



# Energy transfer driven tunable emission of Tb/Eu co-doped lanthanum molybdate nanophosphors

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## ABSTRACT

Tb<sup>3+</sup>/Eu<sup>3+</sup> co-doped lanthanum molybdate nanophosphors were synthesized by conventional co-precipitation method. The Powder X-ray diffractogram revealed the formation of highly crystalline tetragonal nanocrystals with space group *I4<sub>1</sub>/a* and the detailed analysis of the small variation of lattice parameters with Tb/Eu co-doping on the host lattice were carried out based on the ionic radii of the dopants. The FTIR spectra is employed to identify the fundamental vibrational modes in La<sub>2-x-y</sub>(MoO<sub>4</sub>)<sub>3</sub>:xTb, yEu nanocrystals. The formation of nanocrystals by oriented attachment was recognized from the HR TEM images and the d-spacing calculated was in accordance with that corresponding to highest intensity diffraction peak in the XRD patterns. The constituent elements present in the samples were identified with the aid of EDAX and elemental mapping analysis. The broad Mo<sup>6+</sup>-O<sup>2-</sup> CTB and the sharp excitation peaks of Tb and Eu identified from the UV-Vis absorption spectra facilitates the suitability of exciting the phosphors effectively over NUV and visible region of the spectra. The possibility of energy transfer from host to Tb<sup>3+</sup>/Eu<sup>3+</sup> ions and from Tb<sup>3+</sup> to Eu<sup>3+</sup> ions were confirmed from the PL excitation spectra monitoring <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition of Eu<sup>3+</sup> ions around 615 nm. The correlated analysis of PL emission spectra, life time measurements and CIE diagram, upon different excitation channels elucidate the excellent luminescent properties of La<sub>2-x-y</sub>(MoO<sub>4</sub>)<sub>3</sub>:xTb, yEu nanophosphors with tunable emission colours in a wide range varying from yellow green region to reddish orange region and the efficient energy transfer from Tb<sup>3+</sup> to Eu<sup>3+</sup> ions in lanthanum molybdate host lattice. The Tb→Eu energy transfer efficiency and probability were calculated from the decay measurements and the values were found to be satisfactory for exploiting the prepared nanophosphors for the development of multifunctional luminescent nanophosphors.

## 1. Introduction

Development of high yield luminescent nano materials and devices is a frontier area of research for the last decades. Even though, there are many competing candidates qualifying for the multifaceted optical applications, rare earth based materials have gained own platform on account of their excellent luminescent properties inherited from intra 4f transitions [1,2]. The wide range of emission of rare earth elements made them an essential part of RGB tricolour phosphors for the generation of White LEDs [3]. The trivalent rare earth activators like Tb<sup>3+</sup> and Eu<sup>3+</sup> can contribute a crucial part to the development of RGB phosphors owing to their sharp green and red emissions by virtue of <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub> and <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transitions respectively [4]. The in depth study of energy transfer processes among trivalent rare earth ions are significant as it extracts information about the possibility of colour tunable emission by varying rare earth doping concentration. The Tb<sup>3+</sup>→Eu<sup>3+</sup>

energy transfer in various host matrices are well established and the emission properties are governed by structural features of the host lattice in which the rare earth ions are embedded. In Tb<sup>3+</sup>/Eu<sup>3+</sup> co-doped host materials, the Tb<sup>3+</sup>→Eu<sup>3+</sup> energy transfer process is determined by the efficiency of Tb<sup>3+</sup>→Tb<sup>3+</sup> energy migration and that of the Tb<sup>3+</sup>→Eu<sup>3+</sup> energy transfer. The energy migration process in turn depends on the symmetry of sites occupied by Ln<sup>3+</sup> ions, inter ionic distances and the presence of disorder in the matrix [5].

Rare earth oxide host lattices made up of d-block transition metal like molybdenum possess high thermal and chemical stability along with strong optical absorption [6]. Recently, rare earth molybdate host matrix acquired a great deal of attention due to their excellent optical absorption properties in NUV region originating from Mo<sup>6+</sup>-O<sup>2-</sup> charge transfer transitions in MoO<sub>4</sub><sup>2-</sup> tetrahedra [7]. As there is an efficient energy transfer channel from the host material to rare earth ions embedded in the lattice, host excited colour tunable emission

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properties can be achieved by varying rare earth doping concentrations [8].

