



Tailoring Bi₂MoO₆ by Eu³⁺ incorporation for enhanced photoluminescence emissions

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ABSTRACT

Here, an experimental study is presented on the structural, electronic, and optical properties of Bi_{2-x}MoO₆:xEu³⁺ (x = 0, 0.5, 1.0, 2.0, and 4.0 mol%) materials, synthesized by means of the microwave-assisted solvothermal method using ethylene glycol as a solvent. Different characterization techniques (X-ray diffraction measurements with Rietveld refinements, Raman and ultraviolet–visible diffuse reflectance spectroscopy, field emission scanning electron microscopy, and photoluminescence emissions) have been employed to examine the structural and electronic properties, energy transfer and defect evolution which control the performance of the as-synthesized materials. Present findings provide deep insights into the substitution of Eu³⁺ cations in Bi₂MoO₆, with focus on their influence on process that dictate the superior optical properties.

1. Introduction

The emergence of precise and scalable synthetic methods for producing new photoluminescent (PL) materials provides opportunities to tune photophysical properties beyond their band gaps, and to incorporate them in optical devices. The substitution of rare-earth (RE³⁺) cations, acting as activators, in inorganic compounds, is capable to change the local structures towards the modulation of their electrical and optical properties, and playing a crucial role in light-emitting materials [1–5]. Moreover, these materials have attracted considerable attention for applications in different fields such as optical amplifiers, biomedical diagnostics, and optical bioprobes [6–10]. In particular, the PL spectra are associated with the abundant 4f orbitals electron configuration, displaying mainly 4f–4f, 4f–5d, and charge transfer transitions, which results in narrow emission lines, high photostability, and an intense luminescence from ultraviolet (UV) to near-infrared [11]. Among RE³⁺ cations, europium (Eu³⁺) is the most promising for this purpose and it exhibits intense PL red emission due to ⁵D₀ → ⁷F₂ transition around 615 nm [12–14]. Examples of Eu³⁺ cations substitution in different kinds of

materials like glasses, organic compounds, polymers, inorganic matrix, among others, are extensively reported [15–24].

Bismuth oxides of formula (Bi₂O₂)²⁺(A_{n-1}B_nO_{3n+1})²⁻ (A = Ca, Sr, Ba, Pb, Bi, Na, K, and B = Ti, Nb, Ta, Mo, W, Fe) are interesting materials due to their layered structure composed of perovskite slabs of (A_{n-1}B_nO_{3n+1})²⁻ between (Bi₂O₂)²⁺ layers. One representative example of this family is the bismuth molybdate, Bi₂MoO₆ (BMO), due to its versatile applications, including gas sensing [25], electrical [26–31] and photocatalytic [32–56] properties. A wide variety of synthesis methods have been employed to obtain BMO, such as co-precipitation and spray-drying [55], sol-gel [57], mechanochemical [34], sonochemical [58], solid-state [38,50,59], hydrothermal [25,32,33,45,47,49,51,52,60–66], polymeric precursor [67], and citric acid complex process [68], among others [69].

The structure, PL and photocatalytic properties of a wide range of BMO materials with presence of RE³⁺ cations were studied in depth [59–64,67,68,70–74]. However, these materials were obtained by expensive and long-lasting methods and most of the time presented low PL emissions. In previous studies, our research group has successfully

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obtained Eu^{3+} substitution in different materials such as $\alpha\text{-Ag}_2\text{WO}_4$ [5, 75–77], ZrO_2 [78,79], CaMoO_4 [80], ZnMoO_4 [81], and CaZrO_3 [82]. Additionally, Eu^{3+} cations substituted in BMO material was only obtained by conventional hydrothermal [61,63,64,83,84], sol-gel [85], solid-state [59,72,86–88], and citric acid complex [68] methods so far. Therefore, environmentally friendly synthetic procedure of these materials with outstanding optical efficiency is still challenging.

