Abstract—Manganese-doped sodium zinc orthophosphate (NaZnPO₄:Mn) phosphor with exceptional features having ultra-violet (UV) to visible absorption (300–470 nm), yellow-green (543 nm) broad-band photoluminescence (PL), and appreciable color co-ordinates (x=0.39, y=0.58) is reported. The phase purity has been checked and structure parameters have also been successfully harmonized by Rietveld refinement studies. The NZP:Mn phosphor is synthesized by three methods namely, solid-state reaction technique (~5 µm), citrate assisted combustion technique (~3-10 nm) and hydrothermal technique (~5 nm) yielding particles in different size ranges. It has a crystal structure consisting of discrete PO₄ tetrahedra linked by ZnO₄ and NaO₄ distorted tetrahedral such that three tetrahedra, one of each kind, share one corner. The presence of UV sensitive Zn-O-Zn bonds and their efficient energy transfer to Mn²⁺ ions resulted in brightest PL and external quantum yield of 63% at 418 nm. This novel phosphor finds many interesting applications in semiconductor photo-physics, light-emitting diodes, solar cells, environmental remediation and nanophysics.

1. INTRODUCTION

For the generation of white light, one of the well-known methods is the employment of yellow-green emitting phosphor on a blue-LED chip. Several different classes of phosphor materials such as oxides [1,2], oxyfluorides [4], and nitrates [5,6] have been explored using this strategy to achieve bright white light emission. However, the most prominent and perhaps the most widely used material remains Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce), which was first made known in 1967 by Blasse and Bril [7,8] and has become undoubtedly the undisputed phosphor material for solid-state white lighting since its evolution [9,10]. Its remarkable features comprises of good chemical stability and high efficiency. Efforts have been focused to shift the emission peak from ~530 nm to longer wavelengths (540-560 nm) regime. Even though there are many serious drawbacks related to it such as: thermal quenching, color rendering and broader emission. There has been no potential replacement of YAG:Ce phosphor till date. Hence, to deal with above listed issues, the quest for new phosphor systems is ongoing. Among different host lattices viz. aluminates, sulphides, borates and phosphates; the orthophosphates (ABPO₄ family) have captivated researchers the most because of the reports stating that these give brighter luminescence using transition metal ions as activators [11,12]. The current work is focused on the discovery of mercury-free inexpensive phosphor material that is environment-concerning energy-efficient with improved luminous efficacy and low-power driven. In order to develop a prominent yellow-green emitting phosphor for display devices, conventional solid-state technique, combustion and solvothermal techniques have been used to synthesize NaZnPO₄:Mn (NZP:Mn) phosphors for the first time. These phosphors were studied by various experimental and theoretical techniques, such as DFT, XRD, SEM, SIMS and PL etc.

2. PREPARATION OF NAZNPO₄:MN²⁺ PHOSPHOR

Green-light emitting NaZnPO₄:Mn²⁺ (NZP:Mn) powder samples were prepared using reductive solid-state reaction method. The precursors namely; trisodium phosphate (Na₃PO₄), zinc oxide (ZnO), manganese chloride (MnCl₂) and ammonium dihydrogen phosphate (NH₄H₂PO₄) of analytical grade were taken in a proper stoichiometric ratio and milled using mortar and pestle for bulk synthesis. The mixture thus formed was fired in a graphite boat in horizontal tube furnace at temperatures ranging from 1000-1200°C for 2-5 hrs and was allowed to cool gradually. For keeping the Mn²⁺ ions in their di-valent states reducing atmosphere is used. The annealed mass was again milled using agate mortar to ensure proper mixing. The concentration of manganese in the NaZnPO₄ system was systematically varied and optimized for maximum brightness. The thermal parameters and time of firing were also optimized.

