International Journal of Current Science Research and Review
ISSN: 2581-8341
Volume 04 Issue 05 May 2021
DOI: 10.47191/ijcsrr/V4-i5-10, Impact Factor: 5.825
IJCSRR @ 2021
www.ijcsrr.org

Luminescence Studies of Transition Metal (Cu^+ and Ag^+ Ions) Activated Alkali Zinc Mixed Phosphate

Milind Jog[1], Y. K. More[2], D. M. Nerkar[3], Chaitali M. Mehare[4], S. J. Dhoble[5]
[1]Department of Physics, Kirti M. Doongursee College, Dadar, Mumbai- 400028, India
[2]Department of Physics, Bhiwapur Mahavidyalaya, Bhiwapur-441201, India
[3]Department of Physics, Sathaye College, Vile Parle(E), Mumbai- 400057, India
[4,5]Department of Physics, R.T.M.Nagpur University, Nagpur-440033, India

ABSTRACT: Because of the importance of inorganic phosphates in the solid-state lighting industry, $KZnPO_4$ doped with some transition metal dopant ions like Cu^+ and Ag^+ ions were prepared by low-cost co-precipitation method at room temperature followed by annealing at a high temperature around 650^0C. The prepared phosphors were characterized by X-ray diffraction. In the case of a Photoluminescence study for $KZnPO_4$ doped with Cu^+, the emission was observed at 425 nm, which corresponds to the emission of Cu^+ ion. In the case of Ag^+ doped $KZnPO_4$, weak emission was observed at 420 nm, which is assigned to the emission of Ag^+ ions. CIE chromaticity coordinate of $KZnPO^4$ doped with Cu^+ and Ag^+ ions phosphor was also evaluated via using OSRAM SYLVANIA color calculator and colour purity of concentration was nearly 95% of Cu^+ and Ag^+ ions. The obtained outcomes revealed that the prepared phosphor shows potential application in the field of solid-state lighting.

KEYWORDS: co-precipitation method, Luminescence, Photoluminescence, Phosphates, Alkali zinc mixed phosphates, and CIE coordinates

INTRODUCTION

Inorganic orthophosphate compounds have attracted a great deal of interest in recent years in the phosphor industry for display and solid-state lighting owing to their numerous merits such as good chemical and thermal stability, structural diversity as well as economical and environmentally friendly. The activated phosphates with rare earth or transition metal ion (as an activator) have attracted much attention for their significant applications in solid-state lighting especially in white light-emitting diodes (W-LEDs) and other radiation dosimetry, solid-state laser, display panel applications [1, 2]. In general, orthophosphate belongs to the structure of $ABPO_4$, where A represents monovalent cation and B stand for divalent cation, when ionic radii of B is smaller than that of A then $ABPO_4$ shows tridymite structure [3]. They have been considered to be efficient luminescence hosts due to their excellent thermal and hydrolytic properties [4–6]. The luminescence of ions with the nd^{10} configuration has been studied in detail for Cu^+ ($3d^{10}$) and Ag^+ ($4d^{10}$) in alkali halide crystals. For Ag^+ the investigations are still limited to studies on the luminescence of Ag^+ in alkali halides. The optical transitions are interpreted as $4d^{10}\rightarrow4s^95s$ transitions on the Ag^+ ion, analogous to the $3d^{10}\rightarrow3d^94s$ transitions on Cu^+. These Cu^+ and Ag^+ ions are very useful for obtaining fundamental luminescence properties. It has been known for a long time that Cu^+ activated phosphors are efficient luminescent materials [7,8]. Silver is one of the most demanding metal ions and revealed wide application in the field of electronic, photographic, and imaging industries. Silver- and copper-doped semiconductors are technologically important phosphors that have been employed in cathode-ray tubes and other devices for many years [9,10].