For the successful manufacturing of such materials, the structure, distribution, and electronic properties of the RE^{3+} cations on the host lattice must be known. To the best of our knowledge, the characterization and studies of optical properties of the as-synthesized $\text{Bi}_{2-x}\text{MoO}_6:x\text{Eu}^{3+}$ (BMOxEu) samples by the microwave-assisted solvothermal (MAS) method are lacking. This study systematically investigated the effect of the addition of different amounts of Eu^{3+} cations into the BMO host lattice on the structural, electronic and optical properties. These samples were obtained by the MAS method using low temperature and short reaction time, and the samples were denoted as BMO, BMO0.5Eu, BMO1Eu, BMO2Eu, and BMO4Eu, corresponding to the pure- Bi_2MoO_6 , 0.5, 1.0, 2.0, and 4.0 mol% Eu^{3+} samples, respectively.

2. Results and discussion

The BMOxEu materials were efficiently synthesized by the MAS method at 160°C for 32 min. X-ray diffraction (XRD) patterns of the BMOxEu crystals, illustrated in Fig. 1A, showed narrow and sharp peaks indicating a high degree of crystallinity in all cases and are in good agreement with an orthorhombic structure with $Pca2_1$ space group according to the inorganic crystal structure database, ICSD 20–1685 [89]. Thus, no impurities were detected and the percentage of Eu^{3+} cations was not sufficient to form secondary phases. Fig. SI-1 (a–e) shows the Rietveld refinement plot of observed versus calculated pattern of the BMOxEu crystals. The difference between XRD profiles for experimentally observed and theoretically calculated was at near zero in the intensity scale, as shown by the line ($Y_{\text{Obs}} - Y_{\text{Calc}}$). Tables SI-1 shows the experimental lattice parameters and details on the quality of the structural refinement. Small deviations of the statistical parameters (R_w and GOF) were observed, attesting the reliability and accuracy of the refinement results.

Fig. 1B shows the unit cell representation of the BMO1Eu structure simulated through the visualization for electronic and structural analysis (VESTA) program [90,91] using the lattice parameters and atomic positions listed in Tables SI-1. The BMO1Eu unit cell observed is

constituted of two types of Bi octahedral clusters, namely $[\text{Bi}(1)\text{O}_6]$ and $[\text{Bi}(2)\text{O}_6]$, and one type of Mo octahedral cluster, namely $[\text{MoO}_6]$. The Bi^{3+} -by- Eu^{3+} substitution is attested by the percentage of the ion radius between the host ion and the doped ion, which usually is less than 30%. Considering Bi^{3+} (CN = 6, IR = 1.03 \AA), Mo^{6+} (CN = 6, IR = 0.59 \AA), and Eu^{3+} (CN = 6, IR = 0.947 \AA) cations [92], the calculated percentages of Bi^{3+} and Mo^{6+} are 8.05% and -60.5% , respectively. As a consequence, the refinement results show that the Eu^{3+} cations may occupy either $[\text{Bi}(1)\text{O}_6]$ or $[\text{Bi}(2)\text{O}_6]$ clusters in the BMO lattice [93]. Also, a percentage of Eu^{3+} cations can also be presented in the interstitial sites of the host lattice, as the lattice parameters do not change systematically. It happens because Eu^{3+} cations are treated as impurities into the host lattice which dramatically decrease the organization of the $(\text{MoO}_4)^{2-}$ and $(\text{Bi}_2\text{O}_2)^{2+}$ layers within the crystal lattice, promoting the formation of structural defects (oxygen vacancies, distortion of bonds, stresses, strains, etc.). These results are similar to those observed for other RE^{3+} substituted BMO materials in which refinement results show a mean of the overall values of substitution, not necessarily indicating the precise location of Eu^{3+} cations [67,71,72].

Fig. 1C presents the obtained Raman spectra for BMOxEu crystals synthesized by the MAS method. The increasing concentration of Eu^{3+} cations in the crystalline network has a marked effect on the intensity of all vibrational modes, indicating that the substitution of Bi^{3+} cations causes changes in the chemical environment capable of promoting octahedral distortions, reducing symmetry and, consequently, decreasing the structural order at a short-range. In particular, the band at 800 cm^{-1} which corresponds to the stretching mode of the Mo–O bond in the octahedral $[\text{MoO}_6]$ cluster, can be considered as a signature

Table 1

FWHM of 800 cm^{-1} Raman band, E_{gap} , and CIE chromatic coordinates of emission spectra of BMOxEu crystals.

