

Photoluminescence studies of $\text{Na}_2\text{Gd}(\text{PO}_4)_2:\text{Sm}^{3+}$ Nano Phosphors for SSL Applications

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Abstract

Trivalent samarium (Sm^{3+}) doped $\text{Na}_3\text{Gd}(\text{PO}_4)_2$ (NGP) phosphors were prepared by citrate gel combustion process. The structure, optical and energy transfer studies were systematically characterized through photoluminescence (PL), X- ray diffraction, and decay measurements, respectively. Upon 406 nm excitation Sm^{3+} doped NGP phosphors emit orange-red luminescence with peak maximum at 602 nm. Sm^{3+} ions were located at the inversion symmetry sites of NGP lattice. The Commission International de l'Eclairage chromaticity coordinates were calculated from the photoluminescence spectra. The NGP: Sm^{3+} phosphors can be used as a promising material for solid state lighting devices.

Keywords: NGP phosphors, Photoluminescence, Solid state lighting.

1. Introduction

Solid state lighting in view of the inorganic LEDs has now turned into the point of extraordinary research enthusiasm for specialists and researchers everywhere throughout the world throughout the previous couple of decades inferable from its awesome favorable circumstances over guideline a lighting gadgets. This arrangement of enlightenment is anticipated to assume control as the future lighting innovation to light up the entire world. There are different approaches to create white light utilizing LEDs. The primary come up to will be to utilize singular LEDs with red, green and blue hues, together in single light, to yield white light. The second path is to utilize bright LEDs, which light up a red, green and blue phosphor. These phosphor materials change over the high vitality UV light from the LED chip, down to bring down vitality wavelengths of red, green and blue light. The aggregate light is consolidated to create white light. The third path is to utilize a blue LED to light up a yellow phosphor. Among the three, these approve is generally doped to create white light since its shading rendering file is viewed as superior to rest of them [1]. Phosphate phosphors have been widely studied as a luminescent host material, particularly eulytite-type materials have attracted much attention because of their muddled structure contributes to the luminescence [2], such as $\text{Sr}_3\text{Y}(\text{PO}_4)_3:\text{Dy}^{3+}$ [3], $\text{Ba}_3\text{Gd}(\text{PO}_4)_3:\text{Ce}^{3+}$, Tb^{3+}

[4], $\text{Ba}_3\text{Lu}(\text{PO}_4)_3:\text{Eu}^{2+}$, Mn^{2+} [5] and $\text{Ba}_3\text{Y}(\text{PO}_4)_3:\text{Ce}^{3+}$, Tb^{3+} phosphors have shown that they can be effectively excited in the NUV-region to generate white light.. The RE^{3+} ions have been playing a significant role in modern SSL applications because of their rich emission colours related to the $4f \rightarrow 4f$ transitions. Moreover, the host matrix has little influence on the positions of $4f^n$ configuration energy levels are almost similar to that of the free-ion levels. Generally, RE^{3+} ions are considered to be the most important optical activators for luminescent devices. Among the RE^{3+} ions, the Sm^{3+} ion emits orange-red luminescence due to the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2,7/2,9/2}$ transitions and acts as an excellent activator with high luminescence output, colour purity and thermal stability [6]-[7]. In the recent years, Sm^{3+} based systems has also proven to be the potential candidates for other opto-electronic applications. Sm^{3+} -doped Ca_2SnO_4 has shown long lasting phosphorescence for more than 7 h in the reddish-orange region which can find applications in lighting, display and detection of high energy rays, etc [8]. Sm^{3+} ions also find applications in phosphor thermometry to measure high temperatures, typically > 800 K. In the case of Sm^{3+} -doped GdVO_4 phosphor the intensity ratio of ${}^4\text{F}_{3/2} \rightarrow {}^6\text{H}_{5/2}$ to ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$ transition is found to be linear in the temperature range of 293-823 K and can find applications in temperature sensing .

As per the author's knowledge concerned, there are less number of available reports on the optical characterization of Sm^{3+} doped NGP phosphors. Hence, in this study the structural and optical properties of NGP: Sm^{3+} phosphors prepared by the citrate gel combustion method are reported. The proposed synthesis method is technically simple and can be used to produce the nano particles in larger quantity.