It was widely reported that white light can be obtained by the phenomenon of activation. Jianwen Zhao and co-workers systematically investigated and studied the crystal structure, photoluminescence properties, and concentration quenching of the $Ca_{10}Na(PO_4)_7$:Eu^{2+} phosphor [11]. It was the clear occurrence of concentration quenching in fluorescence emission of Eu^{2+} ions in $Ca_{10}Na(PO_4)_7$ host phosphor is attributed to dipole-dipole interaction. The phosphor was reported to be a potential green-emitting phosphor for near-ultraviolet w-LEDs. Single doped and Mn^{+2}/Tb^{3+} co-doped in $NaCaPO_4$ host was prepared and reported, which can be explored for near-ultraviolet light [12]. Bhonsule et.al studied the photoluminescence in Tb doped $NaCe(PO_3)_4$ phosphor synthesized by solid-state diffusion method. The reported phosphor shows a wide application in the lamp industry [13]. Blue-emitting Eu^{2+} doped $Ba_2Ca(PO_4)_2$ was studied by Zhang et al. for its luminescence properties, and elaborate the phase structure,

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photoluminescence, and PL thermal stability [14]. single-composition phosphors $Ca_9MgM(PO_4)_7$:xEu^{2+},yMn^{2+} (M'=Li, Na, K and $0.003 \leq x \leq 0.03$; $0 \leq y \leq 0.1$) were synthesized and reported by Hou et al. [15], wherein, due to an effective resonance-type energy transfer, the emission peaks corresponding to the $4f^6\ 5d^1 \rightarrow 4f^7$ transitions of Eu^{2+} ions for $Ca_9MgM'(PO_4)_7$: Eu^{2+} phosphors were observed to be centered at 417 nm, 457 nm and 453 nm in $Ca_9MgLi(PO_4)_7$:Eu^{2+}, $Ca_9MgNa(PO_4)_7$:Eu^{2+} and $Ca_9MgK(PO_4)_7$:Eu^{2+} respectively for excitation at 337 nm. While in the phosphors co-doped with Mn^{2+} exhibit a series of coloured emissions for various concentrations of Mn^{2+} which indicated that the phosphor can be potentially used as a UV excited phosphor for W-LEDs. Luminescence study of some zinc based compounds and their applications have been reported by many researchers. The Jing Gou et al. reported the development of Dy^{3+} singly doped $KZnPO_4$ phosphor via conventional high temperature solid state reaction method [3]. From the PL emission spectrum clear the enhancement of photoluminescence intensities of $KZnPO_4$:Dy^{3+} with an increase in the concentration of Dy^{3+} ions in the host along with the chromaticity coordinates was tuned from cold-white to warm-white region by varying the concentration of Dy^{3+} ions dopant. The deep level emissions of ZnO_4 presented at different wavelengths using different excitation energy, affect the photoluminescence and chromaticity coordinates of $KZnPO_4$:0.8%Dy^{3+}. It revealed the effect of ZnO_4 on the photoluminescence of $KZnPO_4$:0.8%Dy^{3+}. Synthesis of Nano-Lamellar $KZnPO_4$ developed by high-temperature solid-state reaction and its Data Mining Technology was reported [16]. In this process, potassium zinc phosphate was synthesized by solid-state reaction using $K_3PO_4 \cdot 3H_2O$ and $ZnSO_4 \cdot 7H_2O$ as reagents. The results showed that two mathematical models can be established by regression analysis according to yield and zinc content, which can be used to obtain the best technology conditions of the solid-state reaction. Ionic conduction in $Zn_3(PO_4)_2$. H_2O was studied and could prove that it enables efficient discharge of Zinc anode serum [17]. Chromatic and near-infrared reflective properties of Fe^{3+} doped $KZnPO_4$ were reported by Da Wang et al. [18]. In this study, a new type of inorganic pigment $KZn_{1-x}(Fe)_xPO_4$ (x = 0.00, 0.05, 0.10, 0.15) with high near-infrared reflective properties was prepared by the co-precipitation method. The results showed that after doping with Fe^{3+}, the crystal structure of $KZnPO_4$ remained unchanged confirm from XRD analysis moreover the colour of the sample deepened with the increasing concentration of Fe^{3+} (x = 0.05–0.15), the band gap decreased from 2.00 eV to 1.95 eV, and the near-infrared reflectance reduced from 74.7% to 67.1%. For the aluminium sheet coated with 312 μm thick layer of $KZn_{0.9}(Fe)_{0.1}PO_4$ pigment, the near-infrared reflectance could reach 46.7%, higher than the reflectance of conventional pigment of similar colour (32.1%). Therefore, the prepared $KZjn_{1-x}(Fe)_xPO_4$ pigments can be well served as "cool colorant".

