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LUMINESCENCE STUDY ON TM^{+3} AND TB^{+} DOPED LAVO$_4$:EU NANO-CRYSTAL MATERIALS

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Abstract:

Tm^{+3} and Tb^{+} doped LaVO$_4$:Eu nano-crystal materials were synthesized using chemical co-precipitation method in water medium. The materials were annealed at 600 ° C for 3 hours and then grained into powder form. The materials were characterized by recording XRD and TEM images. The materials showed monoclinic and tetragonal structures and their estimated crystallite sizes were in the range 30-40 nm. And, photoluminescence studies of as prepared materials were carried out at room temperature.

Keywords: Co-precipitation, Nanocrystal materials, Co-doping.

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Introduction:

In the last few decades, the study on material sciences has been actively promoted to enable new technologies for the applications in solar energy, displays, cathode ray tubes, solar cells, LEDs, telecommunications, biotechnology, medical diagnostics etc. [1-4]. These new scientific technologies are basic tools to the development of our global. Lanthanide ions have unique photo-physical properties which have an important role in material sciences with respect to the generation and amplification of light [4]. Usually, luminescent of lanthanide ions are basic components of fluorescent lamps, cathode ray tubes, lasers and other light-generating devices especially white light-emitting diodes (LEDs) because they can emit light in very narrow spectral bands, high chromatic purity, long lifetime, and thus making efficient phosphors [5]. White-LEDs have some excellent features - energy efficient, mercury-free, low cost, long lifetimes etc. Due to these excellent features, white LEDs have been replacing the conventional light sources in a broad range, including visual signals, lighting and illumination and non-visual applications [6]. Generally, white LED can be produced by combination of red, green, and blue LEDs [7]. To achieve ideal white LED having high colour-rendering property, one needs to prepare a new phosphor emitting blue, green and red lights in the visible region. The basic ideas to produce these three colours emitting phosphor are to modify the composition of the host lattice through solid solution with similar crystal structure and to utilize the energy transfer between the co-doped activators (lanthanide ions) [8]. On the basis of the above facts, the author hopes to investigate an alternative phosphor emitting white light by co-doping blue, green and red emitting lanthanide ions to a suitable host lattice.

The commonly used oxide based host lattice having high luminescent potential are Y_2O_3, Gd_2O_3, $GdVO_4$, YVO_4, $LaVO_4$ etc. which can make solid solution with lanthanide ions even at high concentration without change in crystal structure because Y^{3+}, Gd^{3+} and La^{3+} have similar ionic radii with optically active lanthanide ions [9 & 10]. Generally, lanthanide ions doped oxide based materials have been most research potential because of their applications in artificial production of light, plasma display panel, field emission etc. [11-13]. Among those phosphors, lanthanum orthovanadate ($LaVO_4$) doped with rare-earth ions luminescence nanocrystals are the most important functional materials which can act as UV filter [14] A. Anees et al reported that $LaVO_4$:Eu and $LaVO_4$:Tb have been emitted strong red and strong green phosphors respectively[15]. And a group of research workers led by J. Wang reported that YVO_4:Tm has been used as strong blue emitting phosphor[16]. However, the luminescence spectra of lanthanide ions are characterized by sharp peaks, whose spectral positions are independent of the embedding matrix, but whose intensities and fine structure may vary [16]. On the basis of the above facts, the authors intend to synthesize Tm^{3+} and Tb^{3+} doped $LaVO_4$:Eu nano-crystal materials and hope to emit the primary colours of white light having high brightness, high density, high stability, long life time etc. for the generation of an alternative white LED. However, to the best knowledge of the authors, the study on the luminescent property of this phosphor has not been reported so far.