2. Experimental details

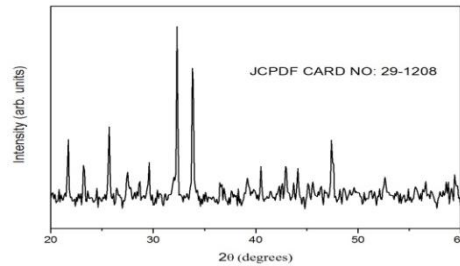
NGP phosphor doped with different Sm^{3+} ion concentrations were synthesized by following the modified citrate gel combustion method. High-purity Na_2CO_3 (A.R), Gd_2O_3 (99.99%), $\text{NH}_4\text{H}_2\text{PO}_4$ (A.R), Sm_2O_3 (99.99%) and $\text{C}_6\text{H}_8\text{O}_7$ (A.R) were utilized as beginning chemicals. Pre-weighted amounts of the considerable number of oxides and carbonates were broken down in concentrated nitric corrosive. An abundance nitrate antecedents were included with citrus extract, which was broken down in water. Citrus extract goes about as the monomer to shape straightforward complex gel after drying a stove at 75°C for 2 h. At that point the gel was taken in a quartz watercraft and tests were let go electric heater at 900°C . At first the citrate complex gel changes to a dark feathery mass almost ten times the gel volume and begins breaking down to CO_2 and H_2O vapors. Following 15 minutes a white voluminous mass of the NGP: Sm^{3+} nanophosphor is gotten. The finalized powdered samples were white and have been used for further characterization [16].

3. Results and discussion

3.1. Structural and compositional analysis

So as to affirm the crystalline idea of the combined host, X-beam diffraction ponders are completed. The XRD examples of NGP nano phosphor is appeared in Fig. 1. An estimation of the crystallite measure for the example was performed utilizing Scherrer's condition from the full width at half greatest (FWHM). The outcomes demonstrate that the readied phosphors NGP are all of stage charge, and the dopant Sm^{3+} particle don't have much power on the gem structure of luminescent materials.

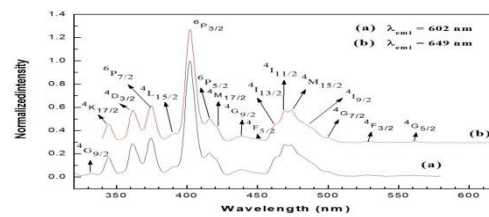
Fig.1. XRD patterns of Sm^{3+} -doped NGP nanophosphors



3.2. Photoluminescence of Sm^{3+} ions

The PLE spectra of independently doped NGP:1.0% Sm^{3+} phosphors by checking the discharge at 602 and 648 nm comparing to the

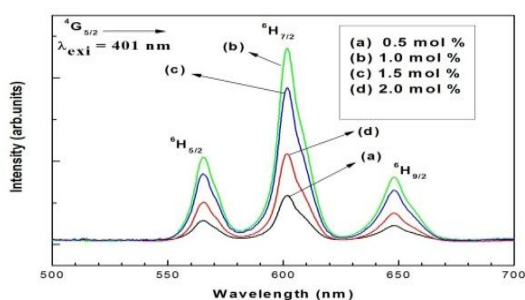
Fig.2. Excitation spectra of 1.0 mol % Sm^{3+} -doped NGP nanophosphors



$^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ changes of Sm^{3+} particle are appeared in Fig.2. The spectra made out of a progression of PLE groups focused at 319, 334, 348, 364, 380, 392, 406, 423, 467, 478 and 488 nm relating to the $^6\text{H}_{5/2} \rightarrow ^4\text{G}_{11/2}$, $^6\text{H}_{5/2} \rightarrow ^4\text{G}_{7/2}$, $^6\text{H}_{5/2} \rightarrow ^4\text{K}_{15/2}$, $^6\text{H}_{5/2} \rightarrow ^4\text{F}_{9/2}$, $^6\text{H}_{5/2} \rightarrow ^4\text{D}_{1/2}$, $^6\text{H}_{5/2} \rightarrow ^6\text{H}_{5/2} \rightarrow ^4\text{L}_{15/2}$, $^6\text{H}_{5/2} \rightarrow ^4\text{L}_{13/2}$, $^6\text{H}_{5/2} \rightarrow ^4\text{M}_{19/2}$, $^6\text{H}_{5/2} \rightarrow ^4\text{I}_{13/2}$, $^6\text{H}_{5/2} \rightarrow ^4\text{I}_{11/2}$ and $^6\text{H}_{5/2} \rightarrow ^4\text{I}_{9/2}$ transitions [9]. The excitation spectra is practically identical to the revealed Sm^{3+} -doped phosphors, for example Lu_2O_3 [10], $\text{Bi}_2\text{ZnB}_2\text{O}_7$ [11] $\text{LaAlGe}_2\text{O}_7$ [12]. It is seen that the power of the f-f progress at 406 nm is higher than that of alternate advances; along these lines, this change is decided for the estimation of the emanation spectra of NGP: Sm^{3+} phosphors. The photoluminescence outflow spectra of NGP: Sm^{3+} phosphor are appeared in Fig. 3. Three noticeable gatherings of discharge lines around running from 500 nm to 700 nm can be ascribed to the intra-4f orbital change from the $^4\text{G}_{5/2}$ 2 level to the 6HJ (J=5/2, 7/2 and 9/2) level in view of their predictable radiance practices with the Sm^{3+} outflow attributes [13]. Among these Three advances, the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ displays extraordinary