$\text{Bi}_{2-x}\text{MoO}_6$: $x\text{Eu}^{3+}$	Raman FWHM	E_{gap} (eV)	Chromatic coordinate			
			$\lambda_{\text{exc}} = 355\text{ nm}$		$\lambda_{\text{exc}} = 290\text{ nm}$	
			x	y	x	y
x = 0	29.01	3.03	0.299	0.263	0.548	0.424
x = 0.5	31.10	3.05	0.230	0.214	0.560	0.415
x = 1	33.28	3.15	0.280	0.297	0.562	0.414
x = 2	34.16	3.14	0.226	0.225	0.549	0.424
x = 4	42.40	3.31	0.281	0.270	0.547	0.426

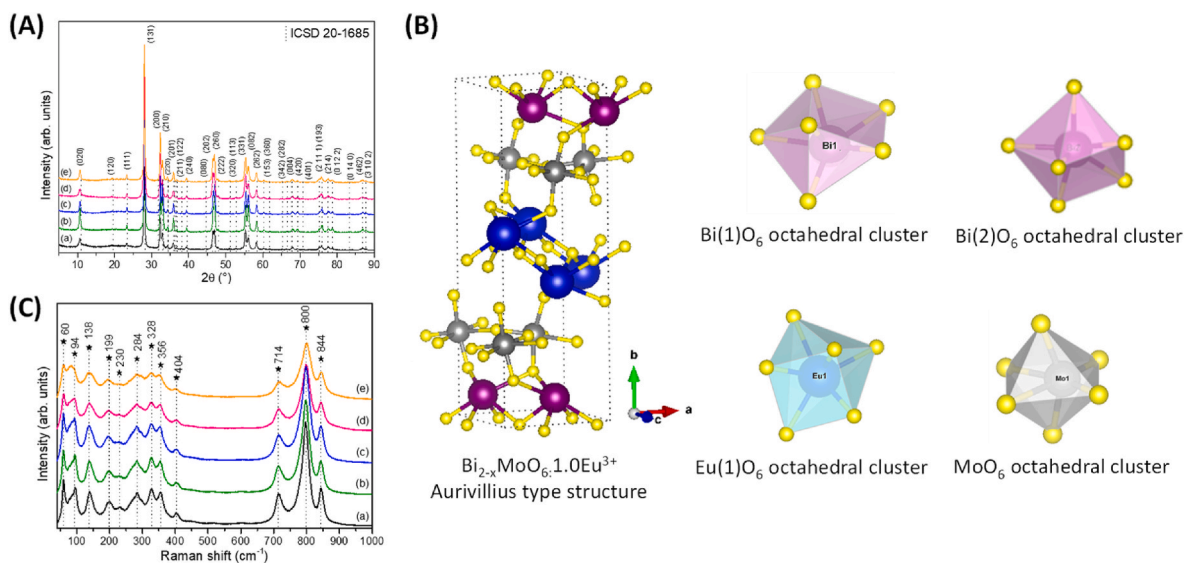


Fig. 1. (A) XRD patterns, (B) Schematic representation of the unit cell of BMO1Eu, and (C) Raman spectra of (a) BMO, (b) BMO0.5Eu, (c) BMO1Eu, (d) BMO2Eu, and (e) BMO4Eu crystals.

of the structural change of the BMO lattice provoked by the inclusion of Eu^{3+} cations. Table 1 presents the values of the full width at half maximum (FWHM) for the mode at 800 cm^{-1} . An analysis of the results renders an increment of the FWHM values as the Eu^{3+} concentration increases, as well as appreciable decrease of the intensity for this band. In addition, we can also sense a general broadening of all vibrational modes as the amount of Eu^{3+} cations increases, and it is also reported in previously studies devoted to the substitution of RE^{3+} cations in the BMO [61,71].