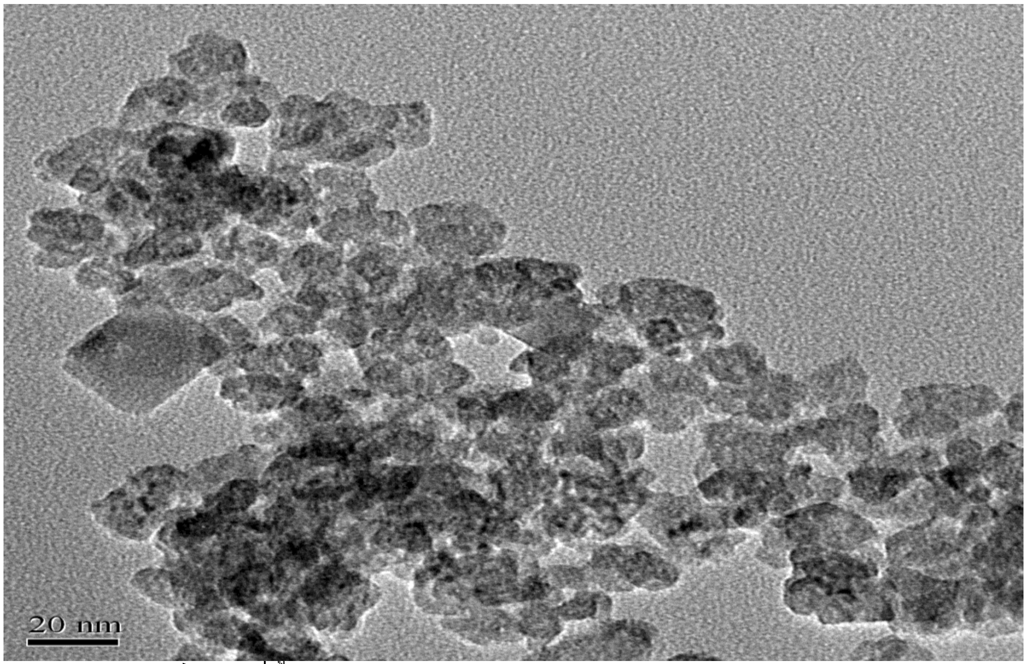
Experimental details:

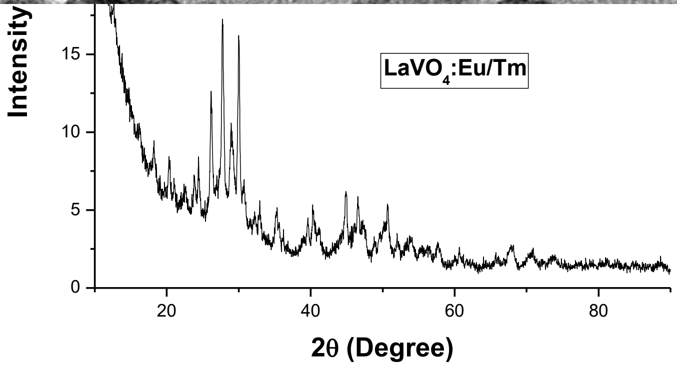
The starting materials were Lanthanum chloride ($LaCl_3.7H_2O$ 99.99% **Sigma**), Ammonium Metavanadate (NH_4VO_3 99.999% Aldrich), Europium Nitrate hydrate ($Eu(NO_3)_3.H_2O$ **Sigma** 99.99%), Thulium Nitrate hydrate ($Tm(NO_3)_3.5H_2O$ **Sigma** 99.99%), Terbium Nitrate hydrate ($Tb(NO_3)_3.5H_2O$ **Sigma** 99.99%) and double distilled water used as solution medium. In a typical synthesis of 5% of Eu^{+3} and 2% of Tm^{+3} co-doped $LaVO_4$ materials, 500 mg $LaCl_3.7H_2O$, 26 mg of $Eu(NO_3)_3.H_2O$ and 13 mg of $Tm(NO_3)_3.5H_2O$ were dissolved in 50 ml of double distilled water and warmed at 40 °C for 5 minutes and then 170 mg of NH_4VO_3 was added to the solution. The solution was maintained pH value at 12 using sodium hydroxide (NaOH) pallet. With the introduction of NaOH, precipitation starts to form. The whole solution was stirred with a speed of 300 rpm at 40 °C for 30 minutes to complete the reaction using magnetic stirrer. The precipitation was collected by centrifugation. The collected precipitation was annealed at 600 °C for 3 hours and made in powder form. Similar procedures were done for synthesis of other samples.

