



Structure and photoluminescence properties of $\text{Na}(\text{Sr},\text{Mg})\text{VO}_4:\text{Eu}^{3+}$ red emitting phosphor

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Abstract

The novel red-emitting phosphors of Eu^{3+} -activated alkaline earth metal (Sr and Mg) vanadate phosphors, $\text{Na}(\text{Sr}_{0.97-x}, \text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ ($x = 0$ to 0.97) has been successfully synthesized using solid state reaction method and characterized through structure, morphology, luminescence (excitation, emission and CIE coordinates) and decay rate properties as a function of Mg ion concentration. The phosphors show an intense and broad excitation band (monitored for ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of Eu^{3+}) in the 220- 400 nm spectral regions which make them highly suitable for GaN-based LED chips. These phosphors can be efficiently excited by near UV light and exhibit a dominant red emission at 611 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$). The decay lifetime and color coordinates were evaluated for $\text{Na}(\text{Sr},\text{Mg})\text{VO}_4:\text{Eu}^{3+}$ phosphors. Therefore, these phosphors could be a potential candidate for light emitting diodes and display applications.

Keywords: Phosphors, $\text{Na}(\text{Sr},\text{Mg})\text{VO}_4$, Eu^{3+} ion, Optical properties, Light-emitting diodes.

1. INTRODUCTION

In recent years, significant efforts have been paid on the development of rare earth (RE) based luminescent materials due to their potential applications in the medical, bio-imaging, display lightening fields, etc. [1]. Developing high efficient and environment friendly lighting instrument to replace the traditional incandescent and fluorescent lamps is a significant subject. The typical method to generate white light is to use a blue LED chip (460 nm) with a yellow-emitting phosphor, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG). However, because of the lack of a red light

component, such white light generated by this method usually obtained poor color rendering. Another way to provide white light is to use an ultraviolet (UV) LED (300–410 nm) to convert phosphors which have red, blue, and green luminescence [2]. Thus, in order to develop this technology, the phosphors with desirable color emission and high efficiency under UV excitation must be explored and developed. Mainly, Vanadate has strong absorption in UV region and ceramics based on alkaline earth metal (such as Sr, Ba, Ca and Mg) vanadates have been identified as an excellent material. The crystal chemistry of many of these alkaline earth metal vanadates is well explored [3-6].

Among the RE elements from La to Lu, Eu ions have a simple electronic energy level scheme and hypersensitive transitions; the red luminescence of Eu^{3+} ions has been extensively studied as an activator ion. The f-electrons of Eu^{3+} ions are well shielded from the chemical environment and own almost retained atomic character. Moreover, Eu^{3+} ions are well known for their intense, narrow and monochromatic red emission as a result of ${}^5\text{D}_0$ - ${}^7\text{F}_2$ transition. In consequence, Eu^{3+} ions have been used in most commercial red phosphors. In the view of the above facts/important the present work concentrates on structural and luminescence properties of Eu^{3+} doped NaSrVO_4 phosphor for lighting applications. In addition, the effect of variation of Mg ion concentration on luminescence properties of Eu^{3+} doped NaSrVO_4 phosphor is also investigated.

2. EXPERIMENTAL DETAILS

The $\text{Na}(\text{Sr}_{0.97-x}, \text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ ($x = 0$ to 0.97) were fabricated by solid-state reaction method. The high purity (99.9%) starting materials were organized from Na_2CO_3 , SrCO_3 , MgCO_3 , V_2O_5 and Eu_2O_3 . The pure raw materials were taken in stoichiometric ratio and mixed with anagate mortar and then sintered at 1150°C for 4 h (heating rate was $10^\circ\text{C}/\text{min}$). The synthesis temperature above 1150°C was not attempted because the evaporation of V ion could take place to a considerable amount above this temperature.

