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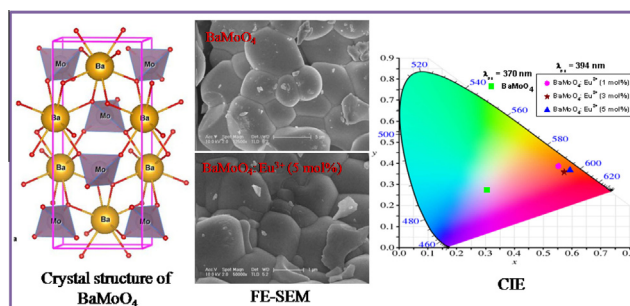
## Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: [www.elsevier.com/locate/saa](http://www.elsevier.com/locate/saa)Synthesis of  $\text{Eu}^{3+}$ -activated  $\text{BaMoO}_4$  phosphors and their Judd–Ofelt analysis: Applications in lasers and white LEDsC. Shivakumara<sup>a,\*</sup>, Rohit Saraf<sup>a</sup>, Sukanti Behera<sup>a</sup>, N. Dhananjaya<sup>b</sup>, H. Nagabhushana<sup>c</sup><sup>a</sup> Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India<sup>b</sup> Department of Physics, B.M.S. Institute of Technology, Bangalore 560 064, India<sup>c</sup> C.N.R. Rao Center for Advanced Materials, Tumkur University, Tumkur 572 103, India

## HIGHLIGHTS

- $\text{BaMoO}_4$ :  $\text{Eu}^{3+}$  phosphors were synthesized using nitrate–citrate gel combustion method.
- Host  $\text{BaMoO}_4$  phosphor revealed white emission upon excitation at 370 nm.
- $\text{Eu}^{3+}$ -activated  $\text{BaMoO}_4$  exhibited red luminescence which was confirmed by CIE chromaticity diagram.
- Judd–Ofelt parameters and other radiative properties of  $\text{Eu}^{3+}$ -activated  $\text{BaMoO}_4$  have been determined.
- These phosphors can be used in red lasers and optical display devices.

## GRAPHICAL ABSTRACT



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## ABSTRACT

$\text{Eu}^{3+}$ -activated  $\text{BaMoO}_4$  phosphors were synthesized by the nitrate–citrate gel combustion method. The Rietveld refinement analysis confirmed that all the compounds were crystallized in the scheelite-type tetragonal structure with  $I4_1/a$  (No. 88) space group. Photoluminescence (PL) spectra of  $\text{BaMoO}_4$  phosphor reveals broad emission peaks at 465 and 605 nm, whereas the  $\text{Eu}^{3+}$ -activated  $\text{BaMoO}_4$  phosphors show intense 615 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ) emission peak. Judd–Ofelt theory was applied to evaluate the intensity parameters ( $\Omega_2, \Omega_4$ ) of  $\text{Eu}^{3+}$ -activated  $\text{BaMoO}_4$  phosphors. The transition probabilities ( $A_T$ ), radiative lifetime ( $\tau_{rad}$ ), branching ratio ( $\beta$ ), stimulated emission cross-section ( $\sigma_e$ ), gain bandwidth ( $\sigma_e \times \Delta\lambda_{eff}$ ) and optical gain ( $\sigma_e \times \tau_{rad}$ ) were investigated by using the intensity parameters. CIE color coordinates confirmed that the  $\text{BaMoO}_4$  and  $\text{Eu}^{3+}$ -activated  $\text{BaMoO}_4$  phosphors exhibit white and red luminescence, respectively. The obtained results revealed that the present phosphors can be a potential candidate for red lasers and white LEDs applications.

