

LUMINESCENCE PROPERTIES OF NaMg₄(PO₄)₃: Mn²⁺ CERAMIC POWDERS

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ABSTRACT

Various concentration of manganese metal ions ($x = 0.01, 0.02, 0.03, 0.04, 0.05$ mol%) doped Sodium Magnesium Phosphate (SMP) NaMg₄(PO₄)₃ compounds were made through combustion-reaction method. The powder X-ray diffraction (XRD) pattern confirms that Mn²⁺ ions were incorporated into the NaMg₄(PO₄)₃ host lattice forming a complete solid solution. Elemental analysis and surface morphology were examined from the EDX spectrum and corresponding element mapping by scanning electron microscopy. The Photoluminescence spectra of Mn-doped SMP samples exhibited a strong visible emission peak at the wavelength of 617 nm, which indicated that spin-forbidden transition takes place from ⁴T_{1g} (G) to ⁶A_{1g} (S) with inversion symmetry. The photoluminescence profiles exhibited the quenching in emission intensity above 0.03 mol% of Mn(NO₃)₂ due to the availability of more octahedral Mn²⁺ ions. These outputs show that Mn²⁺ activated NaMg₄(PO₄)₃ material can fulfill application in red-emitting phosphor-based LEDs devices.

Keywords: Combustion Method, Structural, Phase Purity, and Photoluminescence.

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INTRODUCTION

Orthophosphate systems of the commonly represent formula AM₄(PO₄)₃ (A –alkali-based metal, M – binary oxidation metal cation) possess excellent thermal and chemical stability for use in potential applications. The frameworks of phosphates stabilize the metal-rich crystal system and its consequence exhibit high mechanical strength, and chemical, and thermal stabilities. This was because of the relatively high charge of the PO₄³⁻ tetrahedral basic units, favoring the development of anionic frameworks. The cost-effectiveness and crystallographic possibilities make it more reliable and suitable for the accommodation of d or f metal cations and investigate their interesting optical, photoluminescence, and ionic conductivity properties.¹⁻⁵

Among transition metal ions, Manganese possesses multiple oxidation states (+1 to +7), of which binary, trinary, the ternary and pentavalent oxidation states of manganese are much attention. Binary and trinary oxidation states of manganese are well-known paramagnetic ions whereas binary and ternary oxidation states of manganese are light emission inducers. Of these states, manganese in the divalent state (Mn²⁺) has attracted much attention owing to its electrically semi-conducting, optical, and magnetic (super-paramagnetic) properties.^{6,7}

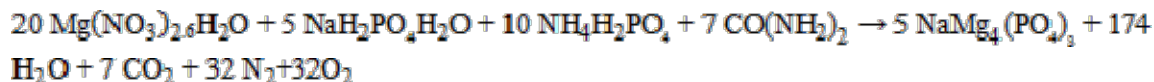
Binary oxidation state of manganese (Mn²⁺) ion with orbital d⁵ electron structure exhibits photoemission from parity-not allowed d–d transitions state. Photoemission originates from a higher energy (⁴T₁) to lower energy (⁶A₁) state was demonstrated through the Tanabe–Sugano plot. Depending on the crystal field strength and the host lattice, Mn²⁺ exhibits photoemission from shorter wavelength to longer wavelength (i.e. green to red). When Mn²⁺ is occupied in the tetrahedral crystal lattice, it radiated green light or if Mn²⁺ is placed in the octahedral structure, it will emit orange to red light. In both crystal lattice conditions, orbital d–d transition (⁴T₁→⁶A₁) of Mn²⁺ is observed due to the spin-not allowed (forbidden) state.⁸⁻¹¹ It is presumed that, if such a stable system is doped with a transition metal ion i.e. manganese, can enhance the luminescence properties.

Therefore, herein we report on the synthesis of NaMg₄(PO₄)₃: Mn²⁺ by solution combustion reaction method and investigated their luminescence properties for testing red-emitting phosphor-based LEDs device applications.