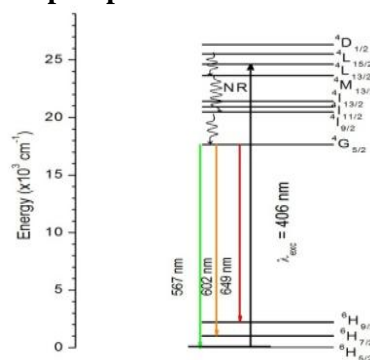
reddish-orange emission. The other two changes, $4G_{5/2} \rightarrow 6H_{5/2}$ and $4G_{5/2} \rightarrow 6H_{9/2}$, indicate direct forces. These emanations are valuable in high-thickness optical information stockpiling, shading presentations and therapeutic diagnostics. From the outflow spectra, it is seen that the pinnacle powers increment with the expansion of fixation from 0.5 to 1.0 mol% and past that the extinguishing in the discharge top intensities has been observed.

Fig.3. Emission spectra for different concentrations of Sm^{3+} ions doped NGP nanophosphors under 406 nm excitation.



The first at 567 nm $4G_{5/2} \rightarrow 6H_{5/2}$ is an attractive dipole (MD) progress, the second at 602 nm $4G_{5/2} \rightarrow 6H_{7/2}$ is an incompletely attractive and mostly compel dielectric-dipole (ED) change, and the third at 649 nm ($4G_{5/2} \rightarrow 6H_{9/2}$) is absolutely ED progress touchy to the precious stone field [14]. Not capably, the $4G_{5/2} \rightarrow 6H_{7/2}$ (602 nm) progress has the most grounded force and can be connected to orange-red discharging show materials. For the most part, the power proportion of ED and MD advances can be utilized to comprehend the symmetry of the nearby condition of trivalent 4f particles in the host framework researched [15]. The kilter nature is more noticeable when the power of the ED progress is higher. Among these, the outflow at 602 nm related with the $4G_{5/2} \rightarrow 6H_{7/2}$ change is observed to be more exceptional. The halfway vitality level outline appeared in Fig.4 portrays the emanation instrument of Sm^{3+} particle in NGP phosphors. The PL spectra of Sm^{3+} co-actuated NGP phosphors uncovered that the radiance force increments with the expansion of Sm^{3+} fixation upto 1.0% and afterward diminishes at higher focuses attributable to the wonder of iridescence extinguishing.

Fig.4. Partial energy level diagram showing the emission channels of Dy^{3+} ions in NGP nanophosphors at 406 nm excitation.



The chromaticity graph of the Commission International del'Eclairage (CIE) demonstrates that directions are very valuable in deciding the correct emanation shading and shading immaculateness of a specimen. The graph speaks to all the chromaticity noticeable to the human eye. Specifically, the edges of the outline compare to monochromatic light, while the area white light arranges exists at the middle. The CIE chromaticity organizes ascertained from the PL spectra are reported in Table 1. The places of every one of these directions are found in the orange-red area. Consequently, the Sm^{3+} doped NGP phosphors display orange-red radiance with 406 nm excitation. The relative power proportions of electric dipole to attractive dipole changes ($4G_{5/2} \rightarrow 6H_{9/2} / 4G_{5/2} \rightarrow 6H_{7/2}$) are utilized to gauge the nearby symmetry around the Sm^{3+} particles. On the off chance that the ($4G_{5/2} \rightarrow 6H_{9/2} / 4G_{5/2} \rightarrow 6H_{7/2}$) force proportion is not as much as solidarity, the Sm^{3+} particles involve reversal symmetry locales of the host cross section and bigger the power proportion more is the twisting from the reversal symmetry [15]. The force proportions ascertained from the PL spectra are additionally exhibited in Table 1. Upon 406 nm excitation, the force proportions are almost steady (~ 0.29) for 1.0% Sm^{3+} - doped phosphors. The littler and steady estimations of ($4G_{5/2} \rightarrow 6H_{9/2} / 4G_{5/2} \rightarrow 6H_{7/2}$) power proportions show that the dopant Sm^{3+} a particles are encompassed by the reversal symmetry locales in the NGP cross section. From these outcomes, it is recommended that the considered phosphors discharge rosy orange emanation under 406 nm excitation wavelength

