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Effect of annealing and excitation wavelength on the downconversion photoluminescence of Sm^{3+} doped Y_2O_3 nano-crystalline phosphor

R.S. Yadav, S.B. Rai*

Laser & Spectroscopy Laboratory, Department of Physics, Institute of Science, Banaras Hindu University, Varanasi 221 005, India

HIGHLIGHTS

- The Sm^{3+} doped Y_2O_3 phosphor was synthesized through solution combustion method.
- The structural analysis shows an increase in the particles size of the phosphor.
- The phosphor emits reddish orange color at 606 nm on excitation with 238, 363, 407, 424 and 464 nm wavelengths.
- The emission intensity of the annealed phosphor is enhanced upto three times.
- The lifetime of the $^4G_{5/2}$ level is increased in the annealed phosphor.

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ABSTRACT

This paper reports the downconversion photoluminescence in Sm^{3+} doped Y_2O_3 nano-crystalline phosphor synthesized through solution combustion method. The structural characterization of the phosphor has been carried out using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques, which reveals its nano-crystalline nature. The particles size of the phosphor increases on annealing it, which has been confirmed by SEM measurement. The energy dispersive spectroscopic (EDS) measurement verifies the presence of Y, Sm and O elements in the phosphor. The Fourier transform infrared (FTIR) measurements show the presence of vibrational bands due to different groups in the phosphor. The photoluminescence excitation spectra of the phosphor show large number of excitation bands due to CTS and 4f-4f electronic transitions of Sm^{3+} ion. The Sm^{3+} doped Y_2O_3 phosphor emits an intense reddish orange color centered at 606 nm due to $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition upon excitation with different wavelengths such as 238, 363, 407, 424 and 464 nm. The photoluminescence intensity is observed larger for 407 nm excitation. Interestingly, the peaks observed in the emission match well with those present in the excitation upon 238 and 363 nm excitations in lower wavelength side. The photoluminescence intensity of the phosphor sample is enhanced upto three times after annealing the as-synthesized phosphor. The improvement in the photoluminescence intensity is due to an increase in crystallinity, particles size and reduction in optical quenching centers. The lifetime of the $^4G_{5/2}$ level is found to be increased in the annealed phosphor. Thus, the Sm^{3+} doped Y_2O_3 nano-crystalline phosphor may be a suitable candidate for displays and photonic devices.

1. Introduction

The spectroscopic studies of the lanthanide doped inorganic phosphors have been fascinated the interest of researchers for their high luminous efficacy. They are chemically and thermally stable for long lifespan and therefore have potential applications in different fields, such as displays devices, plasma panel devices (PPDs), flat panel devices (FPDs), optical devices and solid state devices. [1–7]. The lanthanide doped phosphors show various interesting optical phenomenon, such as energy transfer, concentration dependency, radiative and non-radiative transitions. [8]. The triply ionized lanthanide ions contain large numbers of energy levels; many of them are metastable, which supports intense radiative transitions. The lanthanide ion in a host matrix serves as an activator ion, which has ability to produce a variety of colors. It gives visible (blue, green, yellow and red) and NIR emissions depending on the lanthanide ions and the host materials [9–15]. It also emits complementary color [16]. The intense photoluminescence in the lanthanide ions occurs due to downconversion

* Corresponding author.
E-mail address: sbrai49@yahoo.co.in (S.B. Rai).

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process in which a high energy ultraviolet (UV) photon is converted into low energy visible photons [11–14]. The appropriate combinations of lanthanide ions also produce tunable colors leading to white light. The tunability strongly depends on the lanthanide ions and their concentrations used in the host matrices [17,18].

The samarium (Sm^{3+}) doped phosphors have been extensively studied in different host materials by different groups [19–24]. They have reported a reddish orange photoluminescence due to $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition. Shivaram et al. have studied the optical properties of the Sm^{3+} doped $CaTiO_3$ phosphor on excitation with 407 nm radiation. They have reported that the emission intensity of the Sm^{3+} ion increases with the increase in temperature and the emission intensity is optimum at 1000 °C [19]. The emission intensity of the Sm^{3+} doped $BaNb_2O_6$ phosphor has been monitored upon 405, 418, 463 and 479 nm excitation wavelengths [20]. It has been reported that the emission intensity is optimum for 405 nm excitation. Lu et al. have also reported an intense orange red emission at 609 nm in the Sm^{3+} doped $Bi_4Si_3O_{12}$ phosphor annealed at 800 °C using the same excitation wavelength [21]. Recently, Li et al. and Hou et al. have carried out the spectroscopic investigations on Sm^{3+} ion in the $NaBaLa_2(PO_4)_3$ and Y_2MoO_6 phosphor materials, respectively [22,23]. These groups have also reported reddish orange emission using 403 and 404 nm excitation wavelengths. The reddish orange emission from Sm^{3+} ion in the Y_2O_3 host has been reported by Kodaira et al. using the same excitation wavelength (406 nm). They have prepared the phosphor samples at 400 °C, 500 °C and 600 °C annealing temperatures and the emission intensity was observed maximum at 600 °C [24]. Herein, we have prepared the Sm^{3+} doped Y_2O_3 nano-crystalline phosphor on annealing at 1200 °C. The significant enhancement in emission intensity has been observed due to the annealing process.