EXPERIMENTAL

Materials and Synthesis

Various concentration of manganese metal ions ($x = 0.01, 0.02, 0.03, 0.04, 0.05$ mol%) doped Sodium Magnesium Phosphate (SMP) compounds were made through combustion method. The constituent nitrates or hydroxides of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (A.R.), $\text{NH}_4\text{H}_2\text{PO}_4$ (A.R.), $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (A.R.), and $\text{Mn}(\text{NO}_3)_2$ (A.R) were weighed stoichiometrically and calculated weight of $\text{CO}(\text{NH}_2)_2$ (A.R.) was added as fuel according to the following reaction scheme:



Those precursor chemicals were transferred into a 50 ml beaker containing an appropriate amount of deionized water. The solutions were stirred vigorously for 1 hr. until a homogeneous solution was formed. Thereafter, the homogeneous solution mix was then transferred into the preheated electric furnace at 600°C and held at this temperature for 5 minutes. Throughout this minimum time, the solution gets boiled and undergoes dehydration followed by decomposition releasing a large number of gasses and producing a foamy and voluminous powder. As soon as the reaction completes, the foamy products were cooled and ground thoroughly and calcined at 1000°C for 5 hours, and naturally cooled to ambient temperature. Thus, the collected powder was transferred to the mortar and followed by crushed to obtain soft nature powders. To make pellets for further measurements by taking the final product and followed by applying only one direction pressed into disks (disk size to be measured 1.2-1.3 mm in thickness and 10 mm in diameter).

Characterizations

The confirmation of title compounds can be examined with the aid of Powder X-ray diffraction (XRD) patterns through an XPERT-MPD diffractometer. Using the above instruments, diffraction peaks were scanned in the 2θ range of 10 - 70° by applying graphite-monochromated $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). Using Hitachi FE-SEM SU8010 instrument, the synthesized compound's element, and surface structure were investigated through Energy Dispersive X-ray (EDX) and Scanning Electron Microscope (SEM) analyses. Using, UV-Vis diffuse reflectance spectra; the optical properties were tested on a PerkinElmer Lambda 950 spectrophotometer were measured under a wavelength range of 200-2500 nm at room temperature. Photoluminescence behaviors were examined on Edinburgh FLS920 and FSP920 fluorescence spectrometer.

RESULTS AND DISCUSSION

XRD Analysis

The XRD patterns of as-prepared Mn-doped SMP compounds are shown in Fig.-1a. The recorded diffraction peaks of all the samples are compared, the results are well-matched with the SMP compounds and are in accordance with standard data of JCPDS card number 76-1377 (ICSD code: 35496).^{12, 13}

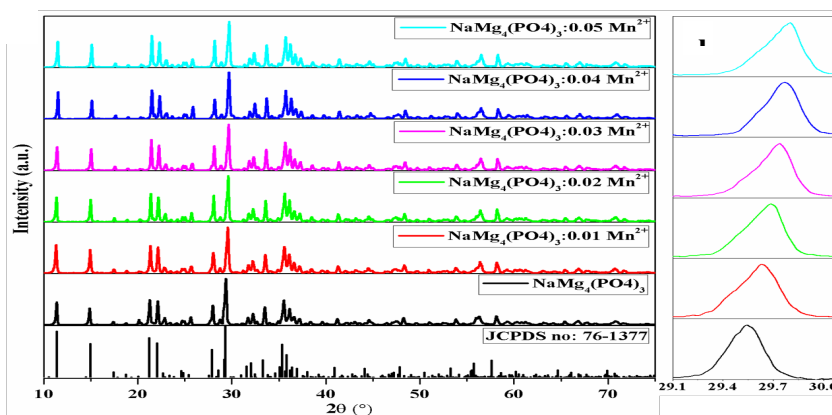


Fig.-1: (a) The XRD Patterns of as- Prepared SMP Compounds with Various Concentration of Mn^{2+} Doped (Left Image), (B) Peak Shift of the XRD Pattern between 29.1° and 30°

Additionally, no impurity signals are identified in the XRD analysis, noticed that does not change the crystal structure with increasing of Mn^{2+} concentration. In addition, the diffraction peaks were shifted towards the higher diffraction angles with an increase in Mn^{2+} content as shown in Figure-1b. This happened due to the various ionic radii between Mn^{2+} , Na^+ , and Mg^{2+} . Here four sites are available for Mn^{2+} to occupy, one from sodium atom and three from magnesium atom.