The phase purity and crystal structure of as prepared materials were examined by powder X-ray diffraction (XRD) technique using **Philips Powder Diffractometer** with *CuKa* (1.5405 Å) radiation with Ni filter and Transmission electron microscopy (TEM) images recorded using JEM-2000 FX microscope at 160 KV. All the luminescence spectra were recorded in LS 55 Fluorometer (Perkin Elmer) at room temperature.

Results and Discussion:

Fig. 1 shows XRD patterns of Tm^{+3} doped $LaVO_4$:Eu materials annealed at 600˚C for 3 hours.





The diffraction peaks show the presence of both monoclinic phase according to JCPDS 70-2392 and tetragonal phase according to JCPDS 32-0504. By the application of Scherrer equation: $t = (0.9\lambda)/(\beta \cos \theta)$, where λ is the X-ray wavelength, β is line broadening at half at the maximum intensity in radians and θ is the Bragg angle, the crystallite sizes of as prepared materials were in the range of 30-40 nm. The sizes of as prepared nano crystal materials were approximately confirmed by TEM images as shown in Fig. 2

Fig. 1 XRD patterns of $LaVO_4$:Eu(5%)/ Tm(2%) nano crystal materials

Fig. 2 TEM images of $LaVO_4$:Eu(5%)/ Tm(2%) nano crystal materials

Fig. 3(a) shows excitation spectra of as-prepared $LaVO_4$:Eu(5%)/Tm(2%) nanocrystal materials annealed at 600° C for 3 hours by monitoring the emission at 615 nm recorded at room temperature. The spectra show a charge-transfer band covered the UV region from 230 to 340 nm with a maximum at approximately 275nm. In the broad band ranges from 230-340 nm, there is efficient energy transfer from VO_4^{3-} groups to the rare-earth ions in $LaVO_4$:Eu. Internally, these broad peaks can be attributed mainly due to charge transfer from the oxygen ligands to the central vanadium atom inside VO_4^{3-} ions [17]. In addition, there exists a small peak at 395 nm which is originated from the f-f transitions of Eu^{3+}. Similar excitation spectra of $LaVO_4$:Eu(5%)/Tb(2%) nanocrystal materials annealed at 600°C for 3 hours by monitoring the same emission wavelength 615 nm are observed as shown in Fig 3 (b).