In the present work, we reported the $KZnPO_4$ phosphors activated with Cu/Ag were investigated, this phosphor has been synthesized by co-precipitation method the phase purity was checked by the XRD measurements, to examine their luminescence properties the photoluminescence characterization, as well as the CIE colour coordinates of the phosphors, have also been carried out.

EXPERIMENTAL

Synthesis of $KZnPO_4$ phosphor

In our present work, a series of $KZnPO_4$: Cu^+, Ag^+ phosphor were synthesized first time by the co-precipitation technique. In this synthesis, required the amount of chemical precursor such as potassium nitrate (KNO_3), zinc chloride ($ZnCl_2$), ammonium phosphate **(**NaH_2PO_4), along with trace amounts of an activator ion like copper nitrate ($Cu(NO_3)_2$), 0.1 mol% for Cu and silver nitrate ($AgNO_3$) 0.1 mol% for Ag in respective phosphors can be accomplished to form the desired compounds and the solvents such as double distilled water are used in this method. All the starting materials are weigh in a stoichiometric amount in a glass beaker and dissolved in double distilled water, mixed thoroughly for 1 hour using stirring. The mixture was then allowed to dry overnight on an oven at 80^O C. This dried solid formed phase sinks to the bottom of the precipitate solution. Then the dried precipitate thus obtained was then washed several times with the help of double-distilled water. Then eventually calcinated at high temperatures up to 650°C for nearly 2-4 hours to form a solid powder form product for characterization.

Chemical Reaction

$KNO3 + ZnCl2 + NaH2PO4 \rightarrow KZnPO4 + NaCl + NH3 + H2O$

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Figure 1. Diagrammatic representation of Co-precipitation method

Characterization

The crystal structure and phase purity of the prepared phosphor are confirmed from the X-ray diffraction (XRD) analysis Bruker Advance D8 Diffractometer with Cu-K α radiation (X-ray tube operated at 40 kV and 40 mA). The photoluminescence emission and excitation spectra were detected on a Shimadzu RF-5301PC spectrofluorophotometer equipped with a Xenon flash lamp recorded using a spectral slit width of 1.5 nm at high and low sensitivity. The CIE chromaticity color coordinates, color purity of the sample are calculated by OSRAM SYLVANIA Color calculator with high accuracy

RESULTS AND DISCUSSION

Phase purity analysis by X-ray diffraction

The XRD pattern of as-synthesized $KZnPO_4$ phosphor is as shown in figure 2, represent homogeneity and phase purity of prepared materials. All the diffraction peaks are well indexed with standard data on the ICDD database (file No. 81-1034), which was reported to crystallize in a hexagonal crystal structure system with a space group of $P6_3$. The lattice parameter of KZP are shows the a = b = 18.155(2) Å, c = 8.504(1) Å, a =b = 90, c = 120, Z = 24, Volume = 2427.43 Å3, [19] with stuffed tridymite family in this structure of $KZnPO_4$ one Zn^{2+} ion coordinates with four O atoms. Its oxygen framework is made up of corner-shared tetrahedral six-membered rings that host the K^+ cation, each PO_4 tetrahedron is connected with four ZnO_4 tetrahedrons and each ZnO_4 tetrahedron is connected with four PO_4 tetrahedrons [4]

Photoluminescence (PL) properties

The photoluminescence excitation and emission spectra of $KZnPO_4$: 0.1 mol% Cu^+ were displayed in figure 3(a). The KZP phosphor is strongly absorb ultraviolet (UV) light and exhibits the emission in blue regions [3,20,21]. The excitation band wavelength in between the range of 220 nm to 400 nm centered at 375 nm with a shoulder peak at 290 nm shown in figure 3 (a) respectively, which is corresponding to the electronic transition $3d^{10}(4S^1)$ of Cu^+ ions. The excitation peak is corresponding well to NUV LED chip.