X-ray diffraction (XRD, SHIMADZU XRD-6000) patterns of the powder phosphors were obtained using Cu-K radiation ($\lambda = 1.54056 \text{ \AA}$). FT-IR spectrum of the powder phosphor was recorded on a FT-IR-200E spectrometer (JASCO) with KBr pellet technique from 4000 cm^{-1} to 400 cm^{-1} . Morphology and particle size of the powder samples were observed by field emission scanning electron microscopy (FE-SEM, Quanta 200, 15 kV). Photoluminescence excitation (PLE) and emission (PL) characteristics were examined by spectrophotometer (FS-2, Scinco) equipped with a monochromator and a xenon lamp (150 W, CW). The lifetime measurements were carried out using JOBIN YVON Fluorolog-3 Spectrofluorimeter using xenon arc lamp as an excitation source. All the measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of $\text{Na}(\text{Sr}_{0.97-x}, \text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ phosphor samples with various Mg ion concentration (x). For $x = 0$ and $x = 0.97$, two pure crystalline phases namely $\text{NaSr}_{0.97}\text{VO}_4$ (JCPDS No. 32-1160) and $\text{NaMg}_{0.97}\text{VO}_4$ (JCPDS No. 79-0672), respectively are obtained. $\text{NaSr}_{0.97}\text{VO}_4:\text{Eu}^{3+}_{0.03}$ phase crystallizes into a cubic structure. As the Mg ion is introduced into the NaSrVO_4 , the Sr ions are replaced by Mg ions resulting into a different crystal structure of $\text{NaMg}_{0.97}\text{VO}_4$ phase (JCPDS No. 79-0672) finally for $x = 0.97$.

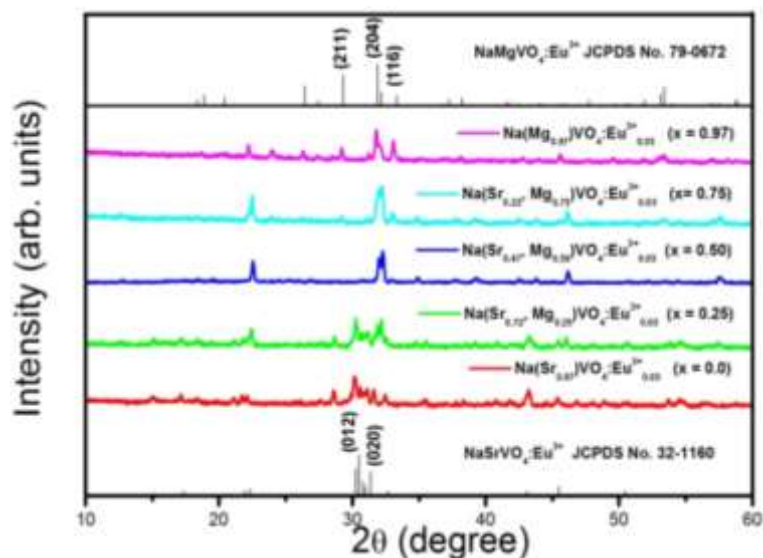


Fig. 1: X-ray diffraction (XRD) patterns of $\text{Na}(\text{Sr}_{0.97-x}\text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ phosphor samples with various magnesium ion concentration.

However, compounds in intermediate steps (for $0 < x < 0.97$) shows a poly-phase structure with the presence of peaks due to both NaSrVO_4 and NaMgVO_4 phases. Remarkably, intensity of the diffraction peaks corresponding to NaSrVO_4 phase becomes weak and also faces a change with increasing concentrations of Mg ion. This is possibly due to strain (shrinkage) in the crystal structure by replacing Sr ions through Mg ions, as the ionic radius of Mg ion (0.65 \AA) is very smaller than that of Sr ion (1.13 \AA) [7]. As a result, incorporation of the Mg ions at this level ($x = 0.25$) is found to form a nearly single-phase compound just having minor impurity phase in its XRD pattern (Fig.1). These unindexed peaks are expected due to the solubility limit of Mg ion in the NaSrVO_4 matrix. It is well known that as the amount of doping ion will increase beyond the solubility limit, impurity phase with unindexed peaks can be obviously observed [8]. The solubility limit of Mg ion in NaSrVO_4 matrix would be an interesting problem for crystallography and needs a detailed Rietveld refinement of XRD data, but beyond the scope of this study. Interestingly, a significant increase in emission intensity is observed by introducing the Mg ion at $x = 0.25$ in the matrix structure which is the focus of the present study.