Colloidal chemical routes for the production of luminescent semiconductor nanoparticles from solutions are well-known. Various techniques such as sol-gel, co-precipitation, and spray pyrolysis have been applied for synthesizing nanoparticles of various phosphate compounds. In last few years, hydrothermal synthesis has
emerged as a promising route for synthesizing phosphate nanophosphors because of its low temperature and high pressure decomposition technique that produces fine, well-crystallized powders with high homogeneity [13]. However, the phosphor under study, NZP:Mn, is a new one of its kind and has not been developed by any of the known nanomaterial synthesis techniques. Thus, in the present study, hydrothermal technique has been followed for synthesis of quantum dots of NZP:Mn. 0.1 Molar solutions of Zinc acetate and Sodium Nitrate were mixed with Manganese Chloride. Under constant refluxing phosphoric acid is added drop wise. Refluxed solution was baked at 55°C to get a gel that was then cooked at 200°C for 30 hrs and the resulting sol was checked for luminescence. The nanophosphor particles were also synthesized using combustion synthesis in order to get high yield. In order to synthesize NZP:Mn nanophosphor and diffuse Mn properly inside the crystal, a modified combustion route using zinc nitrate, sodium nitrate and diammonium hydrogen phosphate as precursor chemicals was developed. In order to incorporate sodium and manganese inside the crystal, a two-step process known as Citrate gel assisted combustion technique was designed and adapted. In the first step, the precursor nitrates were polymerized with citric acid and made into a non-luminescent transparent gel. In the second step, the gel was combusted to form the desired phosphate nanophosphor product at 800°C. Redox mixture comprising of nitric acid and citric acid as fuel was used, where nitric acid acted as oxidizer for citric acid.

3. CHARACTERIZATION

The phase purity of the synthesized phosphors was checked by X-ray diffraction (XRD) analysis using Bruker D-8 advance powder X-ray diffractometer with CuKα radiation operated at 35 kV and 30 mA. The XRD patterns were recorded and refined through Rietveld analysis technique using the FULLPROF software. The mass spectra were acquired using ToF-SIMS 5 (ION-TOF GmbH Germany), during which the pulsed primary ion beam of Bismuth having energy ~25keV was used to produce secondary ions from the sample surface. The beam current was ~1pA. The analysis area was fixed at 500 x 500 µm² in negative ion mode. The vacuum inside the main chamber was kept at 5 x 10⁻¹⁰ mbar. Scanning electron micrographs were taken to observe the morphology and particle size of the phosphor material, using Zeiss EVA MO-10 Scanning Electron Microscope (SEM). The steady-state photoluminescence excitation (PLE) and photoluminescence (PL) spectra were recorded at room temperature (~25°C) using Edinburgh luminescence spectrometer (model: FLSP920) in the range 300-470 nm and 500-650 nm, respectively. The lifetime measurements were recorded using the same instrument but with microsecond xenon flash lamp as the source of excitation.

The schematic diagram of the crystal structure of NaZnPO₄ viewed along (0 2 0) direction is shown in Figure 1. It is assumed that Mn²⁺ substitute for Zn²⁺ ions in the tetrahedral sites of the NaZnPO₄ system [14].

The crystal structure of NZP consists of discrete PO₄ tetrahedral linked to distorted tetrahedra of ZnO₄ and NaO₂. Na, Zn and P form the tetrahedra with O. In the present case, the NaZnPO₄ (NZP) phosphor samples exhibited monoclinic type of system where the XRD peak values are very well matching with JCPDS card no.79-0217 shown elsewhere [15]. Most of the observed peaks in XRD profile of NZP:Mn at room temperature synthesized by two step combustion route with X-ray wavelength 1.54060 Å matched with the monoclinic unit cell (space group; P21/n) structure of NZP with JCPDS card. Apart from standard peaks of NZP two peaks of zinc phosphate (precursor used for combustion) were also observed in the XRD pattern indicating the presence of un-reacted precursor in the final compound. As compared to the XRD peaks of solid-state reaction sample the peaks observed are broader indicating reduction in the crystallite size. The calculated mean particle size using Scherrer equation was around 35 nm.

