

Optical properties of Cu^+ ions activated $\text{Na}_2\text{Zn}(\text{PO}_4)\text{Cl}$ phosphor

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This paper reports optical properties of copper doped $\text{Na}_2\text{Zn}(\text{PO}_4)\text{Cl}$ phosphor prepared by wet-chemical. The phosphor was characterized by photoluminescence (PL) spectroscopy, Scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FT-IR) and Ultraviolet (UV) -Visible diffuse reflectance spectroscopy. Incorporating Cu^+ ions in the $\text{Na}_2\text{Zn}(\text{PO}_4)\text{Cl}$ host resulted in blue emission peaking at 438 nm under 357 nm excitation. The FT-IR spectrum revealed the characteristic vibrational bands of the prepared phosphor material. Band gap was calculated from UV-diffuse reflectance spectra. The investigated halo-phosphate $\text{Na}_2\text{Zn}(\text{PO}_4)\text{Cl}:\text{Cu}^+$ may be a good candidate as blue phosphor.

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1. Introduction

Luminescence phenomenon has always fascinated mankind owing to its wide range of applicability in displays, lighting, scintillation and medical field [1]. In recent years, phosphate-based inorganic phosphors doped with transition metal ions and rare earth ions have gained huge recognition as potential luminescent materials due to excellent thermal as well as chemical stability, low sintering temperature, low phonon energy and large band gap of phosphate group. [2–4]. $\text{Ca}_9\text{La}(\text{PO}_4)_7:\text{Eu}^{3+}$ [5], $\text{SrZn}_2(\text{PO}_4)_2:\text{Eu}^{3+}$, Tb^{3+} , Li^+ [6], $\text{A}_{(1-3x)}\text{Eu}_x\text{Zr}_2(\text{PO}_4)_3$ (A = Na, K, Rb, Cs) [7], $\text{Ca}_{6-x}\text{BaP}_4\text{O}_{17}:\text{xSm}^{3+}$ [8], $\text{Ca}_3\text{Y}(\text{PO}_4)_3:\text{Eu}^{2+}, \text{Mn}^{2+}$ [9], $\text{Sr}_8\text{MgLa}(\text{PO}_4)_7:\text{Ce}^{3+}/\text{Eu}^{2+}/\text{Mn}^{2+}$ [10], $\text{Ca}_9\text{LiGd}_{0.667}(\text{PO}_4)_7:\text{Ce}^{3+}$, Mn^{2+} [11] are some of the recently reported phosphate phosphors. Phosphors made up of halides (i.e. F, Cl, Br) and phosphate/ borates/silicate group are called as halo-phosphors and they are preferably studied to get intense and novel luminescence due to the strong crystallographic field exerted by halide ions in the lattice. $\text{Ba}_4\text{Gd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}$ [12], $\text{Ca}_9\text{La}(\text{PO}_4)_5(\text{SiO}_4)\text{Cl}_2:\text{Dy}^{3+}$ [13] and $\text{Sr}_{5(1-x)}\text{Ba}_{5x}(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ [14] are some of the recently reported halo-phosphors.

Nowadays, most of the research is focused on developing transition metal ion doped phosphors due to their superiority over rare earth ion doped phosphor in terms of cost-effectiveness and eco-friendliness. A phosphor is a combination of a suitable host material along with an activator. Cu^+ is one of the most efficient transition metal ion activators that exhibit characteristic luminescence corresponding to $3d^9 4s^1 \leftrightarrow 3d^{10}$ transitions which is strictly forbidden for free ion but become allowed in crystal and glasses due to mixing of odd state of parity [15]. It shows broad photoluminescence emission in UV to visible region when it gets doped in suitable host.