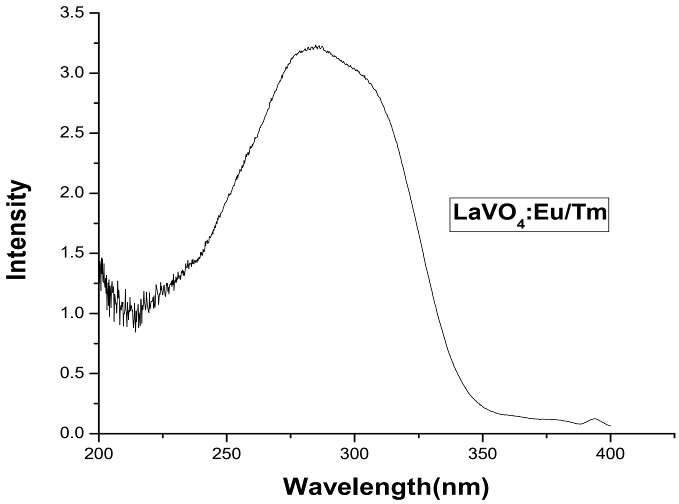


Fig. 3 (a) Excitation spectra of $LaVO_4$:Eu (5%)/Tm(2%) nanocrystal materials

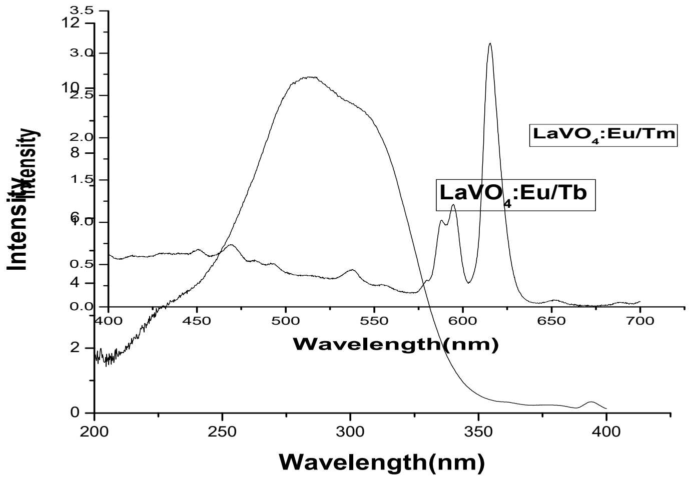


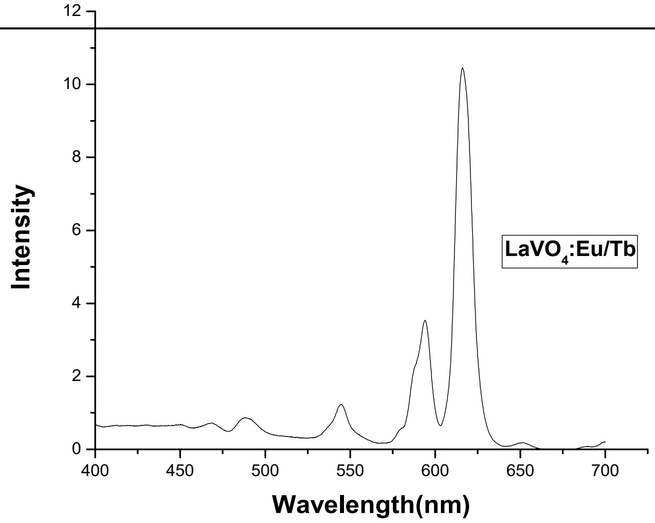
Fig. 3 (b) Excitation spectra of $LaVO_4$:Eu (5%)/Tb(2%) nanocrystal materials

Fig. 4 (a) shows the emission spectra of as-prepared $LaVO_4$:Eu (5%)/Tm(2%) nanocrystal materials annealed at 600˚ C for 3 hours by monitoring the excitation at 275 nm recorded at room temperature. The emission spectra exhibit the main characteristic emission lines of (i) Eu^{3+} in the red region of spectrum at 590 and 615 nm corresponding to $^5D_0 – ^7F_1$ and $^5D_0 – ^7F_2$ transitions respectively [18] (ii) Tm^{3+} in the blue region at 473 nm corresponding to $^1G_4 – ^3H_6$ transition [19] and(iii) a small green emission peak at 539 nm corresponding to $^5D_4 – ^7F_5$ transition [20].

Fig. 4 (a) Emission spectra of $LaVO_4$:Eu (5%)/Tm (2%) nanocrystal materials

The emission spectra of as-prepared $LaVO_4$:Eu (5%)/Tb(2%) nanocrystal materials annealed at 600˚ C for 3 hours by monitoring the excitation at 278 nm recorded at room temperature is shown in 4(b). The spectra exhibit the main characteristic emission lines of (i) Eu^{3+} in the red region of spectrum at 590 and 615 nm corresponding to $^5D_0 – ^7F_1$ and $^5D_0 – ^7F_2$ transitions respectively (ii) Tb^{3+} at 486 and 543 nm corresponding to $^5D_4 – ^7F_6$ and $^5D_4 – ^7F_5$ transitions respectively [20].

Fig. 4 (b) Emission spectra of $LaVO_4$:Eu (5%)/Tb(2%) nanocrystal materials



Conclusions: $LaVO_4$:Eu (5%)/Tm(2%) and $LaVO_4$:Eu (5%)/Tb(2%) nanocrystal materials were synthesized by chemical method in water medium. The crystallite sizes of as prepared materials estimated from XRD data are in the range 30-40 nm which were critically confirmed by TEM images. Photoluminescence study of both as prepared naoncrystal materials was observed to emit strong red small green and small blue. Both the nanocrystal materials were much closed to white light emitting phosphor.

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