The photoluminescence emission spectra of the $KZnPO_4$: 0.1 mol% Cu^+ with excited by the 375 nm are revealed in figure 3(b). The PL emission intensity wavelength range between 380 nm to 500 nm with Cu^+ ions concentrations. Under the 375 nm excitation wavelength, the PL emission spectra show a sharp emission band at 425 nm [22]. The stoke shift for the phosphor was found to be 55 nm.

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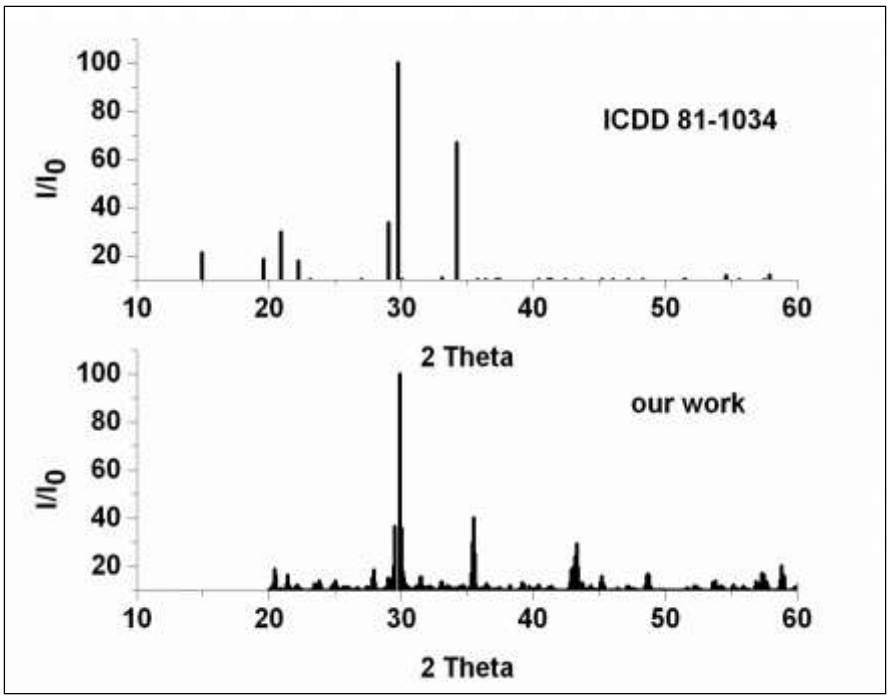