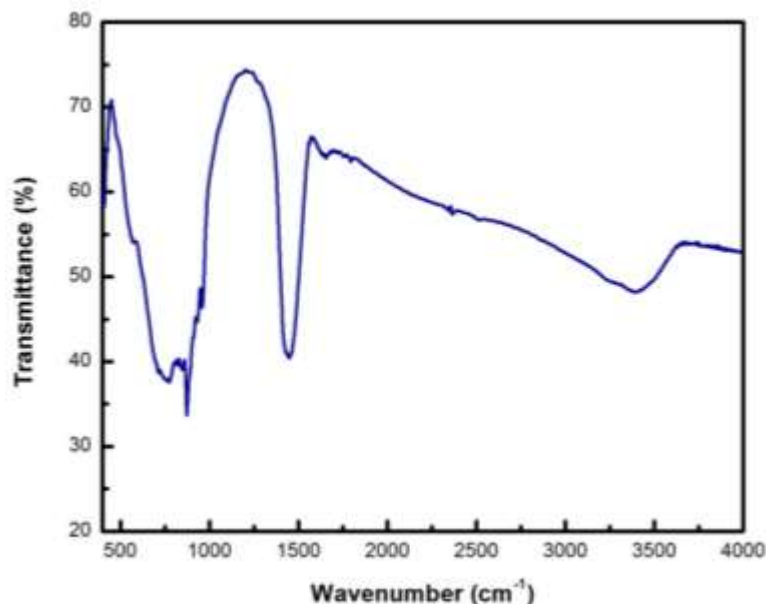


Fig. 2: FT-IR spectrum of $\text{Na}(\text{Sr}_{0.47}, \text{Mg}_{0.50})\text{VO}_4:\text{Eu}^{3+}_{0.03}(x = 0.50)$ phosphor.

Fig. 2 shows the FT-IR spectrum of $\text{Na}(\text{Sr}_{0.47}, \text{Mg}_{0.50})\text{VO}_4:\text{Eu}^{3+}_{0.03}$ phosphor in the spectral region of 400-4000 cm^{-1} . The FT-IR spectrum shows three absorption regions. In the first region, the broad band in the range of 2400-3700 cm^{-1} with maximum at 3391 cm^{-1} assigned to the O-H stretching vibration, the second region in the range of 1200-1600 cm^{-1} , which originated from the absorption of the H-O-H bending vibrations centered at 1441 cm^{-1} . These two bands are the characteristic vibrations of water from air, physically absorbed on the sample surface [9] and third region, Modes in the range of 450-600 cm^{-1} and 740-1150 cm^{-1} are due to $(\text{VO}_4)^{3-}$ absorption bands, which are assigned to the O-V-O bending vibrations and V-O stretching vibrations, respectively [10,11]. It is known that the presence of OH content increases the optical losses and then decreases the quantum efficiency of RE doped materials. However, for the present phosphors, the intensity of the IR band associated to OH group is extremely low, which indicates that these prepared phosphors are suitable for practical applications. The peak assignments of the FT-IR spectrum of the present phosphors have been compared with the results reported in literature [10].

FE-SEM has been used to study the morphology and particle size of the phosphor with various concentrations of Mg ions, as shown in Fig. 3(a-e). The particles show irregular and polygonal shape morphology. The average grain size for almost all the phosphor powders lies in the range of sub-micrometer to a few micrometers. In addition, the synthesized samples showed some aggregation also which is due to high temperature involved in the synthesis of phosphor material.