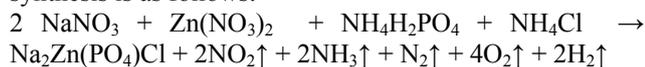
$\text{NaCaAlPO}_4\text{F}_3:\text{Cu}(\text{II})$ [16], $\text{ZnS}:\text{Cu}^+$ [17], $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}^+$ [18], $\text{Na}_2\text{SO}_4:\text{Cu}^+$ [19], $\text{SrS}:\text{Cu}^+$ [20], $\text{MgS}:\text{Cu}^+$, $\text{BaS}:\text{Cu}^+$, $\text{CaS}:\text{Cu}^+$ [21], $\text{BaZnOS}:\text{Cu}$ [22], $\beta\text{-BaB}_2\text{O}_4:\text{Cu}^{2+}$ [23], $\text{SrAl}_2\text{O}_4:\text{Cu}^{2+}$ [24], $\text{BaFCl}:\text{Cu}^+$, $\text{K}_2\text{SO}_4:\text{Cu}^+$, $\text{Na}_2\text{SO}_4:\text{Cu}^+$, $\text{Cs}_2\text{SO}_4:\text{Cu}^+$, $\text{Rb}_2\text{SO}_4:\text{Cu}^+$, $\text{Li}_2\text{SO}_4:\text{Cu}^+$, $\text{Li}_3\text{PO}_4:\text{Cu}^+$, $\text{SrLiPO}_4:\text{Cu}^+$, $\text{BaLiPO}_4:\text{Cu}^+$ [25], $\text{KMgSO}_4\text{Cl}:\text{Cu}^+$, $\text{KZnSO}_4\text{Cl}:\text{Cu}^+$, $\text{Na}_3\text{SO}_4\text{F}:\text{Cu}^+$, $\text{NaMgSO}_4\text{F}:\text{Cu}^+$ [26] and $\text{Na}_2\text{Zn}(\text{PO}_4)\text{Cl}:\text{Cu}^+$ [27] are some of the Cu^+ doped phosphors studied for their photoluminescence (PL) properties.

Shinde et. al. synthesized $\text{Na}_2\text{Zn}(\text{PO}_4)\text{Cl}:\text{Cu}^+$ halo-phosphate phosphor via combustion route and reported its photoluminescence properties [27]. Synthesis methods can alter the intensity as well as peak position of PL emission [28]. In this work, wet-chemical technique was employed for synthesis of $\text{Na}_2\text{Zn}(\text{PO}_4)\text{Cl}:\text{Cu}^+$ compound and we observed the shift in PL emission peak as compared to previously reported results. The present paper describes detail study of Cu^+ ion-doped $\text{Na}_2\text{Zn}(\text{PO}_4)\text{Cl}$ phosphor synthesized by wet-chemical route. Wet-chemical is an easy and low-temperature procedure as compared to other traditional methods of preparation [11]. The prepared phosphor material was characterized by scanning electron microscopy (SEM) along with Energy dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FT-IR) and Ultraviolet (UV) -diffuse reflectance spectroscopy. The photoluminescence (PL) characteristics of the prepared phosphors were studied at room temperature for different dopant concentrations.

2. Experimental

2.1. Synthesis

$\text{Na}_2\text{Zn}(\text{PO}_4)\text{Cl}:\text{Cu}^+$ phosphor was prepared by wet-chemical technique. The precursors NaNO_3 , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ and NH_4Cl of high purity, analytical grade were taken in a stoichiometric ratio. Each compound was separately dissolved in double distilled de-ionized water taken in beaker and stirred on magnetic stirrer. The solutions were added to each other one by. Thereafter, water soluble salt of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was added to the solution. The transparent solution was then evaporated at 80°C in a hot air oven to obtain dry powder. The powder was further heated at 150°C for 1h. The sample was then slowly cooled to room temperature. The resultant powder was crushed to fine particles in a mortar pestle and was used for further characterization. For different molar concentrations of Cu, the ratio of copper nitrate was changed in the proportion of 0.002, 0.01, 0.05 and 0.1 mol %. The expected chemical reaction in the synthesis is as follows:



2.2. Characterization

Photoluminescence (PL) emission and excitation spectrum of the samples were recorded using Spectrofluorophotometer (Shimadzu RF – 5301 PC). Excitation and emission spectra were obtained using a spectral slit width of 1.5 nm. Scanning electron microscope (SEM) and energy dispersive spectrum (EDS) images were obtained using JEOL 6380-A. The Fourier transform infrared (FTIR) spectrum of the phosphor was recorded in the mid-infrared range of $450\text{--}4000\text{ cm}^{-1}$ using KBr pellet by means of FTIR (IR Affinity-1, Shimadzu) spectrophotometer. UV-Visible Spectrophotometer model

JASCO V-670 with diffuse reflectance accessory (integrated sphere) was used for studying diffuse reflectance spectra.

3. Results and discussion

3.1. Morphological studies

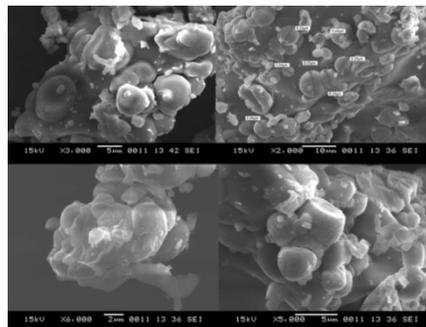


Fig. 1. Scanning electron microscope images of the Cu (0.1 mol %) doped $\text{Na}_2\text{Zn}(\text{PO}_4)\text{Cl}$ phosphor

The morphology and chemical composition of synthesized phosphor are investigated by SEM and EDS technique. Fig. 1 shows the SEM micrographs of copper doped $\text{Na}_2\text{Zn}(\text{PO}_4)\text{Cl}$, taken with different magnifications. The SEM images of the samples show agglomeration with an irregular morphology. SEM images reveal that the sample consists of irregular and round shaped structures. The crystallite size was estimated to be between 3 to $8.05\ \mu\text{m}$. The assimilation of copper into the host material was confirmed by EDS measurements. The EDS pattern is given by Figure 2. The pattern shows the presence of Zn, Na, P, O, Cl and Cu element. From this EDS pattern confirmed that the prepared samples contains doped copper species.

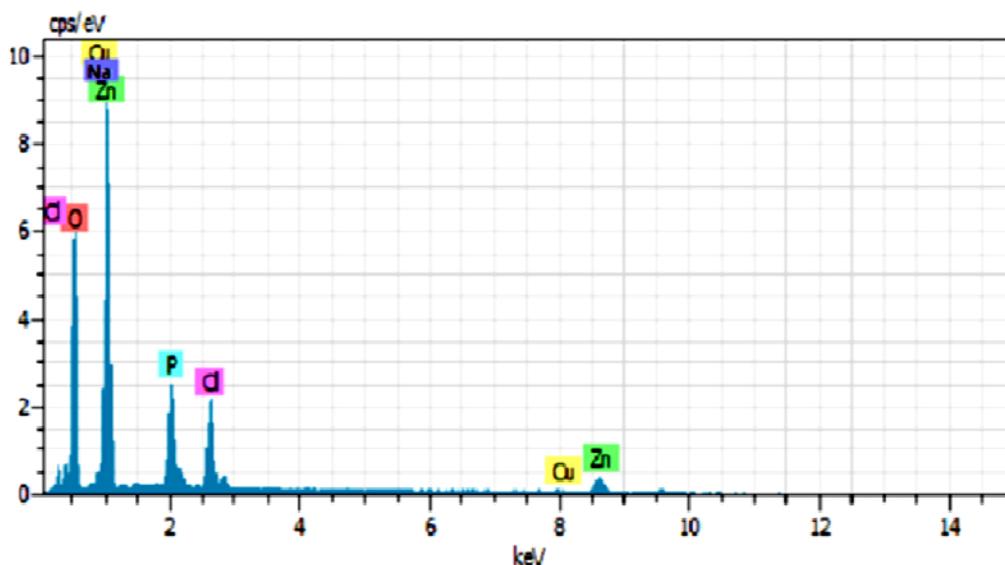


Fig. 2. Energy dispersive spectra of Cu (0.1 mol %) doped $\text{Na}_2\text{Zn}(\text{PO}_4)\text{Cl}$ phosphor