The phosphor contains an activator ion and the inert host material. The host should possess low phonon frequency to get larger photoluminescence. We have used Y_2O_3 as a host material as it contains low phonon frequency (~430–550 cm^{-1}) and it is a chemically, structurally and thermally stable host with optical band gap as 5.7 eV [10,12,15]. The Sm^{3+} ion has been used as an activator as it gives intense emissions from the meta-stable $^4G_{5/2}$ state to different low lying states. The excitation spectra of the Sm^{3+} ion show large number of energy states in the UV region [20]. The presence of emission bands from the ultraviolet (UV) to blue regions in the Sm^{3+} doped Y_2O_3 phosphor has been not reported to our knowledge. The effect of excitation wavelengths on the emission intensity of the Sm^{3+} doped Y_2O_3 phosphor has been also not reported. In the present work, the emission intensity of the phosphor has been monitored on excitation with different wavelengths, such as 238, 363, 407, 424 and 464 nm. It is worth noting that the emission spectra contain various emission bands on excitation with 238 and 363 nm wavelengths, which are clearly present in the excitation spectra of the Sm^{3+} ion.

In this paper, we have synthesized the Sm^{3+} doped Y_2O_3 nano-crystalline phosphor through solution combustion method. The structural measurements of the phosphor samples have been carried out using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The energy dispersive spectroscopic (EDS) measurement reveals the presence of different elements in the nano-phosphor sample. The Fourier transform infrared (FTIR) measurements have been carried out to know the vibrational frequency present in the phosphor sample. We have monitored the photoluminescence emission of the synthesized phosphor samples with different concentrations of the Sm^{3+} ions on excitation with 238, 363, 407, 424 and 464 nm radiations. The Sm^{3+} doped Y_2O_3 nano-phosphor gives intense reddish orange photoluminescence. The synthesized phosphors have been annealed at 1200 °C to reduce the surface defects and optical quenching centers. The annealing improves the crystallinity and the particles size of the phosphor. The lifetime measurements have been carried out to confirm an increase in the photoluminescence intensity for the doped phosphor samples.

2. Materials and method

2.1. Synthesis of Sm^{3+} doped Y_2O_3 nano-crystalline phosphors

The Sm^{3+} doped Y_2O_3 nano-crystalline phosphor has been synthesized through solution combustion method using urea, as an organic fuel for combustion [7,10,25]. The Sm_4O_7 and Y_2O_3 were used as starting materials with the following compositions:

$$(100 - x)\ Y_2O_3 + x\ Sm_4O_7$$

where x represents the concentration of the lanthanide ion and it was varied from 0.5 to 1.5 mol% concentrations.

The starting materials were weighed in the above stoichiometric proportions. They were dissolved in 5 ml concentrated nitric acid followed by dilution with de-ionized water under constant stirring. The urea solution was added to this solution further under constant stirring. The final solution was stirred at 60 °C continuously until it turned into a transparent gel. It occurs due to evaporation of water molecules. The gel thus formed was placed in a closed furnace maintained at 500 °C. An auto ignition took place within few minutes with evolution of different gases due to the exothermic reactions. The sample was obtained in powder form, which is termed as the as-synthesized phosphor. The sample was finally annealed at 1200 °C for 5 h to get a better structure and reddish orange emission in the phosphor samples.

2.2. Characterization

The XRD patterns of the synthesized samples have been monitored to identify crystallinity and to confirm the pure phase formation using 18 kW rotating anode (Cu) based Regaku XRD powder diffractometer attached with a graphite monochromator in the diffracted beam path in the range of 20–80°. The morphology of the phosphor has been recorded using a scanning electron microscope (SEM) from a JEOL-TM Model JSM 5410 unit. The energy dispersive spectroscopic (EDS) measurement has been carried out to verify the elements present in the synthesized sample. The FTIR spectra of the phosphor samples were monitored using Frontier-I spectrometer (Perkin Elmer). The photoluminescence excitation and photoluminescence spectra of the synthesized phosphors have been recorded using Fluorolog-3 attached with 450 W Xenon lamp equipped with photomultiplier tube. The lifetime of $^5G_{5/2}$ level of Sm^{3+} ion emitting at 606 nm in the doped phosphor sample has been monitored using Fluorolog-3 spectrofluorometer in the phosphorescence mode attached with 25 W pulsed Xenon lamp.

3. Results and discussion

3.1. Structural characterization

3.1.1. XRD measurements

The X-ray diffraction (XRD) patterns of the as-synthesized and the annealed (at 1200 °C) 1.0 mol% Sm^{3+} doped Y_2O_3 nano-crystalline phosphors have been recorded in the range of 20–80° and they are shown in Fig. 1. The XRD patterns thus obtained match well with JCPDS File no. 43-1036 (with lattice parameters a = 10.60 Å and $\alpha = \beta = \gamma = 90°$) in both the cases. The phase of the phosphor is C-type cubic with space group *la*3(206). The XRD peaks were also indexed using JCPDS file. The positions of XRD peaks remain the same as it is in the as-synthesized sample. However, in the case of the annealed sample they are slightly shifted towards lower 2θ angle side. It is also evident from the inset in the figure that the full width at half maxima (FWHM) of the annealed sample is also reduced slightly, which suggests an increase in crystallinity of the phosphor sample. Thus, an ordered crystal structure is formed in the annealed phosphor.

The reduction in FWHM and thereby improvement in crystallinity has been studied in our earlier work on Tb^{3+} doped Y_2O_3 nano-