Elemental and Morphology Analysis

Figure-2 shows the EDX spectrum and corresponding element mapping by scanning electron microscopy of $\text{NaMg}_4(\text{PO}_4)_3 \cdot x\text{Mn}^{2+}$ samples. The SEM micrograph exhibits a smooth surface with grains, crystallites, or microsites in the sample. The five elements were traced as Na, Mg, P, Mn, and O in the EDX study. The atomic weight% of O (47.45), Na (5.46), Mg (19.19), P (25.18), and Mn (2.73) were also detected in the EDX study. Further, SEM-EDX mapping quantifies the basic composition of $\text{NaMg}_4(\text{PO}_4)_3 \cdot \text{Mn}^{2+}$ material demonstrating the presence of Na, Mg, P, and Mn elements.

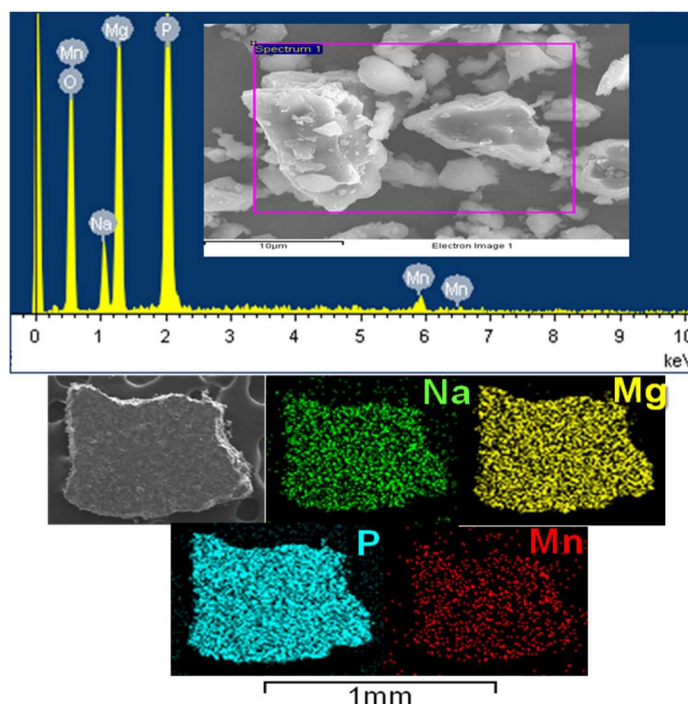


Fig.-2: SEM, EDX Spectra, and Corresponding Element Mapping by Scanning Electron Microscopy of $\text{NaMg}_4(\text{PO}_4)_3 \cdot x\text{Mn}^{2+}$ Powder Samples

Photoluminescence Analysis

In the excitation spectrum of the SMP compounds, a 0.05% concentration of Mn^{2+} phosphor was displayed in Fig.-3a. It revealed that a weak peak at 367 nm and a strong peak at 411 nm, which are ascribed to the ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{2g}(\text{D})$ and ${}^6\text{A}_{1g}(\text{S}) \rightarrow ({}^4\text{A}_{1g}(\text{G}), {}^4\text{E}_{1g}(\text{G}))$ d-d transitions state of Mn^{2+} . The intense excitation band, 411 nm was chosen and it recorded the photoemission behavior of the SMP compounds, and the various concentration of Mn^{2+} doped, which are shown in Fig.-3(b).