3.2 .FT-IR analysis

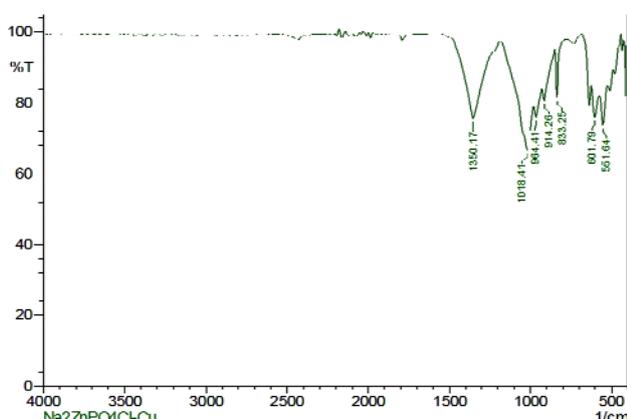


Fig. 3. FTIR spectrum of Na₂Zn(PO₄)Cl:Cu⁺ phosphor

The FT-IR spectra of the synthesized Na₂Zn(PO₄)Cl:Cu⁺ phosphor is displayed in Figure 3. The FT-IR measurement was carried out at room temperature in the mid-infrared region i.e. 4000–450 cm⁻¹. The mid-infrared spectrum can be divided in four regions are as follows: the X–H stretching region (4000–2500 cm⁻¹), the triple-bond region (2500–2000 cm⁻¹), the double-bond region (2000–1500 cm⁻¹) and the fingerprint region (1500–600 cm⁻¹). The bending or stretching of a particular bond, a molecular deformation and the movement of a group of atoms can be ascribed by each band in an infrared spectrum [29]. FT-IR spectra of samples in the frequency range 500 to 1400 cm⁻¹ shows a number of strong bands that can be attributed to characteristic vibrations of (PO₄)³⁻. The phosphate ion (PO₄)³⁻ in a free state exists in T_d symmetry and exhibits four fundamental modes of vibrations viz. non-degenerated ν_1 , doubly degenerated ν_2 and triply degenerated ν_3 and ν_4 vibrations. These are infra-red active modes of vibration [16]. IR bands associated with vibrations of (PO₄)³⁻ group can be divided into two regions 1120 - 940 cm⁻¹ and 650-540 cm⁻¹. Band located at 1018.41 cm⁻¹ can be assigned to triply degenerate (ν_3) antisymmetric stretching vibrations of (PO₄)³⁻ ion. 833.25 cm⁻¹ and 964.41 cm⁻¹ band can be assigned to non-degenerate (ν_1) symmetric stretching vibrations of (PO₄)³⁻ ion. 914.26 cm⁻¹ vibration mode can be assigned to the HPO₄⁻² - PO symmetric stretching vibrations [30]. The out-of-plane bending mode observed at 601.79 cm⁻¹ and 551.64 cm⁻¹ corresponding to triply degenerate (ν_4) vibrations of (PO₄)³⁻ ion. The absorption at 1350.17 cm⁻¹ is due to vibrational modes of P-O-H bond [16].

3.3. Photoluminescence characterization

Photoluminescence (PL) excitation spectrum of Na₂Zn(PO₄)Cl:Cu⁺ (0.002 mol %) phosphor, recorded by monitoring emission wavelength (λ_{em}) at 438 nm, is as shown in Fig. 4. Excitation spectrum shows broad excitation peak centered at 357 nm. This excitation peak

