

Structure and Photoluminescence properties of $\text{Na}_4\text{Mg}(\text{PO}_4)_2 : \text{Sm}^{3+}$ Phosphor

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Abstract— The combustion approach was used to produce a series of reddish orange-emitting phosphate phosphors, $\text{Na}_4\text{Mg}_{1-x}(\text{PO}_4)_2 : x\text{Sm}^{3+}$ ($0.01 \leq x \leq 0.1$). To describe the structure and luminescence characteristics of as-produced phosphors, X-ray diffraction and photoluminescence spectra have been used. The optimized $\text{Na}_4\text{Mg}(\text{PO}_4)_3 : 0.08\text{Sm}^{3+}$ phosphor showed several excitation bands from 350 to 500 nm and exhibit intense reddish orange-emission. The energy transfer type between Sm^{3+} ions was confirmed as dipole-dipole (*d-d*) interaction. The chromatic properties of the typical sample $\text{Na}_4\text{Mg}(\text{PO}_4)_3 : 0.08\text{Sm}^{3+}$ phosphor have been found to have chromaticity coordinates of (0.583, 0.405), which are located in reddish orange region under the excitation of 403 nm. Due to their effective excitation in the near-ultraviolet range, our results suggested that $\text{Na}_4\text{Mg}(\text{PO}_4)_3 : \text{Sm}^{3+}$ phosphors have prospective uses in the field of lighting and display.

Index Terms— Phosphors, Display, Photoluminescence, Chromaticity, Red emission.

I. INTRODUCTION

Highlight a Spectroscopic investigations play key role in elucidating various radiative properties of lanthanide doped glass materials along with its energy level structure and other properties [1]. Such materials are useful for LED's, next generation lighting applications, upconversion luminescent materials and optical filters[2]. Due to the long lifetimes of 4f-4f transitions and sharp spectral width, rare earth doped materials had much attractive[3]. Phosphate glasses has distinctive features like thermal stability, low melting point, high transparency, high gain density owing to high solubility for rare earth ions, low dispersion and low refractive index.

The energy level structure, other features, and other radiative characteristics of lanthanide doped phosphors can only elucidated by spectroscopic investigations [1]. Such materials are helpful for

optical filters, upconversion luminescent materials, LEDs, and next-generation lighting applications [2, 4]. Rare earth doped materials have a great deal of appeal because of the longer lifetimes of 4f-4f transitions and considerable spectral width[3]. Phosphate phosphors are prominent by having qualities like high solubility for rare earth ions, low dispersion, high transparency, high gain density, low refractive index, and thermal stability. UV LED pumped phosphors are a focus of current solid state lighting technology research. Such phosphate hosts play a significant role and make it possible for the rare earth ions to exhibit their distinctive properties at larger levels, which is especially crucial for phosphors with co-doped and tri-doped rare earth ions.

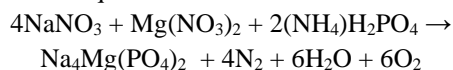
Additionally, the additional components can improves the effectiveness of rare earth ions while also strengthening the network. In addition to improving thermal and optical qualities, past research shows that these kind of phosphate hosts are more mechanically and chemically stable[2]. Trivalent Sm^{3+} ions, can exhibit intense reddish-orange (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$) luminescence. Sm^{3+} ions are crucial and helpful as an optical activator in many hosts, including phosphate, borate, silicates, and others[5–10]. Studies on the luminescence of Sm^{3+} ions in various hosts have been widely documented in the literature. However, it is still important to understand the host matrix's underlying workings and its structural reliance on the luminous centre. Both structural variation of host, concentration effect of Sm^{3+} ions host are two different phenomenons to understand. As a result, earlier research establishes the effectiveness of Sm^{3+} ions in various hosts for photonic applications. Additionally, Sm^{3+} doped glasses and phosphors are used for applications such as white light generation in addition to red emitting lasers and photonics[11–13].

Phosphate hosts are one of the best among other hosts because to their exceptional properties, which include high rare earth ion solubility, wide transmission, high thermal expansion coefficient, and forming ability [14, 15].

Our research seeks to investigate the Sm^{3+} ions-activated $\text{Na}_4\text{Mg}(\text{PO}_4)_3$ phosphor's emission process at various dopant concentrations. Furthermore, the structural variation is investigated and examined with the reference data. The results of this work could significantly advance our knowledge of the Sm^{3+} ions' luminescence behavior in $\text{Na}_4\text{Mg}(\text{PO}_4)_3$ phosphor environments.