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## Introduction

Rare earth ions have been extensively employed as activators for various phosphors. Lanthanide ions ( $\text{Ln}^{3+}$ ) exhibit sharp emission peaks due to intra 4f–4f transitions which were quite characteristic [1]. Trivalent europium ions ( $\text{Eu}^{3+}$ ) activated phosphors

were considered to obtain a red-emitting phosphor with proper CIE chromaticity coordinates. This was because the lowest excited level ( ${}^5\text{D}_0$ ) of the 4f<sup>6</sup> configuration in  $\text{Eu}^{3+}$  was situated below the 4f<sup>5</sup>5d configuration.  $\text{Eu}^{3+}$  provides a particularly favorable situation for substitution in  $\text{A}^{2+}$  sites with favorable isostructural replacement. Trivalent europium ions exhibited narrow band emissions, long lifetimes and large Stokes shifts (emission of lower energy radiation upon excitation by higher energy radiation). The intensities and splitting of the spectral lines provide useful

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information concerning the local site symmetry, sizes of cations and properties of the chemical bonding [2]. Luminescent europium complexes, in particular, act as light conversion molecular devices by absorbing ultraviolet (UV) light and by emitting light in the red visible spectral region.  $\text{Eu}^{3+}$  ions exhibit intense  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  emission in the red spectral region at 615 nm, when they occupy the lattice sites without centrosymmetry. This was highly favorable for improving the color purity of the phosphor. These phosphors were relatively stable and have strong absorption in the near-UV region; therefore, they were promising candidates as a red component for white LED emission devices [3].

Over the past few years, metal molybdates have received great research interest because of their potential applications in various fields, such as photoluminescence [4], optic fiber [5], humidity sensor [6], catalysts [7], microwave applications [8] and solid-state lasers [9]. Metal molybdates of relatively large bivalent cations (e.g., Ca, Ba, Pb and Sr; ionic radius  $> 0.99 \text{ \AA}$ ) mainly exist in a scheelite-type tetragonal structure, whereas those with small cationic radii (e.g., Zn, Fe, Mn, Co and Ni) generally have a wolframite-type monoclinic structure. Among them, scheelite-type  $\text{BaMoO}_4$  is one of the most important inorganic materials which exhibit self luminescence in almost entire visible spectrum. Also, they serve as excellent host materials for trivalent lanthanide ions, which produce spectral emission lines due to f-f transitions [10].

Several synthetic routes have been employed for the formation of  $\text{BaMoO}_4$ , such as solid state reaction [11], Czochralski technique [12], spontaneous crystallization [13], hydrothermal method [14] and complex polymerization [15]. All these synthesis methods exhibit several problems, such as presence of organic compounds, surfactants, expensive precursors, very high temperature and long processing time. For instance, Wu et al. [11] reported the synthesis of  $\text{BaMoO}_4: \text{Eu}^{3+}$  phosphors by the solid state method at  $1000^\circ\text{C}$  for 3 h. Similarly, in the Czochralski technique ( $1100\text{--}1200^\circ\text{C}$ , 30–40 h) [12] and spontaneous crystallization method ( $950^\circ\text{C}$ , 72 h) [13], high temperatures and long processing time were required for the preparation of barium molybdate. Zhang et al. [14] prepared the  $\text{BaMoO}_4: \text{Eu}^{3+}$  microspheres via a hydrothermal route by using sodium dodecyl benzenesulfonate (SDBS) as surfactant. Nitrate–citrate gel combustion method overcome these problems and offer advantages such as low heating temperature, short reaction time, phase purity of products, less expensive, low energy requirements, better compositional control and relative simplicity of the process.

As per our knowledge, the spectroscopic Judd–Ofelt investigation of  $\text{Eu}^{3+}$ -activated  $\text{BaMoO}_4$  have not been reported so far and need careful examination. In the present work,  $\text{Eu}^{3+}$ -activated  $\text{BaMoO}_4$  phosphors were synthesized by the nitrate–citrate gel combustion technique. The crystallographic structural parameters, surface morphology and functional groups were analyzed by powder X-ray diffraction (XRD), Field emission Scanning electron microscopy (FESEM), and Fourier transform infrared (FTIR) spectroscopy, respectively. Further, we have used the Judd–Ofelt theory to calculate the intensity parameters and various other radiative properties such as transition probability, radiative life time, branching ratio, stimulated emission cross-section, gain bandwidth and optical gain for possible optical applications.