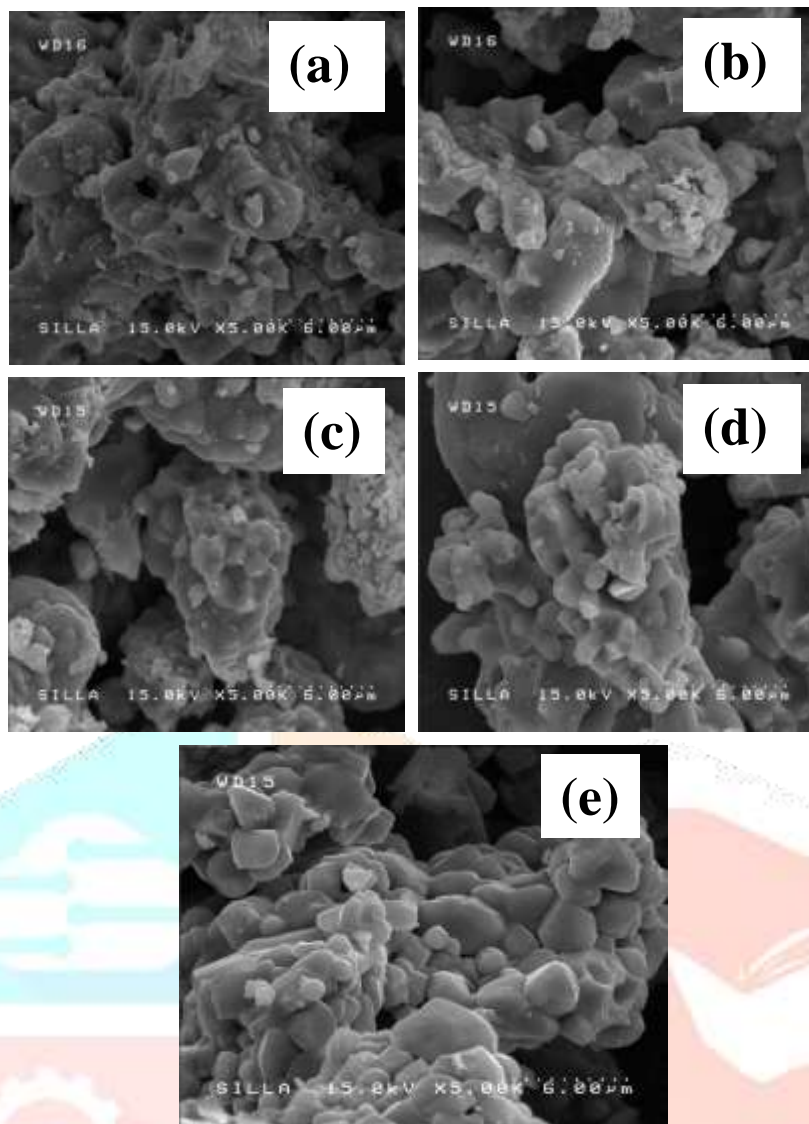


Fig. 3: The field scanning electron microscopy (FE-SEM) micrograph of $\text{Na}(\text{Sr}_{0.97-x}\text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ phosphor with varying concentration of Mg ion (a) $x = 0.0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 0.97$.

Detailed composition of the prepared $\text{Na}(\text{Sr}_{0.47}\text{Mg}_{0.50})\text{VO}_4:\text{Eu}^{3+}_{0.03}$ ($x = 0.50$) phosphor is further analyzed by EDS. A representative EDS spectrum is shown in Fig. 4. EDS spectrum shows several specific lines, the signal of Na, Sr, Mg, V, O and Eu elements in the prepared samples. This confirms the phase purity of the obtained phosphor and is in consistent with XRD analysis.