![Crystal Structure of NaZnPO₄](image)

**Fig. 1:** Schematic diagram of the crystal structure of NaZnPO₄ viewed along (0 2 0) is shown. (Color figure online)

![Rietveld refinement of the powder data of the as-synthesized powder.](image)

**Fig. 2:** Rietveld refinement of the powder data of the as-synthesized powder. (Color figure online)
Figure 2 shows the comparison of the calculated and observed NaZnPO$_4$ system patterns as well as the difference curve between them. The calculated and observed diffraction profiles are not only peak position identical, but similar in relative peak intensities as well. The structure refined parameters as revealed from Rietveld analysis are $R_p = 25.7$, $Rwp = 29.7$ and $Rexp = 6.96$. The compound crystallizes have monoclinic space group $P 2_1/n 1$, with lattice parameters; $a = 8.73$ Å, $b = 8.09$ Å and $c = 15.06$ Å. Further, Kohn-Sham [16] density functional theory (DFT) is applied to analyse density of states and band structure of lattice as shown in Figure 3 (a-c). DFT calculations have been carried out using all-electron-full potential linearized augmented plane wave (FP-LAPW) method as implemented in WIEN2K [17]. NaZnPO$_4$ crystallizes in monoclinic space group $P 2_1/n 1$, with lattice parameters; $a = 8.73$ Å, $b = 8.09$ Å and $c = 15.06$ Å. It comprises of 21 atoms in total: there are 3 atoms each for Na, Zn and P; 12 oxygen atoms.

Figure 3: The (a) total density of states and (b) partial density of states for NaZnPO$_4$ calculated using all electron approach. (c) Band structure calculations of NaZnPO$_4$ material near Fermi-level calculated using all electron approach. (Color figure online)

In our case, we have treated NaZnPO$_4$ crystal as orthorhombic (since $\beta > 89^\circ$) and then calculated exchange correlation energies using Perdew-Burke-Ernzerhof [18] generalized gradient approximation (GGA) functional. The optimization has been done by using 36 k-points in the Irreducible Brillouin Zone (IBZ). Prior to this, a minimized structure of NaZnPO$_4$ has been used to carry out self-consistent DFT calculations. The self-consistent field tolerance is $10^{-4}$ Ry. The self-consistency is obtained using 100 k-points in the IBZ). The calculations done using DFT reveals that NaZnPO$_4$ is a semi-conductor with an energy band gap of ~4.1eV. To get more knowledge about bandgap formation in NaZnPO$_4$, we study its band structure. Figure 3 (c) shows the band structure of NaZnPO$_4$ near the Fermi level. The compound shows a direct band gap of ~4.1eV along $\Gamma$. Both the valence band maxima and conduction band minima have originated from p orbitals of O atom, as revealed by density of states depicted in Figure 3. However, it is well-known that DFT calculation always underestimates the band gap by 20-50%. The band structure analysis of NaZnPO$_4$ reveals it to be a degenerate semiconductor.

Extensive surface analysis of NZP:Mn from the outermost surface using Time of flight secondary ion mass spectroscopy (ToF-SIMS) is shown in Figure 4. Figure 4 distinctively shows Na, Zn, P and O peaks of characteristic elements used to make the phosphor with signals of binder material in the negative polarity mode. From the chemical imaging analysis of the sample shown elsewhere, scatter plot between horizontal (Zn) and vertical (Mn) axes has high correlation along 45$^\circ$ line. But for Mn$^{2+}$ and Na$^+$ ions, color overlay diagram inclines more towards Na$^+$ ions.

The SEM micrograph of NZP:0.12Mn phosphor shown in Figure 5 depicts melting morphology. The phosphor grains show irregular shape with elongated rod-like micron sized structures having distinct boundaries.