II. MATERIALS AND METHODS

$\text{Na}_{4-x}\text{Mg}(\text{PO}_4)_2 \cdot x\text{Sm}^{3+}$ (where $x = 0.01, 0.03, 0.05, 0.08$ and 0.1 mol%) phosphors are prepared by using renowned combustion synthesis. NaNO_3 , $\text{Mg}(\text{NO}_3)_2$, Sm_2O_3 , and $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ used as starting materials. The balance equation is



All precursors are taken in stoichiometric ratio along with urea as fuel and H_3BO_3 as flux. All the compounds are weighed by following the procedure reported by K.N. Shinde et. al. [16] and mixed thoroughly for 30 min by using pestle and mortar. Each batch of the resultant mixture placed in a high temperature furnace at 800°C for few minutes. The reaction takes place as ignited and burned. As a result, solid white foam specimen remained in the crucible. This combustion synthesis is also known as self-propagating high-temperature synthesis and it doesn't required oxygen from the air in formation of desired metal complex. The remained powders are grinded and annealed at 650°C for 3h to reduce their hardness, making them more workable.

III. RESULTS AND DISCUSSION

X-ray diffraction patterns of prepared $\text{Na}_4\text{Mg}(\text{PO}_4)_2$ phosphors are shown in Fig 1 and compared with standard structure.

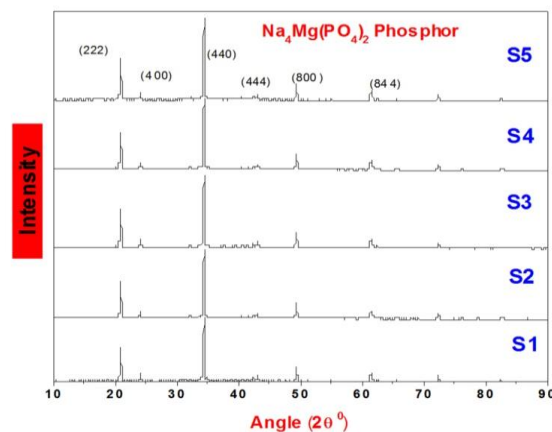


Figure 1(a) X-ray diffraction of pattern of $\text{Na}_4\text{Mg}(\text{PO}_4)_2$ phosphor(s)

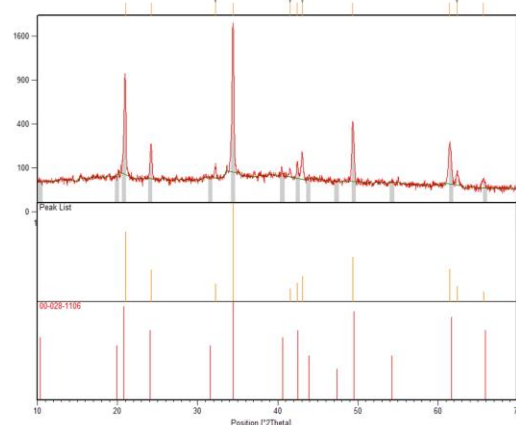


Figure 1(b) Correlation of X-ray diffraction of pattern of $\text{Na}_4\text{Mg}(\text{PO}_4)_2$ phosphor with standard JCPDS data

It shows that the prepared samples are well crystallized and matched with the standard structure (JCPDS No.28-1106). It exhibits an cubic crystal structure. There are no other impurity phases found. This confirmed the single phase $\text{Na}_4\text{Mg}(\text{PO}_4)_2$ phosphor. In addition, no structural variations are also observed upon Sm^{3+} addition. From this x-ray diffraction pattern, crystallite sizes are calculated by using Debye-Scherrer's formula ($D = 0.9\lambda / \beta \cos \theta$), where D -crystallite size, β -full width half maximum, λ – x-ray wavelength. The calculated average crystallite size is ~ 73 nm.