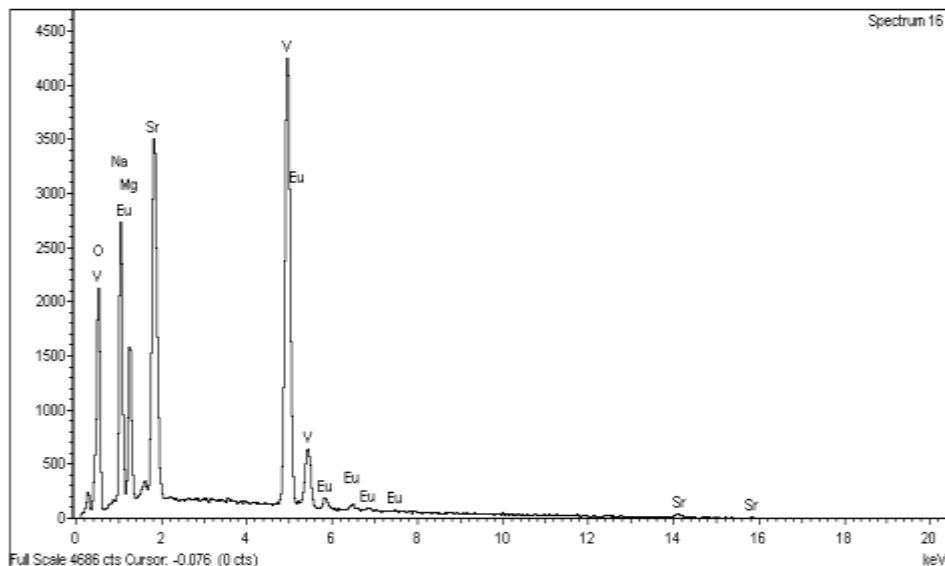


Fig. 4: EDS profile of $\text{Na}(\text{Sr}_{0.47}, \text{Mg}_{0.50})\text{VO}_4:\text{Eu}^{3+}_{0.03} (x = 0.50)$ phosphor.

The PLE spectra of $\text{Na}(\text{Sr}_{0.97-x}, \text{Mg}_x)\text{VO}_4 : \text{Eu}^{3+}_{0.03}$ phosphors as a function of Mg ion concentrations are presented in Fig. 5. As can be seen from Fig. 5 shows the changes in the PLE spectra by monitoring the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of Eu^{3+} at 611 nm. In the excitation spectra, there are not only sharp lines between 350 nm and 450 nm belonging to the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_7$ (383 nm), ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ (394 nm) and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_3$ (415 nm) transitions of Eu^{3+} ions, but also broad-bands excitation ranging from 220 to 390 nm. These broad band excitations are assigned to the CTB transitions of VO_4^{3-} , Mg^{2+} and $\text{Eu}^{3+}-\text{O}^{2-}$, but not attributed to the charge transfer from O^{2-} to Eu^{3+} [12], because the charge transfer of $\text{V}^{5+} - \text{O}^{2-}$ is easier than that of $\text{Eu}^{3+} - \text{O}^{2-}$ due to the quite difference in the charge and the small difference in radii between $\text{V}^{5+} - \text{O}^{2-}$ [13]. The strong CTB from host group is favorable for the effective energy transfer and luminescence of Eu^{3+} ion.

The replacement of Sr ion by Mg ion shows a significant change in the peak position corresponding to broad excitation band while the peak positions of the sharp bands remain almost unaltered. The intensity of PLE band in 220-390nm region gain in broad intensity with an increase in Mg ion concentration and attains a maximum at for $x = 0.75$ (with its maxima at 339 nm wavelength). This broad band excitation of the material makes it highly suitable for GaN-based LEDs and display applications[14]. The UV/blue emission will be strongly absorbed by the host band edge which will activate the Eu^{3+} ion for efficient red emission.

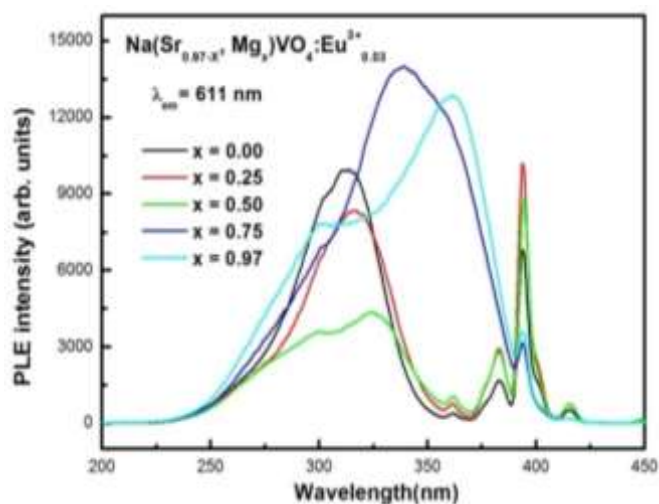


Fig. 5: Photoluminescence excitation (monitored at $\lambda_{em} = 611$ nm) spectra of $\text{Na}(\text{Sr}_{0.97-x}, \text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ phosphor as a function of magnesium concentrations.