Figure 2. XRD Pattern of $KZnPO_4$ Phosphor

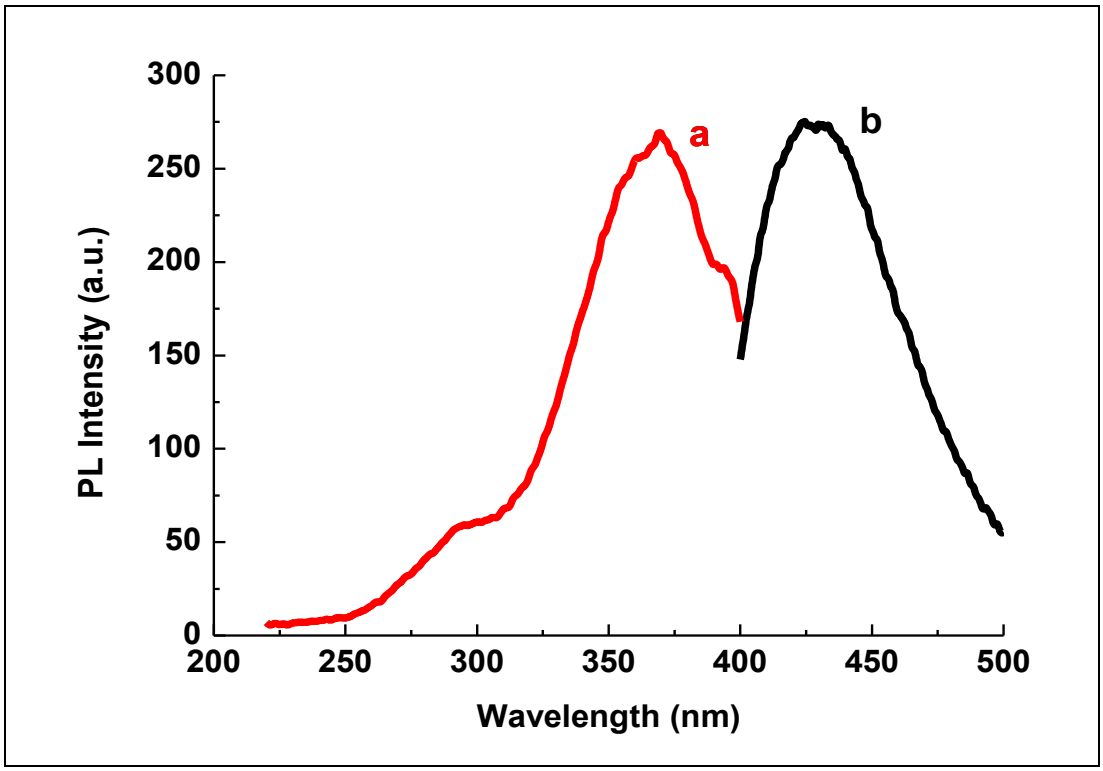

Figure 3. (a) PL excitation spectra of Cu activated $KZnPO_4$ under 420 nm emission wavelength and **(b)** PL emission spectra of Cu activated $KZnPO_4$ phosphor under 380 nm excitation wavelength.

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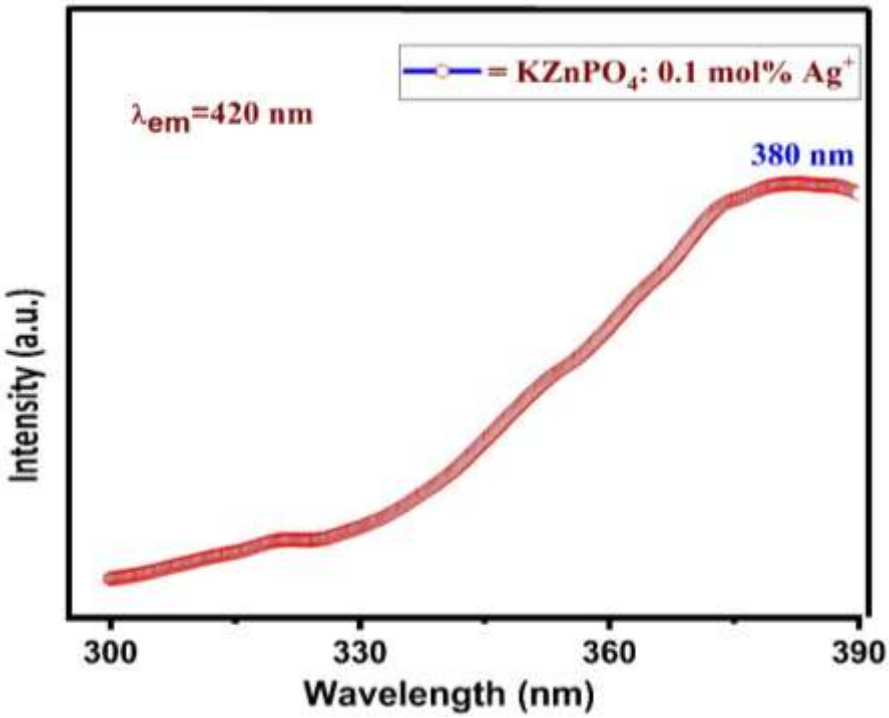

Figure 4 (a) PL excitation spectra of Ag activated $KZnPO_4$ under 420 nm emission wavelength