The luminescent properties of bulk and nano NaZnPO$_4$:Mn were investigated thoroughly. The dependence of luminescence upon firing temperatures and doping concentrations was also investigated. Figure 6 shows the room temperature photoluminescence excitation (PLE) and photoluminescence emission (PL) spectra monitored at 543 nm and at 418 nm respectively for bulk sample of NZP:0.12Mn$^{2+}$ phosphor. The photoluminescence excitation (PLE) spectrum shows the five characteristic peaks corresponding to well-known Mn$^{2+}$ transitions.
The excitation and emission transitions of Mn$^{2+}$ ions are from ground level $^{4}A_{1}(^{6}S)$ to $^{4}E(^{4}D)$, $^{4}T_{2}(^{4}D)$, $[^{4}A_{1}(^{4}G)$, $^{4}E(^{4}G)]$, $^{4}T_{1}(^{4}G)$ and $^{4}T_{1}(^{4}G)$ excited levels, respectively [19]. Maximum excitation peak (418 nm), recorded in the range 500-650 nm. The PL spectrum depicts a single broad band centered at 543 nm giving yellow-green emission as Mn$^{2+}$ ions substituted tetrahedrally coordinated (C.N. - 4) Zn$^{2+}$ in the monoclinic NaZnPO$_4$ lattice. The spin forbidden d-d transition ($^{4}T_{1}$→$^{4}A_{1}$) of Mn$^{2+}$ being exposed to weak crystal field gives rise to such a strong PL emission. By using Tanabe-Sugano diagrams it is concluded that the emission for divalent Manganese ion originates from parity forbidden $^{4}T_{1}$-$^{6}A_{1}$ d-d transition [20].

As d electrons are outermost electrons, they are strongly affected by the crystal field strength of the host matrix. It has been predicted that energy differences between $^{4}T_{1}$ and $^{4}T_{2}$ excited states and $^{3}S_{1}$ ground state of Mn$^{2+}$ are highly influenced by the crystal field and give green emission in weak and red emission in strong field conditions.
some local field effect associated with lattice perturbations due to doping. Thus, a blue shift is observed from bulk to nano in both excitation and emission spectra.

Figure 9 (a) shows the photoluminescence excitation spectra for the nanoparticles synthesized via combustion route recorded in the range 200-400 nm monitored at 530 nm emission. The spectra consist of three different peaks at 275, 293 and 347 nm with the most intense peak at 347 nm. Compared to bulk spectra a blue shift is observed owing to the size effects. The photoluminescence emission spectra for the nanoparticles synthesized via combustion route in the range 500-650 nm monitored at 347 nm excitation is as shown in the Figure 9 (b). The shift in emission as in case of quantum dots may be due to some local field effect or presence of impurity like zinc phosphate that has been detected in XRD pattern.

The CIE color coordinates of NZP:0.12Mn phosphor was calculated and was found out to be (x=0.39, y=0.58) using equidistant wavelength method [22]. These are comparable to the coordinates of commercially used β-SiAlON:Eu²⁺ (green) and Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce, yellow-green) Nichia phosphors for white-light emitting diodes. The external quantum yields were also determined and was found out to be as 41% @ 405 nm, 63% @ 418 nm and 74% @ 460 nm for β-SiAlON:Eu²⁺, NZP:Mn and YAG:Ce phosphors by using integrating sphere assembly and single photon counting system as shown in figure 11.

4. CONCLUSIONS

In conclusion, a bright yellow-green emitting and rare-earth free NaZnPO₄·Mn²⁺ (NZP:Mn) phosphor with bespoke photoluminescence is identified. Thermal parameters and concentration of activator manganese were varied and optimized. The maximum PL brightness at 418 nm excitation was obtained for 12 mol% of manganese in NaZnPO₄ lattice synthesized at 1050°C having monoclinic structure. Moreover, for all characteristic excitation wavelengths the phosphor showed a strong yellow-green (~543 nm) PL emission owing to spin forbidden d-d transition of Mn²⁺ ions. Dissolution of Mn²⁺ ions in the host lattice was confirmed by ToF-SIMS analysis and chemical imaging techniques. It has been evidenced that Mn²⁺ ions replace Zn²⁺ ions in the NaZnPO₄ lattice, which are sites of weak crystal field

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I = I_0 \left\{ \exp(-t/\tau_1) + \exp(-t/\tau_2) \right\}
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The relatively inexpensive phosphor has an external quantum yield (QY) of 63% at 418 nm and is comparable to industrially used phosphors. Further it is established that NZP:Mn$^{2+}$ phosphor could be simulated to commercial UV LED for producing general-purpose white light if a suitable red-emitting phosphor is also included to improve color rendering of white light generated.

ACKNOWLEDGMENTS

The authors’ sincerely acknowledge the Council of Scientific and Industrial Research (CSIR) for the financial support under the scheme 31/1(413)/2014-EMR-I and Academy of Scientific and Innovative Research (AcSIR) to carry out the research work.

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