$\text{Na}(\text{Sr}_{0.97-x}, \text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$

Fig. 6 (a) shows the PL spectra of $\text{Na}(\text{Sr}_{0.97-x}, \text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ phosphors. The PL spectra ($\lambda_{ex} = 345$ nm) show the presence of most of the characteristic bands ($^5\text{D}_0 \rightarrow ^7\text{F}_j$, $j = 1, 2, 3, 4$) due to Eu^{3+} ion. The bands are observed and could be assigned to the transitions of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (591 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (611 nm and 624 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_3$ (653 nm) and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ (688 nm and 706 nm) Eu^{3+} ions. The intensity of the PL spectra also follows a similar trend, as PLE, and thus the PL intensity also shows an increase with increase in Mg ion concentration and attains the maximum emission intensity for $\text{Na}(\text{Sr}_{0.97-x}, \text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ phase (for $x = 0.50$), and then it decreases due to the effect of Mg ion concentration. The increase in the intensity of the emission with a variation in Mg ion concentration could be related to the variation in asymmetry around the rare earth ion which could be estimated by monochromaticity (R).

The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is used as a reference to judge the environmental asymmetry of the rare earth because it is allowed by the magnetic-dipole transition and its intensity is independent of the environment where as the hypersensitive transition ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) strongly depends on it. The ratio of the intensities of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions gives a measure of the degree of distortion from inversion symmetry of the local environment of the Eu^{3+} ion in glasses [15]. Lower value of R signifies higher symmetry and vice-versa. Fig. 7(b) shows intensity ratio (R), versus Mg ion concentration (in x% value). The intensity ratio of $\text{Na}(\text{Sr}_{0.97-x}, \text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ phosphors increases with the increase in Mg ion content up to a value of $x = 0.50$ is reached, and then it decreases due to the slight changes in local symmetry around the Eu^{3+} ion. The higher value of intensity ratio of $\text{Na}(\text{Sr}_{0.97-x}, \text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ ($x = 0.50$) phosphor is found to be 5.90. This is favorable to improve the color purity of the red phosphor.

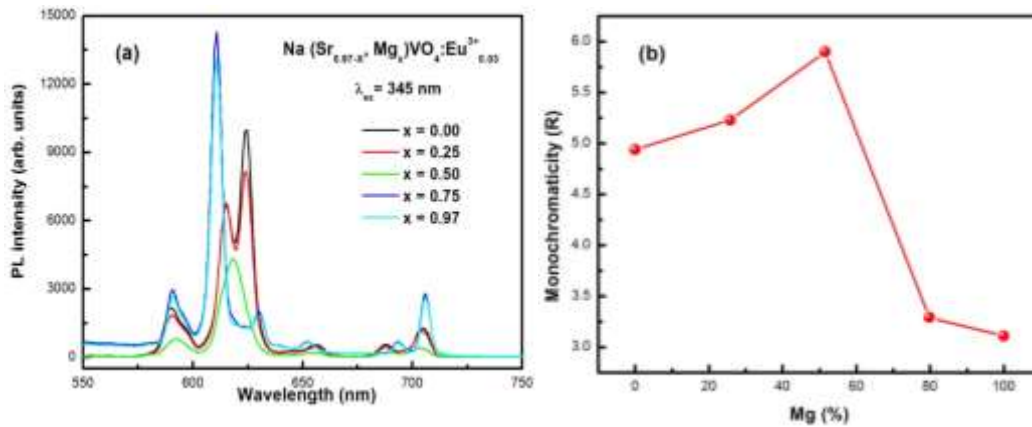


Fig. 6: (a) Emission ($\lambda_{ex} = 345$ nm) spectra of $\text{Na}(\text{Sr}_{0.97-x}\text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ phosphors as a function of magnesium concentrations and (b) Intensity ratio of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition (called monocromaticity, R), versus Mg concentration (in % value) graph.

The decay curve of $\text{Na}(\text{Sr}_{0.97-x}\text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ phosphors by monitoring the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ emission transition of Eu^{3+} ions at 611 nm are shown in Fig. 7. All the decay curves are well fitted by the single exponential equation [4]. The estimated lifetime values from the fits are summarized in Fig. 7.