can be attributed to 3d¹⁰ → 3d⁹4s¹ transition of Cu⁺ ion in this host. Fig. 5 shows the PL emission spectra of Na₂Zn(PO₄)Cl:Cu⁺ phosphor for 0.002, 0.01, 0.05 and 0.1 mol% doping of Cu⁺ ions, obtained by keeping excitation wavelength at 357 nm. The spectra exhibit a strong blue emission centered at 438 nm ranging from 400 nm to 525 nm. This emission peak can be attributed to 3d⁹4s¹ → 3d¹⁰ transitions of Cu⁺ ions [22]. The variation in PL emission intensity with the change in the Cu⁺ ion concentration in Na₂Zn(PO₄)Cl host is shown in Fig. 6. An increase of PL emission intensity is observed with increase in copper concentration for the present phosphor and maximum PL intensity is observed for 0.05 mol% of Cu⁺ ion.

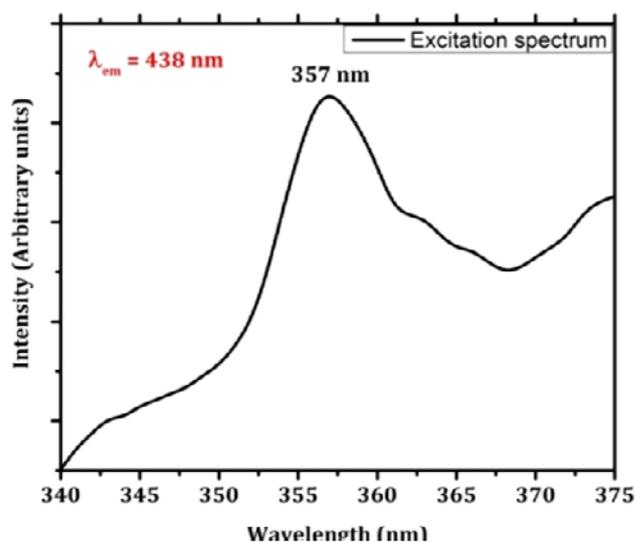


Fig. 4. PL excitation spectrum of Na₂Zn(PO₄)Cl:Cu⁺ monitored at 438 nm emission

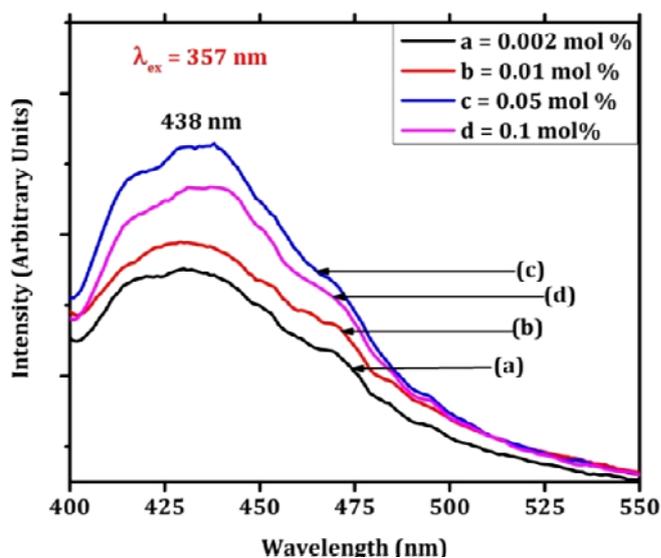


Fig. 5. PL emission spectra of Na₂Zn(PO₄)Cl:Cu⁺ for different Cu concentration monitored at 357 nm excitation

