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Sol-gel synthesis and photoluminescence analysis of $\text{Sm}^{3+}:\text{NaGd}(\text{WO}_4)_2$ phosphors

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ABSTRACT

$\text{Sm}^{3+}:\text{NaGd}(\text{WO}_4)_2$ sub-micron phosphors were synthesized by a sol-gel method. The tetragonal crystalline structure was observed from X-ray diffraction analysis and the crystallite size was calculated by Williamson-Hall approximation. Raman results elucidate the presence of phonon vibrations corresponding to tungstate tetrahedra and free metallic ions. The morphology and average grain size were obtained using scanning electron microscopy. Luminescence spectra reveal the emission peaks at 563 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$), 600 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$), 645 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$) and 700 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}$) under the excitation wavelength of 406 nm. The maximum emission intensity was observed for 3 mol% of Sm^{3+} ions concentration in $\text{NaGd}(\text{WO}_4)_2$ phosphors. The temperature dependent luminescence and luminescence decay were measured. The CIE color co-ordinates of 3 mol% $\text{Sm}^{3+}:\text{NaGd}(\text{WO}_4)_2$ phosphors were calculated as (0.558, 0.416).

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1. Introduction

In recent years, trivalent rare-earth ions-activated oxides-based phosphors occupy an important role in solid state lasers, white light emitting diodes (WLEDs) in the flat panel displays and field-emission display (FED) [1–3]. In particular, near-ultraviolet phosphors-converted WLEDs have attracted great attention because of their low power consumption, chemical stability, high brightness, long lifetime and environment-friendly characteristics in solid-state lighting devices [4,5]. To attain high-quality devices, it is necessary to develop phosphors with high crystalline nature, uniform size and shape, closely packed with good chemical stability, high luminescence efficiency and near monochromatic emission. At present, commercial phosphor materials are synthesized using solid state reaction but it has drawbacks like requirement of high purity oxides, high temperature and long time for synthesis, non-uniformity of particle size and morphology. Several wet chemical methods like sol-gel [6,7], hydrothermal synthesis [8], spray-pyrolysis [9,10], and co-precipitation synthesis [10] can be used for synthesis of these phosphor material. These methods yield uniform size and morphology with the use of low cost nitrates or other water soluble chemicals as precursors at low

temperature. Among these methods, the sol-gel method is one of the most convenient to synthesize a multicomponent metal oxide system because of its better composition flexibility, shaping versatility and higher homogeneity. One of the strongest advantages of this method is that the individual metal ions are mixed with one another in the atomic level [11–13].

Alkaline rare-earth double tungstates $\text{A}^+\text{B}^{3+}(\text{WO}_4)_2$ ($\text{A}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$ and Cs^+ ; $\text{B}^{3+} = \text{Y}^{3+}, \text{Bi}^{3+}$ and Ln^{3+}) have monoclinic or tetragonal structures. These compounds with a tetragonal structure, related to scheelite CaWO_4 like materials, have great interest for solid state lasers and LEDs [14–16]. In this structure there is no individual site for alkaline and the rare-earth ions, so both ions share the same sites and that lead to structural disorder. Also the tetragonal structure of W^{6+} ions is tetrahedrally coordinated by four oxygen ions and the A^+ and B^{3+} cations are coordinated in between tetrahedrals at two different distances and form a S_4 symmetry. In tungstate-based phosphors, like $\text{NaGd}(\text{WO}_4)_2$ (NGW) host lattice is more stable and environmentally friendly compared to other host materials like fluorides, sulfides and silicates [17]. In recent years an increasing number of reports are available in rare earth doped NGW phosphors prepared by the sol-gel method [18–20]. For practical applications, the light emitting at longer wavelength (red or orange) are the most suitable sources for solid state lighting and display devices. Among the rare-earth ions, Sm^{3+} ions doped inorganic oxides produce reddish orange emission due to its $^4\text{G}_{5/2} \rightarrow ^6\text{H}_J$ ($J=5/2, 7/2, 9/2$, and

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11/2) transitions [21–23]. Hence, in this work, Sm^{3+} : NGW phosphors are synthesized by the sol–gel method. The structural and luminescent properties of Sm^{3+} : NGW phosphors are analyzed and the results are discussed.

2. Synthesis procedure

The sub-micron sized Sm^{3+} : NGW phosphors are prepared by the sol–gel method. Stoichiometric amounts of ammonium paratungstate ($(\text{NH}_4)_{10}(\text{H}_2\text{W}_{12}\text{O}_{42}) \cdot 4\text{H}_2\text{O}$), sodium nitrate tetrahydrate ($\text{Na}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and gadolinium oxide (Gd_2O_3) were used to prepare the NGW host materials and the samarium oxide (Sm_2O_3) was used as an activator. Dilute nitric acid is used to convert the Gd_2O_3 and Sm_2O_3 to its nitrates. After that, all reactants are dissolved individually in appropriate amount of de-ionized water for complete dissolution. The chelating agent (citric acid) is added in each of the solution individually to form the appropriate metal citrate complex. Then, the metal citrate complexes were mixed together thoroughly using a magnetic stirrer. The synthesis was maintained at 80°C for 1 h. The pH of the solution was adjusted to 6.5 with ammonia solution and ethylene glycol was added as a binder. The solution was stirred continually at 80°C until the formation of the gel. After that, the gel was dried at 120°C for 24 h, the xerogel was formed. The xerogel was treated at 250°C for 30 min to get black flakes. Finally, the black flakes were calcined at 800°C for 2 h in a resistive furnace at air atmosphere [7].