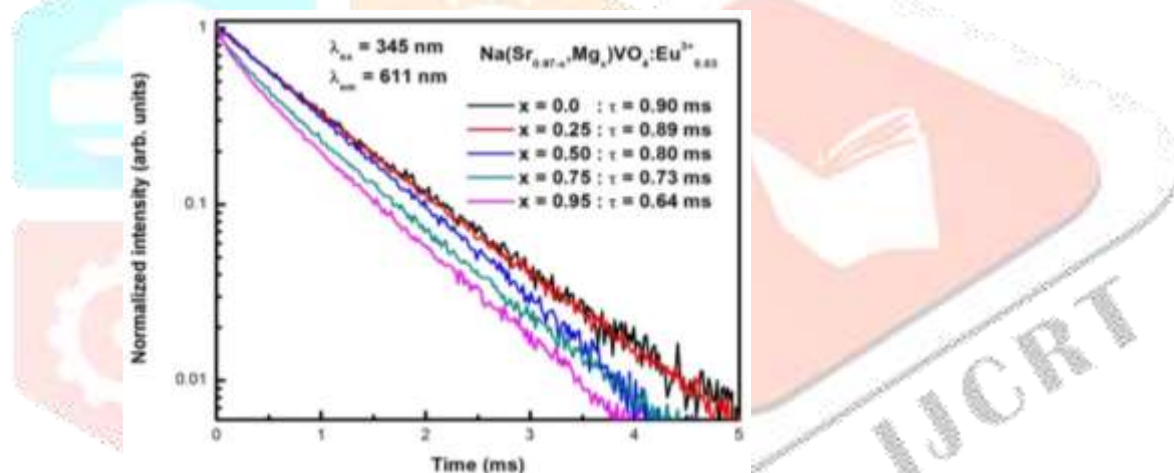


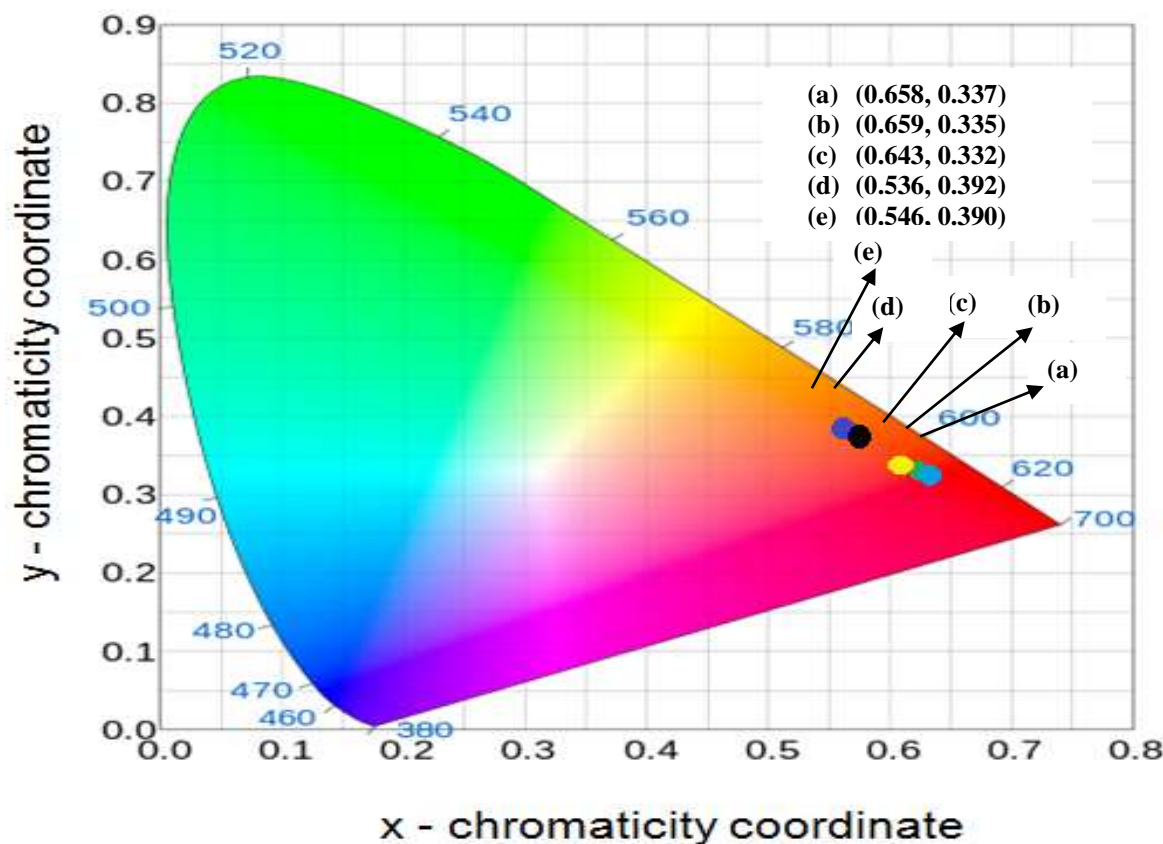
Fig. 7: Photoluminescence decay curves of $\text{Na}(\text{Sr}_{0.97-x}\text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ ($x = 0.0, 0.25, 0.50, 0.75$ and $x = 0.97$) phosphors ($\lambda_{ex} = 345$ nm and $\lambda_{em} = 611$ nm).