The main concern of the present work is to develop Tb<sup>3+</sup>/Eu<sup>3+</sup> co-doped lanthanum molybdate nanophosphors with doping concentration dependent tunable emission ranging from green to red region of visible spectra depending on the rare earth doping concentrations. To the best of our knowledge, this is the first reported work on the relevance of Tb<sup>3+</sup>/Eu<sup>3+</sup> co-doping for colour tunable emission in La<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> host matrix. A detailed investigation on the intense green emission of Tb<sup>3+</sup> in La<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> lattice was already reported in our previous work [7]. On the basis of this work, Tb<sup>3+</sup> concentration is fixed as 15% in all Tb<sup>3+</sup>/Eu<sup>3+</sup> co-doped samples examined. The Eu<sup>3+</sup> doping concentration is varied from 0.5% to 25% for analyzing the colour tunable emission properties. The present investigation details the synthesis of Tb<sup>3+</sup>/Eu<sup>3+</sup> co-doped lanthanum molybdate nanophosphors and a systematic analysis of the host, Tb<sup>3+</sup> and Eu<sup>3+</sup> sensitized tunable photoluminescence and decay behaviour.

## 2. Experimental

A series of Tb<sup>3+</sup>/Eu<sup>3+</sup> co-doped Lanthanum molybdate nanophosphors, La<sub>2-x-y</sub>(MoO<sub>4</sub>)<sub>3</sub>:xTb,yEu; (x = 0.3; y = 0.01, 0.02, 0.1, 0.2, 0.3, 0.4, 0.46, 0.5) [Eu 0.5%, Eu 1%, Eu 5%, Eu 10%, Eu 15%, Eu 20%, Eu 23% and Eu 25%] were synthesized by conventional co-precipitation method. Stoichiometric amounts of Lanthanum (III) nitrate hexahydrate [La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Alfa Aesar, 99.9%], Terbium (III) nitrate pentahydrate [Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, Sigma Aldrich, 99.9%], Europium (III) nitrate hexahydrate [Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Alfa Aesar, 99.9%] and Sodium molybdenum oxide dihydrate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, CDH, 99%) were used in the synthesis of nanocrystals. In a typical synthesis procedure, proposed amounts of Lanthanum (III) nitrate hexahydrate, Terbium (III) nitrate pentahydrate and Europium (III) nitrate hexahydrate were dissolved in deionized water. The rare earth solution was gently added to aqueous solution of sodium molybdenum oxide dihydrate under vigorous stirring for 15 min. The white coloured precipitate thus formed was thoroughly washed with deionized water, acetone and then dried at 80 °C for 10 h. The samples were further annealed at 650 °C for 5 h at a heating rate of 50 °C/hour in a muffle furnace to get fine white powders. The obtained white powders were grinded for 30 min in a clean agate mortar and used for further studies. The optimization of annealing temperature, heating rate and annealing time of the nanocrystals were carried out through a set of repeated experiments as all these parameters can decide the phase purity of the prepared samples.

## 3. Characterization

The X-ray powder diffraction analysis was accomplished with X'Pert PRO PANalytical X-ray powder diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) with step size 0.02° and scan step time 0.8 s. The Fourier Transform Infra Red spectra of the nanocrystals in the range 350–4000 cm<sup>-1</sup> were recorded using Shimadzu IR Prestige 20 spectrometer. In order to probe the morphological identities of the samples, Transmission Electron Microscopic analysis was carried out using a JEOL JEM 2100 transmission electron microscope. The elemental mapping and EDS spectra of the sample were recorded using JSM-6490LA scanning electron microscope. The Agilent Cary 5000 UV-Vis-NIR spectrophotometer with Barium sulphate as reference was used to collect the UV-Vis absorption spectra of the samples in the wavelength range 200–700 nm. The room temperature photoluminescence excitation and emission spectra of the samples were carried out using Horiba Jobin- Yvon Fluoromax-4 Spectrofluorometer in the wavelength range 200–750 nm. An Edinburgh UV-VIS-NIR (FLS-980) spectrometer with a spectral resolution of 0.05 nm was used to record the decay profiles. A microsecond flash lamp is used as the excitation source for the sample with excitations in the range 200–1000 nm operating in Multi Channel Scaling (MCS) mode. The

