP}_2\text{O}_7$) have potential applications in phosphors [1], X-ray and gamma radiation scintillators [2, 3], solid state lasers [4], catalysts and ion conductors [5]. The layered structure of $\text{A}_2\text{MP}_2\text{O}_7$ is characterized by MO_4 tetrahedron sharing corners with four different $[\text{P}_2\text{O}_7]$ groups and monovalent A^+ ions located between these layers [6]. Quaternary phosphates in the A–M–P–O system (A=alkali or alkaline earth; M=transition metal ion) have attracted considerable attention due to their interesting structural geometries and potential applications. The $\text{Na}_2\text{ZnP}_2\text{O}_7$ pyrophosphate family has been extensively studied here because materials belonging to these classes possess an open framework structure facilitating the mobility of cations (A^+) leading to good ionic conductivity and are possible sources for intercalation/deintercalation reactions [7].

Rare earth compounds have been widely studied for their superior photoluminescence properties.

Rare earth and transition metal ions have been studied as excellent luminescence materials, and these materials have been widely used as phosphors [8], fiber amplifiers [9, 10], solid state laser [11], etc. Phosphates and pyrophosphates have been considered as hosts for rare earth doped phosphor materials [12]. The materials containing Eu^{3+} ions have applications in such diverse fields as illumination device, display devices and medical diagnostics. Phosphor-converted white light-emitting diodes (LEDs) have gained much attention as a new generation solid state lighting device due to their

advantageous features such as of low energy consumption, long lifetime and environmentally friendly [13–17]. At present, $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ is often used as the red phosphor for near UV InGaN-based LEDs [18]. However, this sulfide-based phosphor is chemically unstable, less efficient and not environment-friendly. Therefore, it is needful to find a new red phosphor that can exhibit intense red emission with high absorption in the near UV spectral region. Eu^{3+} ions have sharp orange-red emission which is almost independent of the host matrix and hence, a number of Eu^{3+} doped inorganic phosphors were synthesized to meet the requirements of the rapid development of promising display and illuminating technologies [19–23]. The present study uses Eu^{3+} ions as activator in pyrophosphates, since pyrophosphates are stable crystalline compounds.

Nowadays research on red, green, blue tricolour phosphors, which are excited by near-UV LED chips, is attracting huge attention. As compared to commercial white LEDs fabricated with a blue chip and yellow YAG:Ce^{3+} phosphor, the white LEDs fabricated with near-UV chips and tri color phosphors have two important advantages: one is the excellent color-rendering index and another is the high color tolerance. Great efforts have been made to discover new host materials as well as activators with high performance for red-emitting phosphors by Shinde et al., e.g. Eu^{3+} -activated $\text{M}_6\text{AlP}_5\text{O}_{20}$ (M= Sr/Ba/Mg) (1), $\text{Na}_2\text{X}(\text{PO}_4)\text{F}$ (X =Mg, Ca, Sr) (2), $\text{Na}_2\text{Zn}_5(\text{PO}_4)_4$ (3), $\text{K}_3\text{Al}_2(\text{PO}_4)_3$ (4) and NaCaPO_4 [24]. These studies mostly concentrated on the choice of the host materials and the central luminescent ions. Phosphate compounds can provide many crystal field environments imposed on emission centres. Moreover, phosphate phosphors doped with rare earth ions have excellent

* Corresponding Author Email: sjdhoble@rediffmail.com

thermal and charge stabilization [25, 26] and also phosphate compounds are known to be multifunctional materials. In particular, orthophosphates have been extensively investigated, due to their structural diversity. This makes them suitable as hosts to accommodate active rare earth ions. The phosphate family symbolizes possibly one of the most attractive kinds of novel inorganic materials, largely owing to the ability of the tetrahedral PO_4^{3-} group to bond with other structural units. Recently, we have reported several phosphate phosphors for lamp applications [27–28]. Both the chemical and thermal stability of the phosphor is a matter of concern in order to prevent degradation with temperature and time that results in loss of efficiency and cause changes in the produced light color. Therefore, development of persistent phosphors, with better physical and chemical stability, water-resistant property, is an important requirement in lamp industry. Recent developments in the field of solid state lighting (SSL) have motivated the demand and development for novel efficient inorganic luminescent materials. In this respect, europium doped materials have received special attention [29–30].