Upon exciting with 411 nm, Mn^{2+} ions in lower energy state are moved to higher excited states followed by non-radiatively relaxing to ${}^4\text{T}_{1g}(\text{G})$ state through intermediate energy levels (${}^4\text{E}_{1g}$, ${}^4\text{T}_{2g}$, (${}^4\text{E}_{1g}$, ${}^4\text{A}_{1g}$) and ${}^4\text{T}_{2g}$). After that, decay radiatively transitions to lower energy state ${}^6\text{A}_{1g}(\text{S})$ through phonon emission creating a wider reddish-orange emission peak at the wavelength of 617 nm ascribed to a spin-not allowed transition state of ${}^4\text{T}_{1g}(\text{G}) \rightarrow {}^6\text{A}_{1g}(\text{S})$ with invariance under a point reflection. A strong emission peak was observed in the PL spectra due to the distribution of dopant sites and perceptivity to changes in coordination and symmetry. The spectral peak position of 617 nm lying in the red emission region confirms octahedral site symmetry of dopant ion in SMP lattice structure. Further, it is realized from the emission spectra that upon varying Mn^{2+} ion concentration from 0.01 to 0.05 mol %, emission intensity

was found to suppress after 0.03 mol% which leads to a quenching effect. Such type of emission intensity occurred due to the presence of active sites of Mn^{2+} ions.

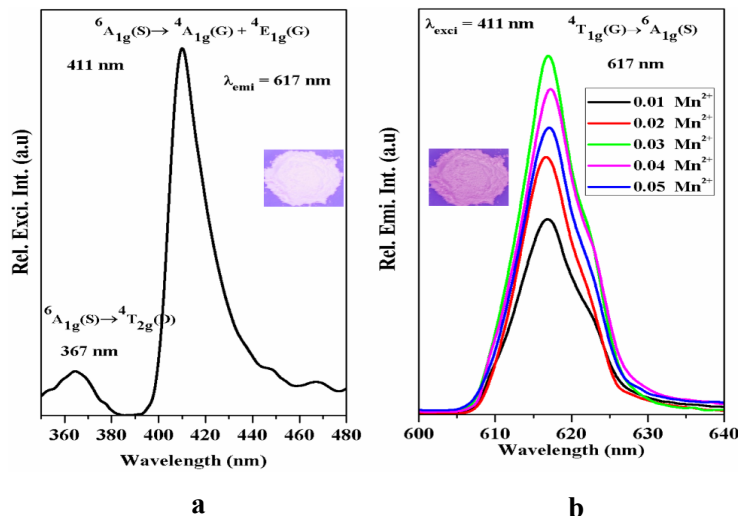


Fig.-3(a): Excitation and (b) Luminescence Spectra of the SMP Compounds: Various Concentration of Mn^{2+} Doped at ($\lambda_{\text{exci}} = 411 \text{ nm}$) and ($\lambda_{\text{emi}} = 617 \text{ nm}$)

Hence, the mean distance between them is less and its consequence collision between these ions will be more, which leads to the transfer of excitation energy non-radiatively between excited and un-excited Mn^{2+} ions in the host lattice.^{14,15} It is also explained that this quenching phenomenon could also be happened due to the formation of ion clusters, which act as a sink to absorb excitation energy instead of radiatively emitting absorbed energy. Furthermore, luminescence quenching has been studied and supported by plotting emission lifetime decay curves. Figure-4(a) exhibits emission decay curves plotted for (0.01-0.05 mol%) Mn^{2+} phosphors at $\lambda_{\text{exi}} = 411 \text{ nm}$ for ${}^4\text{T}_{1g}(\text{G}) \rightarrow {}^6\text{A}_{1g}(\text{S})$ emission transition using a single exponential fitting eqn.-1.