The structural, vibrational properties and morphology of Sm^{3+} :NGW phosphors were analysed using an X-ray diffractometer (XRD, Mac Science, M18XHF-SRA) equipped with monochromated $\text{CuK}\alpha$ irradiation ($\lambda = 1.54056 \text{ \AA}$), a Raman spectrometer (Jobin Yvon HR800 system $\lambda = 630 \text{ nm}$) and scanning electron microscopy (SEM, Hitachi SU-70) respectively. The reflectance spectra were measured using an UV/VIS Spectrophotometer (Shimadzu UV-2101PC). The excitation and emission spectra were recorded at room temperature in a spectrofluorimeter (Jasco-6233) with a 150 mW xenon lamp watt Xe lamp with shielded house and silicon photomultiplier (minimum spectral resolution 2.5 nm).

3. Results and discussion

The powder XRD patterns of the different concentration Sm^{3+} : NGW phosphors are shown in Fig. 1. The observed XRD peaks match well with the tetragonal phase of NGW (JCPDS NO. 25-829) with space group $I4_1/a$ and its lattice parameter values are $a = b = 5.243 \text{ \AA}$, $c = 11.384 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. There are no additional peaks observed due to the incorporation of Sm^{3+} ions in NGW matrix. This is because of the fact that the dopant Sm^{3+} (0.958 \AA) ions easily replace the Gd^{3+} (0.938 \AA) sites in the NGW matrix because of the almost equal ionic radii and same coordination number (6) of both ions. However, the predominant peak (112) of the tetragonal structure is shifted towards the lower angle side due to the larger size of Sm^{3+} ions. The lattice constant values of Sm^{3+} : NGW powders were calculated by using well known the Maud software and presented in Table 1. These lattice parameter values are in good agreement with the standard value of NGW crystals. The substitution of Gd^{3+} (0.938 \AA) ions by the larger ionic radii of Sm^{3+} (0.958 \AA) ions leads to an increase in the value of the lattice parameters monotonically with increase of Sm^{3+} concentration.

The crystallite sizes of synthesized phosphors were calculated from XRD data using Debye–Scherrer approximation. But the crystallite size calculated by this method was smaller than the

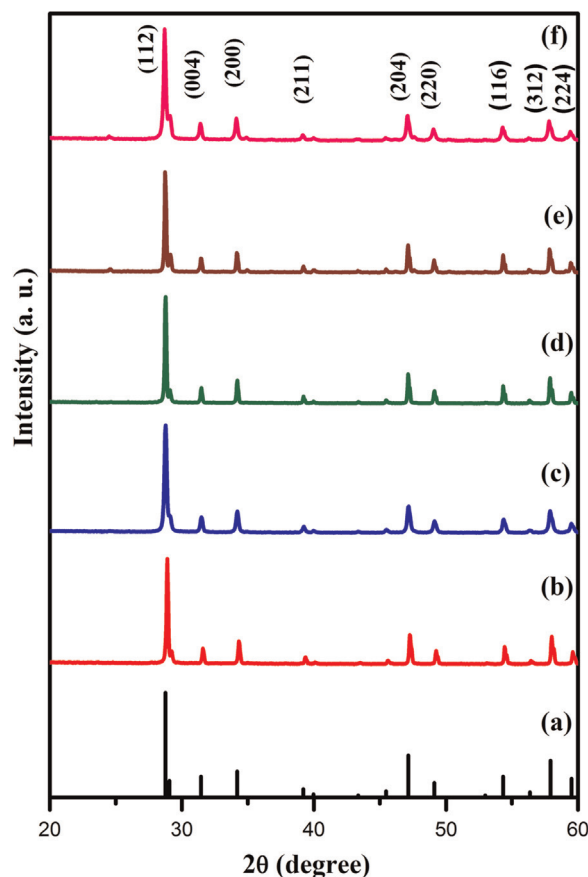


Fig. 1. XRD patterns for the phosphor Sm^{3+} : NGW, (a) JCPDS NO. 25-829, (b) 1 mol%, (c) 2 mol%, (d) 3 mol%, (e) 4 mol% and (f) 5 mol%.

Table 1

Calculated lattice parameters, CIE coordinates and decay time of Sm^{3+} : NGW phosphors.

Composition	Lattice parameters		CIE coordinates (x, y)	Decay time (ms)
	a (Å) (± 0.002)	b (Å) (± 0.003)		
1 mol% Sm^{3+} : NGW	5.243	11.368	(0.545, 0.406)	0.97
2 mol% Sm^{3+} : NGW	5.249	11.371	(0.522, 0.412)	0.84
3 mol% Sm^{3+} : NGW	5.252	11.373	(0.558, 0.416)	0.75
4 mol% Sm^{3+} : NGW	5.260	11.381	(0.554, 0.414)	0.61
5 mol% Sm^{3+} : NGW	5.288	11.456	(0.554, 0.423)	0.39

actual size, this may be due to the reason that this method did not include the shape induced strain contribution. In this scenario several authors followed the Williamson–Hall method as a refinement of the Debye–Scherrer approximation including the components of shape induced strain during estimation of size [24]. In this approach, the X-ray line broadening is considered as a sum of contribution from small crystallites and the broadening caused by lattice strain present in the material (*i.e.*)

$$\beta_{FWHM} = \beta_{size} + \beta_{strain} \quad (1)$$

Here, $\beta_{size} = \lambda/D \cos \theta$ (Scherrer's approximation) where λ is the wavelength of X-ray used, D is the crystallite size and θ is the corresponding angle. $\beta_{strain} = 4\epsilon \tan \theta$, where ϵ is the strain

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