2. EXPERIMENTAL

In recent past, many methods have been developed to prepare various phosphors. Most commonly used methods are sol-gel, precipitation, wet chemical, solid state reaction, spray pyrolysis, etc.

We prepared the Eu^{3+} -doped $\text{Na}_2\text{ZnP}_2\text{O}_7$ pyrophosphate phosphor by the wet chemical synthesis assisted with precipitation technique because of its simplicity, low cost and relatively fast processing which maintains thermodynamically stable phases with high purity at relatively low temperature. To form Eu^{3+} -doped $\text{Na}_2\text{ZnP}_2\text{O}_7$ compound, the starting materials Na_2SO_4 , ZnSO_4 and $(\text{NH}_4)_2\text{HPO}_4$ of analytical grade (pure) were weighed in the proper molar ratio and each precursor was thoroughly mixed in double distilled water to form transparent solutions in separate beakers. All the solutions were added together and stirred well on a magnetic stirrer at room temperature.

The rare earth ion (Eu^{3+}), in the nitrate form, was introduced in proper stoichiometric ratio as a dopant with different concentrations varying as 0.05 mol%, 0.1 mol%, 0.5 mol% and 1 mol%.

It was observed that after adding di-hydrogen ammonium phosphate $[(\text{NH}_4)_2\text{HPO}_4]$, the precipitate formed instantly and a thick solution like paste of creamy whitish color was obtained. The obtained solution was washed several times to separate the unwanted by-products with distilled water, filtered with best quality filter paper and allowed to dry in an oven at 90°C for 24 hours. All the doped samples of this series were prepared in this way. Completely dried samples were in fine yellowish white powder form.

The prepared hosts lattice $[\text{Na}_2\text{ZnP}_2\text{O}_7]$ was subjected to scanning electron microscopy (SEM) for surface morphology and Fourier Transform Infrared (FTIR) spectroscopic study for chemical identification. For testing their optical properties, the phosphors were tested for photoluminescence (PL) analysis. The PL measurements were done by a Shimadzu RF-5301PC spectrofluorophotometer fitted with a 150 W 'Xenon flash lamp' as an excitation source and sensitive photomultiplier tube. The excitation and emission spectra were recorded using a spectral slit width of 1.5 nm. This spectrofluorophotometer provides corrected excitation and emission spectra in the wavelength range from 220–420nm and 300–650 nm respectively. All measurements were done at room temperature.

3. RESULTS AND DISCUSSION

3.1 SEM Studies

Fig.1 shows the SEM micrographs of $\text{Na}_2\text{ZnP}_2\text{O}_7$ pyrophosphate phosphor for studying the particle size and shape. It can be seen that the particles are agglomerated with a narrow size, since the pyrophosphate phosphor particles were quenched at a rather low temperature. The particles exhibited a quadrate shape with an average diameter of 1–2 μm , which suggests that the phosphors are suitable for solid-state lighting devices [32].

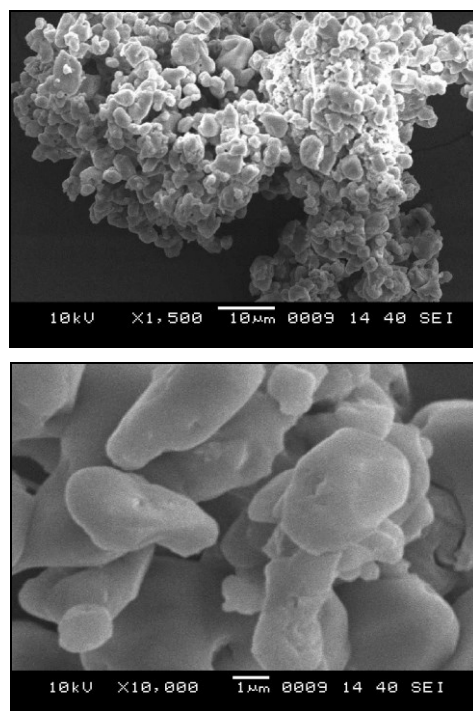


Fig. 1: SEM of $\text{Na}_2\text{ZnP}_2\text{O}_7$ phosphor.