$$I = A \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

Where I represent the photoluminescence intensity at a time, τ denotes the decay component, and A is ascribed fitting parameter. Non-exponential to exponential nature transformation with a decrease in their lifetimes with increasing manganese dopant concentrations was confirmed through decay curves. Thus, a decrement in a lifetime could be more pronounced due to the non-radiative energy transfer process between manganese dopant ion pairs at a smaller distance and its consequence luminescence quenching occurred. This may another reason for an increase in non-radiative nature which is governed by numerous-phonon relaxations and energy transfer between dopant ions. Figure-4(b) represents a schematic energy level picture of Mn^{2+} doped in the SMP host matrix. Different types of possible interactions like dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, and exchange between charges through the energy transfer process, when the dopant is introduced into the synthesized host lattice. Initially, energy transfer happened due to the radiation re-absorption is verified from excitation and emission spectral overlap, which could not be taking place between them indicating energy transfer could be interchange interaction or diverse-polar interactions. Therefore, the critical distance (R_c) of energy transfer between Mn^{2+} ions was calculated by using the formula given in eqn.-2.

$$R_c = 2 \left(\frac{3V}{4\pi x_c N} \right)^{\frac{1}{3}} \quad (2)$$

Where V represents the volume of the unit cell, x_c denotes critical concentration, and N indicates the number of accessible sites for the dopant in the unit cell of the obtained compounds. V , N , and x_c values are found to be $955.7 \text{ \AA}^3$, 4, and 0.03. Using V , N , and x_c values, the R_c of energy transfer between Mn^{2+}

ions in the SMP host is calculated to be $24.7 \text{ \AA}^\circ$. From obtained R_c it is understood that exchange interaction has a fewer role to play in this transfer process because it is valid when R_c is about $5 \text{ \AA}^\circ$. Therefore, diverse interchange interaction and non-radiative energy transfer processes between Mn^{2+} ions were verified using Dexter theory. The type of interaction responsible energy transfer process between doped ions into the host lattice was computed by employing the formula below:¹⁶⁻¹⁸

$$\frac{I}{x} = K \left[1 + \beta(x)^{\theta/3} \right]^{-1} \quad (3)$$

Where I represent the emission intensity, x denotes activator concentration, θ represents electric multipole-multipole interactions, i.e. $\theta = 6, 8$, and 10 represent the dipole-dipole, dipole-quadrupolar, and quadrupole-quadrupole transition. K and β are representing excitation constants. Based on the eq.-3 the $\log(I/x)$ versus $\log(x)$ plot of manganese doped SMP as shown in Fig.-4c, which is well fitted to a straight line with a slope $(-\theta/3) = -1.77$. The θ value is calculated to be 5.31 , which is near 6 denoting energy transfers through the quenching mechanism between Mn^{2+} ions is an electric dipole-dipole interactions type.