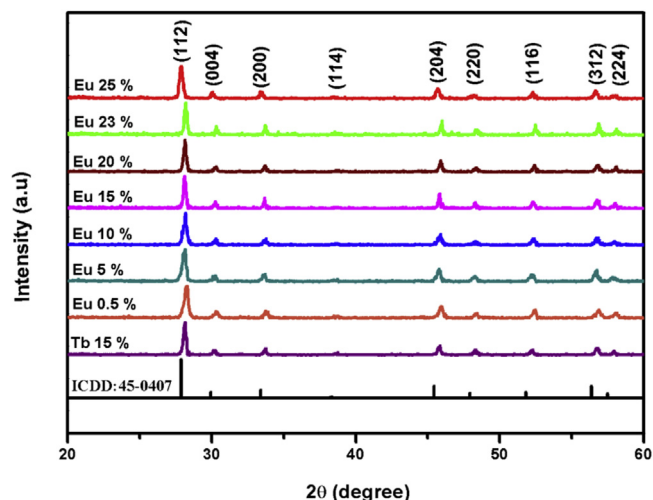


Fig. 1. X-ray diffraction patterns of La<sub>2-x-y</sub>(MoO<sub>4</sub>)<sub>3</sub>:xTb, yEu nanocrystals.

emission intensity of the sample was collected using a photomultiplier detector and monitored as a function of time.

## 4. Results and discussions

### 4.1. X-ray powder diffraction analysis

The X-ray powder diffraction analysis was employed to confirm the crystal structure of the prepared La<sub>2-x-y</sub>(MoO<sub>4</sub>)<sub>3</sub>:xTb, yEu samples. The typical X-ray diffractograms recorded in the 2 $\theta$  range 20–60° are shown in Fig. 1. The sharp and strong diffraction peaks in the pattern ascertain the highly crystalline nature of the samples. The diffractograms were consistent with ICDD 45–0407 of tetragonal La<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> with space group I4<sub>1</sub>/a, indicating that the crystal structure is not altered significantly on doping [7,9]. The calculated lattice parameters of the synthesized La<sub>2-x-y</sub>(MoO<sub>4</sub>)<sub>3</sub>:xTb, yEu samples along with that of pure La<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> were given in Table 1. A slight shift in the peak positions and lattice parameters were observed due to doping of rare earth ions in La<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> lattice. It is worth mentioning that there was a higher angle shift for Tb 15% sample when compared with ICDD of pure lanthanum molybdate and as the Eu<sup>3+</sup> concentration increases in Tb/Eu codoped samples, the diffraction peaks retrace to lower angle side towards the ICDD of pure tetragonal lanthanum molybdate.

It is expected that Tb<sup>3+</sup> or Eu<sup>3+</sup> ions occupy the La<sup>3+</sup> sites in La<sub>2-x-y</sub>(MoO<sub>4</sub>)<sub>3</sub>:xTb, yEu samples owing to their comparable ionic radii and identical valency. When Tb<sup>3+</sup> ions of ionic radii 0.98 Å replaces La<sup>3+</sup> ions of higher ionic radii (1.16 Å), there will be a shrinkage of lattice and a small reduction in lattice parameters. As a result the diffraction peaks shift to higher angle in accordance with Bragg's Law [10]. In the present work, the Tb<sup>3+</sup> doping concentration is fixed and subsequently

Table 1  
Lattice parameters of La<sub>2-x-y</sub>(MoO<sub>4</sub>)<sub>3</sub>:xTb, yEu nanocrystals.

Sample code	Lattice parameters		
	a (Å)	c(Å)	Volume (Å) <sup>3</sup>
ICDD 45-0407	5.368	11.945	344.20
Tb 15%	5.325	11.836	335.693
Eu 0.5%	5.326	11.833	335.737
Eu 5%	5.324	11.847	335.871
Eu 10%	5.327	11.838	335.962
Eu 15%	5.329	11.828	336.010
Eu 20%	5.324	11.812	334.873
Eu 23%	5.344	11.871	339.088
Eu 25%	5.343	11.878	339.206

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