3.2 Fourier Transforms Infrared (FTIR) Spectroscopy

For confirming the molecular structures of the synthesized compounds, FT-IR spectroscopy was used.

An infrared spectrum represents a finger print of a sample with absorption peak, which corresponds to the frequencies of vibrations between the bonds of the atoms making up the materials. The infrared spectra of pyrophosphates give information regarding the internal and external modes of $P_2O_7^{4-}$ group and metal-oxygen vibration peaks. Fig.2 shows the FTIR spectrum of the $Na_2ZnP_2O_7$ pyrophosphate.

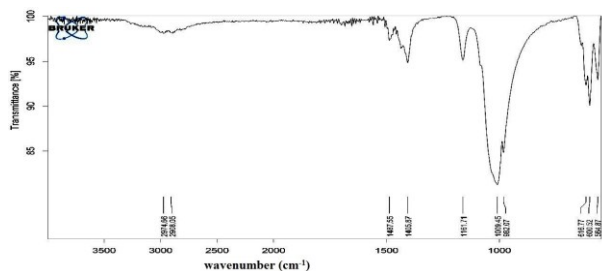


Fig. 2: FTIR spectrum of the $Na_2ZnP_2O_7$ pyrophosphate.

Fig.2 shows the IR spectra of $Na_2ZnP_2O_7$ in the range $1600-500\text{ cm}^{-1}$. The frequencies of the $P_2O_7^{4-}$ anion are assigned on the basis of the characteristic vibrations of the P–O–P and PO_3 groups [33]. From the above spectra, it is observed that the phosphate units are characterized by two IR absorption bands near 1009.45 and 600.52 cm^{-1} . It shows prominent multiple absorption bands in the regions $1487.55-564.87\text{ cm}^{-1}$. The broad band is observed at 1000.45 cm^{-1} due to Na_2SO_4 . The sulphate vibration absorbing near $1000-1100\text{ cm}^{-1}$ is triply degenerate and this may be case of splitting of the degeneracy as a result of altering the crystal symmetry.

3.3 Photoluminescence (PL) Study for $Na_2ZnP_2O_7:Eu^{3+}$ Phosphor

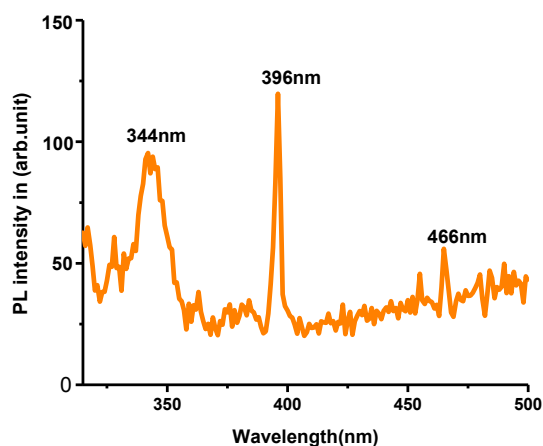


Fig. 3: Excitation spectra for $Na_2ZnP_2O_7:Eu$ phosphor.

Fig.3 shows the PL excitation spectra of $Na_2ZnP_2O_7:Eu^{3+}$ phosphor. The excitation spectrum shows the highest intensity peak at 396 nm wavelength with two small intensity peaks at 344 nm and 466 nm . The narrow excitation peak lines appearing at longer wavelengths correspond to the characteristic f-f transitions of Eu^{3+} . The