## Experimental

### Synthesis

$\text{BaMoO}_4: \text{Eu}^{3+}$  (0, 1, 3 and 5 mol%) phosphors were prepared by the nitrate–citrate gel combustion method. In the synthesis of  $\text{Eu}^{3+}$  doped  $\text{BaMoO}_4$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ,  $\text{Eu}_2\text{O}_3$  and citric

acid were used as the starting materials. The typical preparation of  $\text{BaMoO}_4: \text{Eu}^{3+}$  (1 mol%) compound was included in the following steps:  $\text{Ba}(\text{NO}_3)_2$  (1.2937 g) and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  (0.8828 g) were dissolved in 50 ml distilled water separately.  $\text{Eu}_2\text{O}_3$  (0.0088 g) was dissolved in 5 ml of 6 N  $\text{HNO}_3$  and added into the barium nitrate solution followed by the addition of ammonium molybdate solution. Citric acid (1.3699 g) was dissolved in 50 ml of distilled water and added to the metal ions containing nitrate solution. The clear solution was heated on a hot plate around  $80^\circ\text{C}$  to remove water and oxides of nitrogen to form a thick viscous gel. The resulting gel was further heated to get dry powder. Finally, the powder was grind in an agate mortar and pestle and calcined in a muffle furnace at  $700^\circ\text{C}$  for 2 h in an ambient atmosphere.

### Characterization

The phase purity of  $\text{BaMoO}_4: \text{Eu}^{3+}$  phosphors was examined by powder X-ray diffraction measurements using PANalytical X'pert Pro diffractometer, Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) with a nickel filter. For Rietveld refinement analysis, data were collected at a scan rate of  $1^\circ/\text{min}$  with a  $0.02^\circ$  step size for  $2\theta$  from  $10^\circ$  to  $80^\circ$ . The structural parameters were refined by Rietveld method using FullProf Suite-2000 programme. The surface morphology of these phosphors were investigated using FESEM (FEI Sirion XL 30) operated at an accelerating voltage of 10 kV. FTIR spectra were recorded using Perkin Elmer Spectrometer, Frontier using KBr as a reference. UV–Visible absorption spectra have been recorded for powders on Perkin Elmer Lambda 750 spectrophotometer. The PL studies have been carried out using a Horiba Fluorolog-3 spectrofluorimeter (450 W Xenon lamp). All the measurements were performed at room temperature.

## Results and discussion

### Powder X-ray diffraction

Fig. S1 shows the powder XRD patterns of  $\text{BaMoO}_4: \text{Eu}^{3+}$  (0, 1, 3 and 5 mol%) phosphors calcined at  $700^\circ\text{C}$  for 2 h. All diffraction peaks could be indexed to the scheelite type tetragonal phase with  $I4_1/a$  (No. 88) space group which were in consistent with the JCPDS Card No. 72–0747. No traces of additional peaks were observed in the XRD patterns, which confirm the formation of single phase compounds. The structural parameters were obtained from the Rietveld refinement method using powder XRD data. The patterns were typically refined for lattice parameters, scale factor, backgrounds, pseudo-Voigt profile function ( $u$ ,  $v$  and  $w$ ), atomic coordinates and isothermal temperature factors ( $B_{\text{iso}}$ ). The refinement result reveals that all the compounds crystallized in the tetragonal scheelite-structure with space group  $I4_1/a$  (No. 88). The observed, calculated and the difference XRD patterns of  $\text{BaMoO}_4: \text{Eu}^{3+}$  phosphors are shown in Fig. 1. There was a good agreement between the observed and calculated patterns. In Table 1, we have summarized refined structural parameters for all compounds. The crystal structure was modeled through VESTA program [16] using the Rietveld refined structural parameters. In scheelite  $\text{BaMoO}_4$  structure (Fig. S2),  $\text{Ba}^{2+}$  atoms were bonded to eight oxygen atoms which results in deltahedral  $[\text{BaO}_8]$  clusters. In case of  $\text{Eu}^{3+}$ -activated  $\text{BaMoO}_4$  compounds,  $\text{Eu}^{3+}$  atoms were also coordinated with eight oxygen atoms. On the other hand, the  $\text{Mo}^{6+}$  atoms were coordinated to four oxygen atoms which form  $[\text{MoO}_4]$  clusters. These  $[\text{MoO}_4]$  clusters were slightly distorted in the lattice and exhibit a particular characteristic related to differences in the O–Mo–O bond angles (Fig. S2).

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