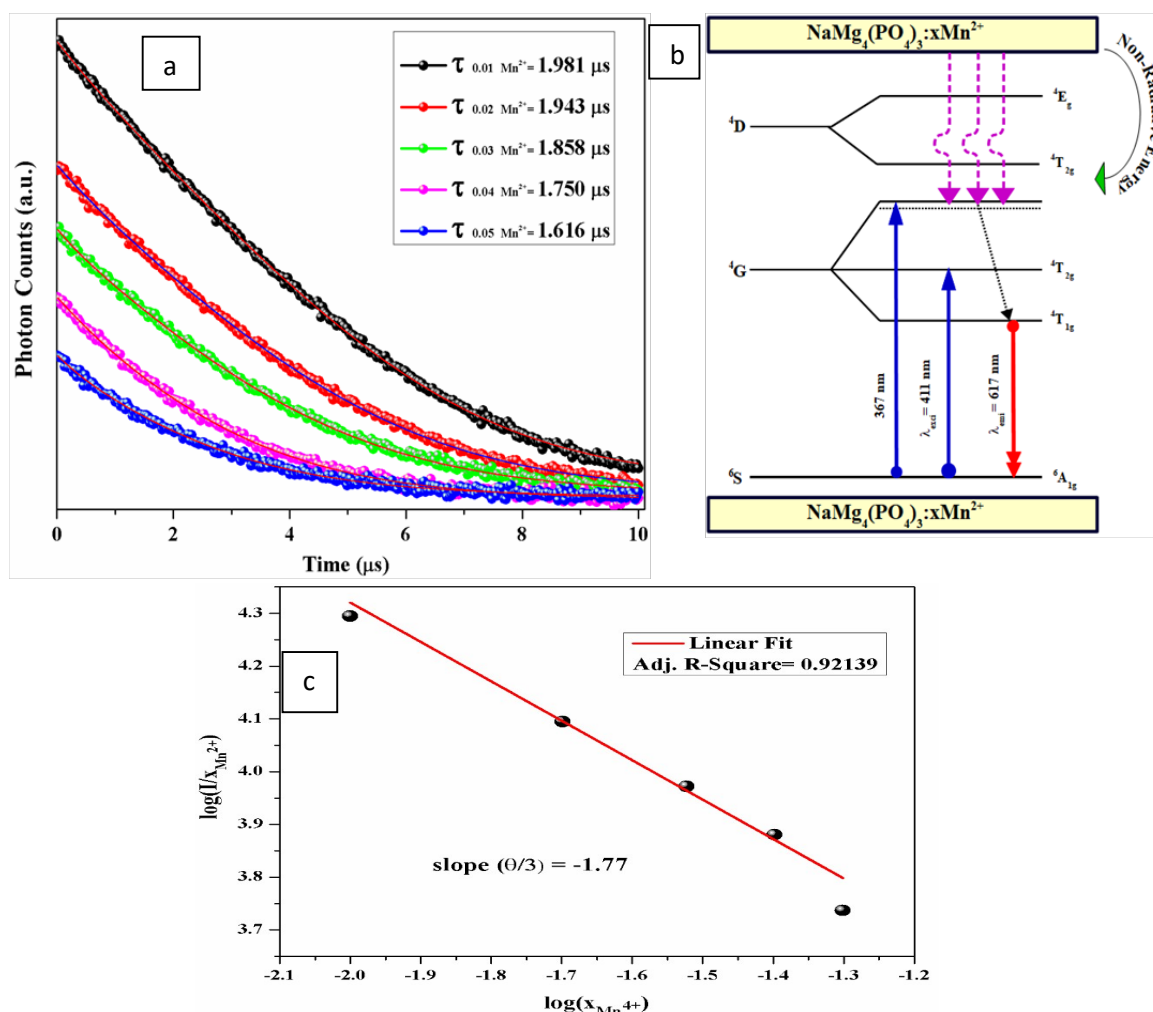


Fig.-4:(a) Emission Decay Curves of Various Concentrations (0.01-0.05 mol%) of Mn^{2+} Phosphors and Excitation Wavelength at 411 nm From $^4\text{T}_{1g}(\text{G}) \rightarrow ^6\text{A}_{1g}(\text{S})$ (b) Schematic Energy Level Diagram of Mn^{2+} Doped SMP Compounds, and (c) $\log(x)$ versus $\log(I/x)$ of Mn^{2+} Doped SMP Compounds

CONCLUSION

Various concentrations of Mn^{2+} doped SMP compounds were made by combustion method and their structural characteristics and photoluminescence behavior are investigated for LEDs device applications.

XRD analysis proved that doped ions are completely soluble in the host SMP lattice point locating Na^+ sites in $[\text{NaO}_6]$ developing a stable and mono-phased solid solution. EDX spectrum and corresponding element mapping by scanning electron microscopy confirm the presence of Na, Mg, P, O, and Mn elements and uniformly admixture of Mn into the host lattice of SMP. The Photoluminescence spectra of the Mn^{2+} doped SMP compounds observed a strong red emission peak at 617 nm, which denotes a spin-not allowed transition state of ${}^4\text{T}_{1g}(\text{G}) \rightarrow {}^6\text{A}_{1g}(\text{S})$ with an inversion symmetry operation. Powder materials containing 0.03 mol% of Mn have exhibited strong visible emission. The weight of Mn is more than 0.03%, the emission intensity was decreased. This was due to the presence of more Mn acceptor ions. In addition, after introducing dopant into the host compounds, the energy transfer process from lower to the excited state, d-d interaction, and photoemission quenching happened. The above characteristic is successfully explained using emission decay curves. Based on the above results suggested that the synthesized materials are used as red-emitting phosphors in the production of white LEDs.

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