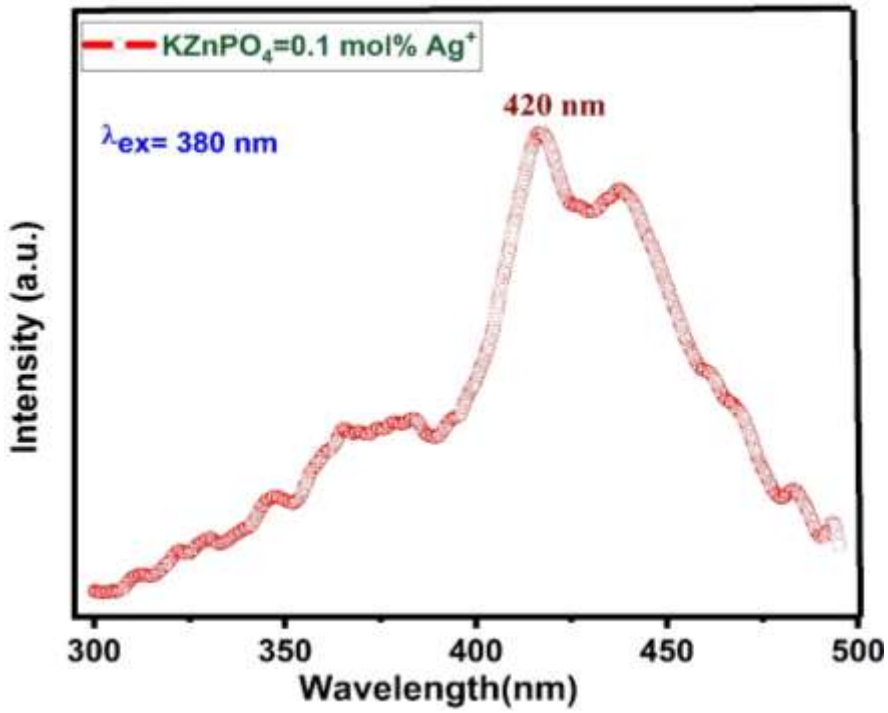

Figure 4(b). PL emission spectra of Ag activated $KZnPO_4$ phosphor under 380 nm excitation wavelength

Figure 4. (a) and (b) display the photoluminescence excitation (PLE) and emission (PL) spectra of Ag ions observed in the $KZnPO_4$ phosphors. However figure 4(a), the excitation peak for the KZP phosphor was observed at 380 nm with a shoulder at 320 nm. we

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have found a broad excitation band in the range of 300 nm to 400 nm attributed to the $3d^{10} \rightarrow 3d^9 4s$ transition of isolated Ag^+ ions [7]. The center of this PL excitation spectra observe at 380 nm but some part of these spectra lies at 350 nm to 400 nm. This is useful for the generation of white light because it may be used as near UV light.

Figure 4(b) represents the photoluminescence emission spectra of the $KZnPO_4$: 0.1 mol % Ag^+ phosphor under the 375 nm excitation wavelength. The PL emission spectra represent broad emission spectra from 300 nm to 500 nm centered at 420 nm. The excitation peak at 380 nm and emission peak at 420 nm is assigned to the $4d^{10}$ ($1\ S_0$)–$4d^9\ 5s^1$ ($^3D_1$) transition of isolated Ag^+ ions. The intensities of both emission and excitation peaks were low as compared to the PL spectra of Cu doped samples.

Chromaticity diagram for KZnPO4: Cu+ and Ag+ phosphors

Figure 5 displays the Commission Internationale de I'Eclairage (CIE) colour (x,y) coordinates of $KZnPO_4$: Cu^+ phosphor which excitation under 375 nm and $KZnPO_4$: Ag^+ ions with under 380 nm for comparative study. In this chromaticity diagram calculate CIE parameters such as colour coordinates, colour purity and correlated colour temperature (CCT). In the emission spectra of KZP: Cu^+ and Ag^+ phosphor is located in the blue region in white light. The calculated CIE coordinates are represented as (x= 0.1492, y= 0.0352) and (x= 0.1480, y= 0.0349); coordinate of (xi, yi) is standard value (xi= 0.333, yi= 0.333) and corresponding dominant wavelength value is (xd= 0.1674, yd= 0.0083) and (xd= 0.1670, yd= 0.0080). The colour purity of KZP: Cu^+, Ag^+ phosphor was found to be high as 95.00%. as synthesized phosphor excitation under (NUV) near-ultraviolet region and emitted in blue colour in wLEDs. So all these results show KZP phosphors are very useful for the fabrication of near UV LED-based w-LEDs.