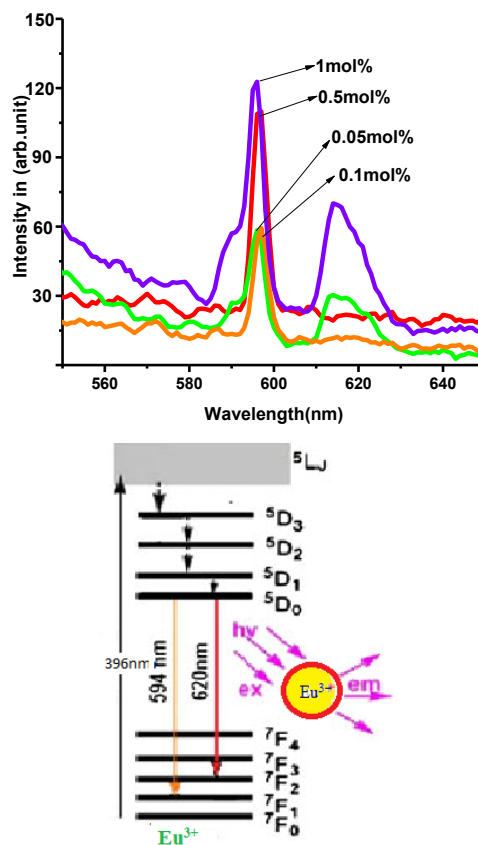


Fig. 4: Emission spectra of $Na_2ZnP_2O_7:Eu^{3+}$ under 396 nm excitation.

main excitation line is assigned to ${}^7F_0 \rightarrow {}^5L_6$ (396 nm) transition. This transition of Eu^{3+} ions, which is far away from Hg excitation, is a main characteristic of solid-state lighting (i.e. in the range $365-396\text{ nm}$ near-UV region) in the lamp industry. The excitation spectrum shows that these phosphors can be effectively excited by near-UV-light, which is exactly required by UV pumped multi-phosphor-converted white LEDs. Therefore, this phosphor may be a suitable candidate to be used as reddish-orange phosphor for LED lighting. Fig.4 shows the PL emission spectrum obtained under 396 nm excitation, and the energy level diagram. PL emission spectra were observed for various concentrations of Eu^{3+} such as 0.05 mol\% , 0.1 mol\% , 0.5 mol\% and 1 mol\% etc. Highest PL intensity, located at 594 nm , is noted for 1 mol\% of Eu^{3+} . This reddish-orange emission at 594 nm , is mainly from the ${}^5D_0 \rightarrow {}^7F_1$ magnetic dipole transitions of Eu^{3+} ions, and the weak red emission peaked around 620 nm is due to the hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ electric dipole transition. The PL intensity of Eu^{3+} emission at 620 nm is found less as compared to 594 nm peaks. From emission spectra, we observed that peak position of emission lines did not change with the concentration of Eu^{3+} .

According to Judd-Ofelt theory, the magnetic dipole transition is allowed. However the electric dipole

transition is allowed only when Eu^{3+} ion occupies a site without an inversion centre and its intensity is prominently affected by local environment around Eu^{3+} ions [33]. The optical properties of Eu^{3+} activated materials also strongly depend on its valence states. Normally, Eu^{3+} ions exhibit emissions from orange to red light, which originated due to 4f–4f transitions of Eu^{3+} ions. However, the efficiency of this type of luminescent material is supposed to be very low, since the 4f–4f transitions of Eu^{3+} are forbidden transitions and their excitations are very ineffective in such pyrophosphate hosts; for most Eu^{2+} ion doped phosphors, the stimulated emission originates from 4f–5d transitions and their emission wavelength can vary in a broad range from ultraviolet to red. Since the 4f–5d transitions of Eu^{2+} are allowed transitions, the absorption and emission of Eu^{2+} in many hosts are very efficient, which makes the Eu^{2+} activated luminescent materials to be good candidates for industrial phosphors as compare to Eu^{3+} doped materials [34–35].