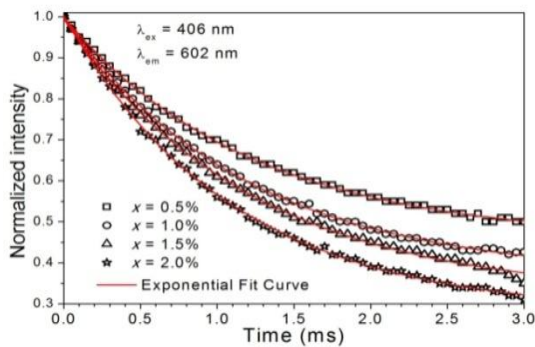
Table 1 CIE chromaticity coordinates (x, y) and $\left(\frac{{}^4G_{5/2} \rightarrow {}^6H_{9/2}}{{}^4G_{5/2} \rightarrow {}^6H_{7/2}}\right)$ intensity ratios in NGP:xSm³⁺ phosphors at 406 excitation.

NGP phosphor doping	$\lambda_{ex} = 406 \text{ nm}$ CIE coordinates		$\left(\frac{{}^4G_{5/2} \rightarrow {}^6H_{9/2}}{{}^4G_{5/2} \rightarrow {}^6H_{7/2}}\right)$
	X	Y	
x = 0.5%	0.582	0.405	0.29
x = 1.0%	0.554	0.376	0.27
x = 1.5%	0.558	0.376	0.28
x = 2.0%	0.575	0.340	0.29

3.3. Decay analysis of ${}^4G_{5/2}$ (Sm³⁺) state

The radiance rate of ${}^4G_{5/2}$ discharge territory of Sm³⁺ in NGP phosphors are contemplated by observing the outflow at 602 nm with the excitation wave length 406 nm. The standardized force versus time bends appeared in Fig.5 are reasonably fitted to single exponential capacity.

Fig.5. Decay profiles of ${}^4G_{5/2}$ level for different concentrations of Sm³⁺ ions in NGP nano phosphors.



The lifetime of ${}^4G_{5/2}$ level in Sm³⁺ doped NGP phosphor has been observed to be 1.23, 1.19, 1.11, 1.09 ms, for x = 0.5, 1.0, 1.5 and 2.0% individually. The continuous decline in lifetime with the expansion of Sm³⁺ particles fixation could be because of the expanded cooperations among the energized Sm³⁺ particles. This unmistakably shows the τ_{exp} of the ${}^4G_{5/2}$ level declines with the expansion of Sm³⁺ particles focus. By and large, phosphors doped with Sm³⁺ activator have along rot time prompted by a taboo change of Sm³⁺ as indicated by a turn choice run the show. This change has a low likelihood and rot time is in the request of millisecond. These outcomes demonstrate that the life time is sufficiently short

for potential applications in presentations and lights.

4. Conclusions

Optical nature of NGP phosphors with various groupings of Sm³⁺ particles were arranged and portrayed for their auxiliary, optical and glow properties through XRD, FTIR photoluminescence and rot estimations. Sm³⁺ doped NGP phosphors were effectively arranged by changed citrate gel burning technique. The phosphor has Three emanation groups focused at 567 nm, 602 nm and 649 nm relating to advances from ${}^4G_{5/2}$ to ${}^6H_{5/2}$, ${}^6H_{7/2}$ and ${}^6H_{9/2}$ of Sm³⁺, separately. The watched consistent otherworldly widths of ${}^4G_{5/2} \rightarrow {}^6H_{5/2,7/2,9/2}$ advances and the $({}^4G_{5/2} \rightarrow {}^6H_{9/2}/{}^4G_{5/2} \rightarrow {}^6H_{7/2})$ force proportions shows that the Sm³⁺ are situated at the reversal symmetry destinations of NGP cross section. . Every one of these attributes recommend that the orange– red emitting NGP:Sm³⁺ phosphor can be an appropriate orange– red segment of nano phosphor changed over WLEDs.

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