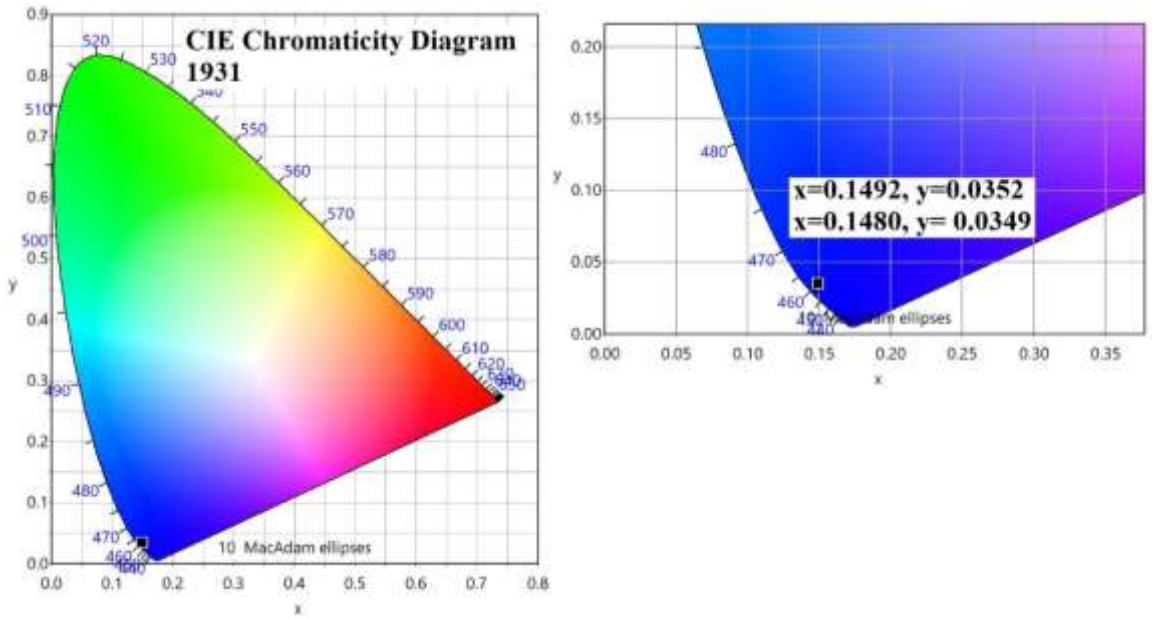

Figure 5: Commission International de I' Eclairage (CIE)-chromaticity diagram for KZP phosphors

DISCUSSION

A novelty of blue-emitting KZP phosphor doped Cu^+, as well as Ag+ alkali zinc mixed phosphate samples have been developed by the low cost co-precipitation method at a high-temperature 650o C. the as-synthesize luminescent phosphor materials, was characterized by the X-ray diffraction analysis confirmed the phase purity of KZP phosphors and crystalizes into the hexagonal structure. The photoluminescence study of prepared phosphor confirms PL spectrum displays both broad brand excitation and emission spectra. When monitored at 375 nm and 380 nm, this phosphor revealed an emission band from 300 nm to 500 nm covering the blue light region in w-LED. CIE chromaticity coordinates are calculated and represented in CIE 1931 chromaticity Diagram. By using CIE coordinate and dominant colour coordinate, the color purity of synthesized phosphor is evaluated. CIE diagram represents synthesized material emits intense blue color with high color purity. This sample show is considered to be excellent optical properties of blue phosphor candidate for solid-state laser and White Light Emitting Diodes (WLEDs) applications.

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Cite this Article: Milind Jog, Y. K. More, D. M. Nerkar, Chaitali M. Mehare, S. J. Dhoble (2021). Luminescence Studies of Transition Metal (Cu+ and Ag+ Ions) Activated Alkali Zinc Mixed Phosphate. International Journal of Current Science Research and Review, 4(5), 386-392