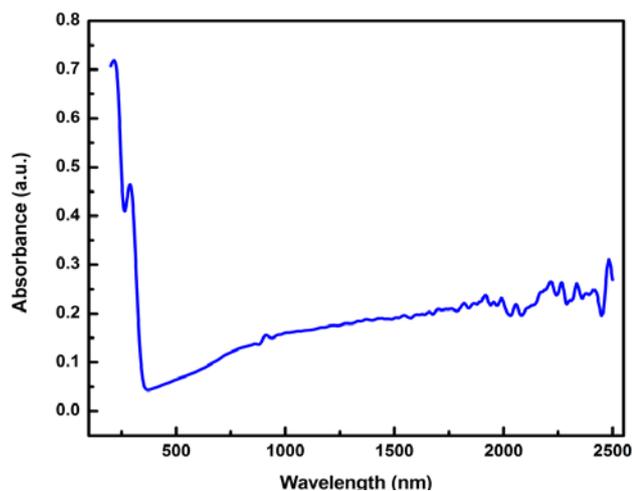


Fig. 10. UV-Visible Absorbance of Na₂Zn(PO₄)Cl:Cu⁺

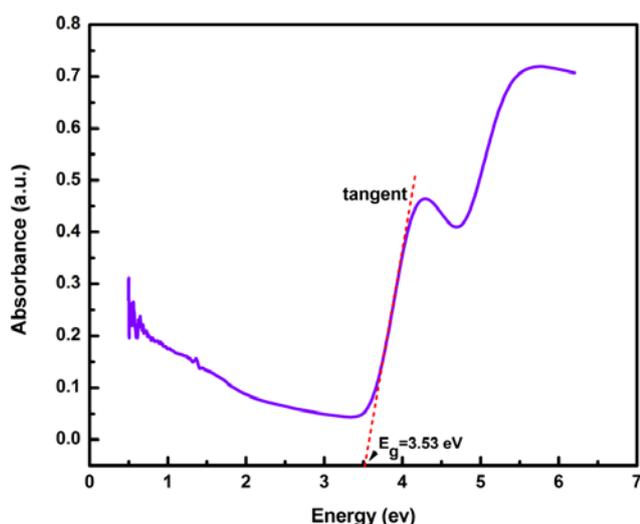


Fig. 11. Absorbance versus Energy of Na₂Zn(PO₄)Cl:Cu⁺

Diffuse reflectance spectroscopy (DRS) is a simple and powerful spectroscopic tool to estimate the band gap energy (E_g) of the powder samples. UV-VIS diffuse reflectance spectra was collected for Na₂Zn(PO₄)Cl in the region of 200 – 2500 nm as shown in Fig. 9. It can be observed from Fig. 9 that the reflection spectra have bands at 215 nm, 261 nm, 364 nm, 750 nm, 891 nm and 2448 nm which are characteristic bands of copper containing compounds [32]. Prominent absorption bands are observed in the UV region between 200-300 nm as seen in Fig. 10. The tangent to the inflection point was determined and the band gap energy was found as the intersection point of the tangent with the horizontal axis i.e. Energy (eV) as depicted in Fig. 11. Band gap was calculated using formula $E_g = 1240 / \lambda$, here, E_g (eV) is band gap and λ (nm) is the wavelength of the absorption edge in the spectrum [33]. Optical diffuse reflectance spectrum studies estimated the optical band gap for Na₂Zn(PO₄)Cl:Cu⁺ as 3.53 eV.

4. Conclusions

Optical properties of Cu⁺ doped Na₂Zn(PO₄)Cl phosphor synthesized via wet-chemical route are discussed in detail in this paper. This phosphor was characterized by PL, SEM, EDS, UV-diffuse reflectance spectroscopy and FT-IR spectroscopy. The EDS pattern showed the elemental compositions of Zn, Na, P, O, Cl and Cu. The characteristic vibrational modes of (PO₄)³⁻ and P-O-H group are evident from FT-IR studies. Under excitation of 357 nm, the phosphor emits in blue region peaking at 438 nm attributed to 3d⁹4s¹ ↔ 3d¹⁰ transitions of Cu⁺ ions. Enhanced luminescence intensity was observed for high Cu⁺ concentration. The color chromatic coordinates (x , y) of the phosphor were calculated as 0.1743 and 0.1202 (Color coordinates for NTSC blue are $x = 0.15$, $y = 0.06$). Band gap (E_g) was estimated as 3.53 eV using UV-Visible DRS studies. The present phosphor is thus, a promising candidate to be used as a blue phosphor.

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