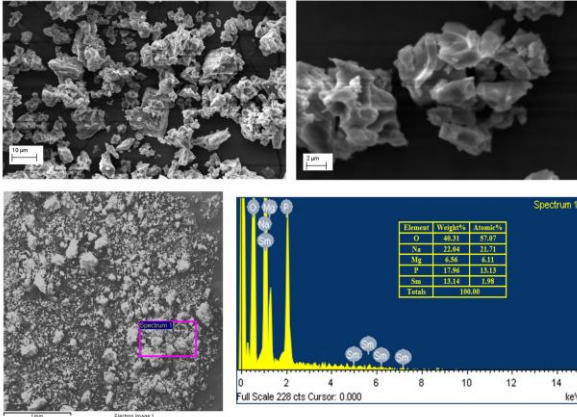


Figure 2 SEM and Energy Dispersive spectra of Sm^{3+} activated $\text{Na}_4\text{Mg}(\text{PO}_4)_2$ phosphor

SEM image clearly shows the agglomeration and irregular shapes. The size of the particles is in the range of 180 – 300 nm. This kind of asymmetrical grains and porous surface is generally obtained in combustion synthesis. The Energy Dispersive X-ray spectra (EDS) (in set) confirm that the particles constitute Na, Mg, P, Sm and O. Further, it shows a clear association Sm with Na and Mg.

Excitation and Emission spectra were recorded in the visible region for the present $\text{Na}_4\text{Mg}(\text{PO}_4)_2$ phosphors and are shown in Figure 3 and Figure 4 respectively. Excitation spectrum indicates the transitions from $^6\text{H}_{5/2}$ to different excited levels $^4\text{D}_{7/2}$, $^4\text{D}_{3/2}$, $^6\text{P}_{7/2} + ^4\text{I}_{17/2}$, $^4\text{L}_{15/2}$, $^6\text{P}_{3/2}$, $(^6\text{H}, ^4\text{P})_{5/2}$, $^4\text{G}_{9/2}$ and $^4\text{I}_{11/2} + ^4\text{I}_{13/2} + ^4\text{M}_{15/2}$. Here $^6\text{H}_{5/2} \rightarrow ^4\text{F}_{7/2}$ (403 nm) level had the maximum absorption and is taken as excited wavelength to record the emission spectra for the present study.

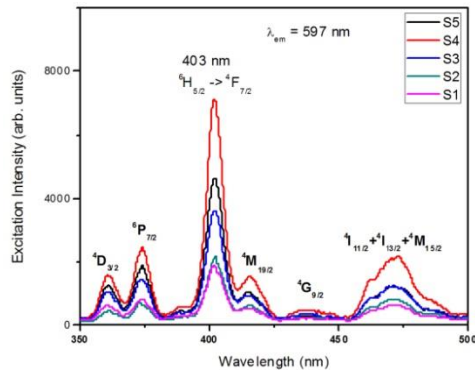


Figure 3 Excitation spectra of $\text{Na}_4\text{Mg}(\text{PO}_4)_2 : \text{Sm}^{3+}$ phosphors (monitored at 597 nm)

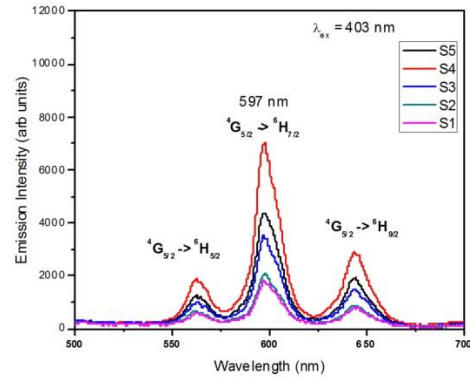


Figure 4 Emission spectra of $\text{Na}_4\text{Mg}(\text{PO}_4)_2 : \text{Sm}^{3+}$ phosphors (upon 403 nm excitation)

Figure 4 shows the Emission spectra of $\text{Na}_4\text{Mg}(\text{PO}_4)_2 : \text{Sm}^{3+}$ exhibits three transitions from the excited level to different ground levels. The transitions are $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ (~563 nm-greenish yellow; magnetic dipole transition), $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ (~597 nm – Orange; electric dipole transition), and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ (~644 nm – Red; electric dipole forced transition)[5]. The transition from $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ (~597 nm – Orange) has maximum intensity in all the samples indicates that these samples are emitting visible orange red colour and are useful in red light emission applications. Here the electric dipole transitions are responsive for local field and magnetic dipole transitions are insensitive to the change of field around Sm^{3+} ion[17].