3.4 Effect of Dopant Concentration on PL Intensity

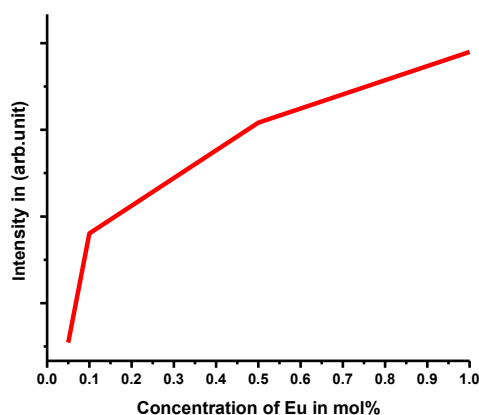


Fig. 5: Concentration in mol% versus PL intensity

Variation of PL emission intensity of $\text{Na}_2\text{ZnP}_2\text{O}_7:\text{Eu}^{3+}$ phosphor with the concentration of Eu^{3+} ions is shown in Fig.5. It is observed that the intensity increases gradually as the concentration of dopant ions increase. The most intense peak was obtained for the concentration of 1 mol% due to the energy transfer between the neighbouring Eu^{3+} ions. With an increase in the concentration of the activator ion, the number of luminescent centre increases and the emission intensity gets enhanced. Ultimately, highest PL intensity was obtained for 1 mol% of Eu^{3+} and lower europium contents result in a substantial decrease in emission intensity. In case of $\text{Na}_2\text{ZnP}_2\text{O}_7:\text{Eu}^{3+}$ phosphors, Eu^{3+} ions entered the host crystal lattice and preferentially substituted alkali metal (i.e. Na^+) ions. This induced the charge imbalance and thus, reduced the lattice distortion and enhanced the luminescence intensity [36]. In this way, the emission intensity is strongly related to the concentration of the Eu^{3+} activator ions.

3.5 CIE Diagram for $\text{Na}_2\text{ZnP}_2\text{O}_7:\text{Eu}^{3+}$ Phosphor

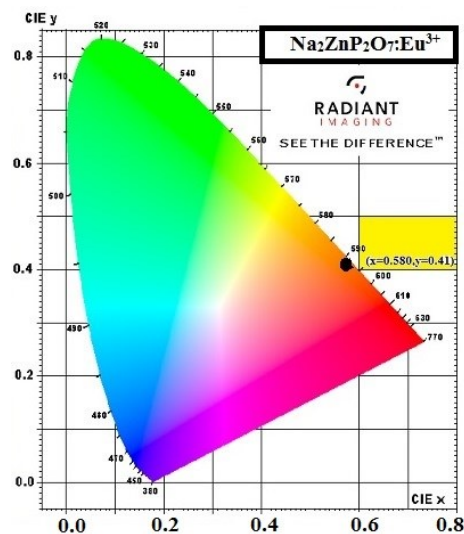


Fig. 6: CIE chromaticity diagram showing the chromaticity coordinates for $\text{Na}_2\text{ZnP}_2\text{O}_7:\text{Eu}^{3+}$ phosphor.

All the results calculated from the emission spectra in Fig. 4 are plotted in the Commission Internationale de l'Eclairage (CIE) 1931 chromaticity diagram, as shown in Fig.6. The $\text{Na}_2\text{ZnP}_2\text{O}_7:\text{Eu}^{3+}$ phosphor is a red phosphor. The location of the color co-ordinates of the $\text{Na}_2\text{ZnP}_2\text{O}_7:\text{Eu}^{3+}$ phosphor on the CIE chromaticity diagram presented is as shown in Fig. 6 by a small circle. Here, the coordinates of only 1 mol% concentration of Eu^{3+} has been plotted, since maximum intensity was obtained for this dopant concentration in the PL emission spectra. In general, the color of any light source can be represented by (x, y) coordinates in this color space. The chromatic coordinates (x, y), were calculated which is equal to (x=0.580, y=0.414) using the color calculator program Radiant Imaging [36]. This indicates that Eu^{3+} -doped $\text{Na}_2\text{ZnP}_2\text{O}_7$ is close to the edge of the CIE diagram, which indicates the high color purity of this phosphor. The CIE diagram indicates that the color properties of this phosphor may have significance in field emission displays. Also, the PL emission in Eu^{3+} -doped $\text{Na}_2\text{ZnP}_2\text{O}_7$ may be efficiently utilized as a red component for solid-state lighting, and is helpful in generating white light with a particular ratio of this phosphor [36].

4. CONCLUSION

A series of Eu^{3+} ions doped $\text{Na}_2\text{ZnP}_2\text{O}_7$ pyrophosphate phosphor was prepared by wet chemical method, for the first time. SEM, FT-IR and PL properties of this phosphor were investigated and systematically analyzed at room temperature. $\text{Na}_2\text{ZnP}_2\text{O}_7:\text{Eu}^{3+}$ phosphors were efficiently excited by near-ultraviolet light of 396 nm wavelength and exhibited bright orange-red emission which is due to the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions of Eu^{3+} ions. Therefore, this phosphor is a potential candidate for an orange-red emitting LED and red component in field emission

displays. The CIE diagram indicates the high color purity of this phosphor. We proposed here a feasible interpretation about the impact of Eu^{3+} doping on photoluminescence properties of the phosphor.

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