It indicates that the reduction of decay times may be attributed to the increase of non-radiative decay rate with the increase of Mg content in $x\%$ value. This result shows that the lifetime is short enough for potential applications in displays and lights.

In 1931, the Commission International de l'Eclairage (CIE) established a universal quantitative model of color spaces. The chromaticity coordinates of $\text{Na}(\text{Sr}_{0.97-x}\text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ phosphors are calculated (using CIE calculated software) from their corresponding emission spectra excited by 345 nm and have shown in Fig. 8. The obtained CIE color coordinates of all the samples are lies in the red region. The changes in **Fig. 8:** CIE chromaticity diagram of $\text{Na}(\text{Sr}_{0.97-x}\text{Mg}_x)\text{VO}_4:\text{Eu}^{3+}_{0.03}$ phosphors under UV (345 nm) excitation, (a) $x = 0.0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 0.97$.

the colorcoordinates may be due to the variation of the asymmetric ratios of various Mg ion concentrations of

$\text{Na}(\text{Sr}_{0.97-x}\text{Mg}_x)\text{VO}_4:\text{Eu}^{3+0.03}$ phosphors. Thus, the present results suggest that the Eu^{3+} -doped $\text{Na}(\text{Sr}_{0.97-x}\text{Mg}_x)\text{VO}_4:\text{Eu}^{3+0.03}$ ($x=0$ to 0.97) phosphors could be a potential candidate as red emitting phosphor in display/white light emitting diode applications.



4. CONCLUSIONS

In conclusion, the Eu^{3+} ion-doped $\text{Na}(\text{Sr}_{0.97-x}\text{Mg}_x)\text{VO}_4:\text{Eu}^{3+0.03}$ ($x=0$ to 0.97) phosphors have been fabricated successfully and analyzed by XRD, FT-IR, FE-SEM with EDS and luminescence properties. Structural analysis depicts that phosphor crystallizes into pure $\text{NaSr}_{0.97}\text{VO}_4:\text{Eu}^{3+0.03}$ and $\text{NaMg}_{0.97}\text{VO}_4:\text{Eu}^{3+0.03}$ phases for $x=0$ and $x=0.97$ respectively. These phosphors show broad absorption bands in the NUV region and the band edges of them locate at around 390 nm, where the NUV-based LED emission occurs. The optimum emission is achieved for mixed $\text{Na}(\text{Sr}_{0.22}\text{Mg}_{0.75})\text{VO}_4:\text{Eu}^{3+0.03}$ phase phosphor. The excellent optical features, such as broad excitation band (monitored for $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+}) lying in the range of 220-400 nm and excellent emission in red region (at 611 nm). The present results indicate that the novel red emitting phosphor is a suitable candidate for the application on white LEDs combine with a near UV chips.

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