In the present study, for S4 (0.08 mol% of Sm^{3+}) phosphor has maximum luminescence intensity compared to others. In many reported phosphors [5, 18–20], illustrates that intensity increases with the dopant concentration increases, is due to the local symmetry changes. So, this study reveals that the change in local environment around Sm^{3+} ions will have a definite effect on emission properties with respect to concentration variation of Sm^{3+} ions.

Lifetime measurements were done at room temperature and shown in Figure 5. Experimental and calculated lifetimes with quantum efficiencies of $^4\text{G}_{5/2}$ level for $\text{Na}_4\text{Mg}(\text{PO}_4)_2 : \text{Sm}$ phosphors were calculated and presented in Table 1.

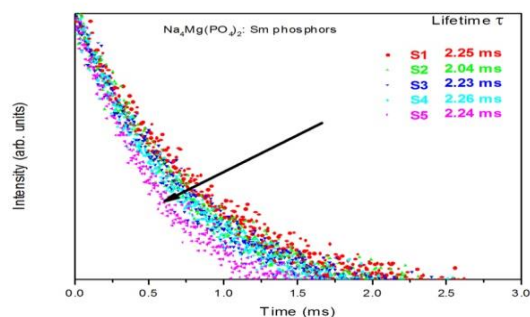


Figure 5 Decay profiles of $\text{Na}_4\text{Mg}(\text{PO}_4)_2$: Sm phosphors

Table 1. Experimental and calculated lifetimes of present $\text{Na}_4\text{Mg}(\text{PO}_4)_2$: Sm phosphors

Phosphor	τ_{exp}	τ_{cal}	η
S1	2.25	3.27	68.8
S2	2.04	2.49	81.9
S3	2.23	2.59	86.1
S4	2.26	2.62	86.2
S5	2.24	2.61	85.8

One can conclude from the obtained values that S2 had more efficiency than the others though lifetimes were increased as concentration decreases and the variation is also almost similar.

From the emission spectra, the calculated CIE colour coordinates for the present phosphors were approximately identical with slight variation and were well placed in orange red region and is shown in Fig 6. The CIE coordinates (x,y) were (0.594,0.392); (0.597,0.386); (0.593, 0.386); (0.588, 0.382) and (0.594, 0.399) for S1, S2, S3, S4 and S5 respectively. Therefore, the above result suggests that these phosphors were useful for development of orange-red lighting devices.

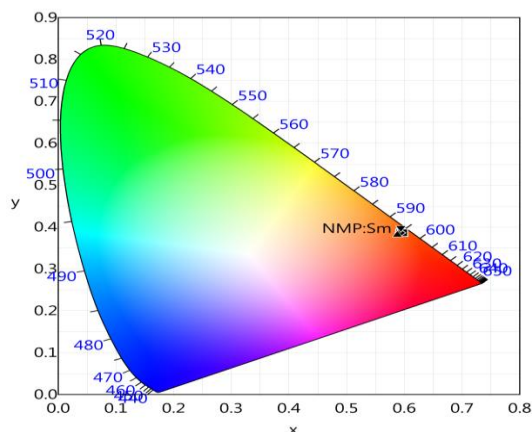


Figure 6 CIE chromaticity diagram for $\text{Na}_4\text{Mg}(\text{PO}_4)_2$: Sm phosphors

IV. CONCLUSION

A series of novel $\text{Na}_4\text{Mg}(\text{PO}_4)_2$: Sm phosphors were prepared by combustion synthesis. Structure and luminescence characteristics of as-produced phosphors, were analyzed by X-ray diffraction, photoluminescence and other tools utilized. The optimized $\text{Na}_4\text{Mg}_{0.92}(\text{PO}_4)_3:0.08\text{Sm}^{3+}$ phosphor showed several excitation bands from 350 to 500 nm and exhibit intense reddish orange-emission. The energy transfer type between Sm^{3+} ions was confirmed as dipole-dipole ($d-d$) interaction. The chromatic properties of the typical sample $\text{Na}_4\text{Mg}(\text{PO}_4)_3:0.08\text{Sm}^{3+}$ phosphor have been found to have chromaticity coordinates of and are located in reddish orange region under the excitation of 403 nm. Due to their effective excitation in the near-ultraviolet range, our results suggested that $\text{Na}_4\text{Mg}(\text{PO}_4)_3:\text{Sm}^{3+}$ phosphors have prospective uses in the field of lighting and display.

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