Fig. SI-2(A) shows the UV-vis diffuse reflectance spectra for the BMOxEu crystals, which showed absorption in the visible range of approximately 450 nm for all crystals. Fig. SI-2(B) shows the graphs obtained by the Kubelka & Munk-Aussig method for BMOxEu crystals and the E_{gap} values obtained are listed in Table 1. It was observed a small increase on the E_{gap} values as the Eu^{3+} concentration increases. Besides the limitation of the equipment and the band gap estimation due to the small percentage of Eu^{3+} cations, the increase on the values can also be attributed to the presence of structural defects, and different acceptor species in the valence band (VB) region associated with donator species in the conduction band (CB) region. Specifically, for the BMOxEu crystals, the variation in the band gap values may be due to Eu^{3+} 4f orbitals which are responsible for generating separation between VB and CB as cited in other published works [61,62,67,71,93].

Photoluminescence (PL) measurements were performed by two distinct equipment. Firstly, Fig. 2 shows the PL emission spectra of the BMOxEu crystals under laser excitation at a wavelength of 355 nm . PL emission band of semiconductor materials are mainly originated by the recombination of photo-generated electron-hole pairs [94]. Particularly, the PL emission band at 445 nm is due recombination of these pairs within the $[\text{MoO}_6]$ clusters. Moreover, for BMOxEu crystals, Eu^{3+} cations are responsible for increasing the structural and electronic defects due to $[\text{EuO}_6]$ clusters, contributing to the broadening and different intensity of this band. These results indicate that the PL behavior arises from intrinsic defects of the host lattice, and extrinsic defects due to Eu^{3+} cations [59]. Additionally, for BMOxEu crystals, a narrow and well-defined peak characteristic of the Eu^{3+} cations at 615 nm was observed, related to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition. Finally, plate/flake-like morphologies tend to have the largest specific surface area and the strongest light absorption, which contributed to the results observed [61].

Secondly, PL excitation and PL emission spectra were performed on a Xe lamp source equipment. Fig. 3A shows the PL excitation spectra of BMOxEu crystals monitoring the emission wavelength at 615 nm , which represents the Eu^{3+} cations maximum PL emission ascribed to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition. A broad band in the range of $250\text{--}375\text{ nm}$ is

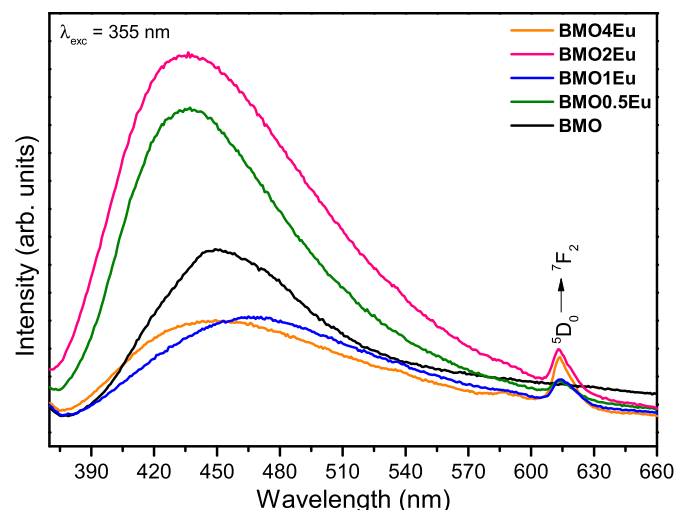


Fig. 2. PL emission spectra of the BMOxEu crystals excited by a 355 nm laser.

observed for all samples which is characteristic of mixed and indistinguishable: i) ligand-to-metal charge transfer (LMCT) state of $\text{O}^{2-} \rightarrow \text{Mo}^{6+}$ of the $[\text{MoO}_6]$ clusters and ii) charge transfer band (CTB) of $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$ [72,93]. A peak located at 394 nm was also observed, which is related to the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition of Eu^{3+} cations [75,76]. Fig. 3B shows the PL emission spectra for BMOxEu crystals when excited at 290 nm , maximum intense of the absorption band observed in the PL excitation spectra. Analyzing Fig. 3B, well-defined peaks can be ascribed to the f-f transitions of the Eu^{3+} cations which are located at 592 nm (${}^3\text{D}_0 \rightarrow {}^7\text{F}_1$), 615 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$), and 695 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$). These results illustrate that Eu^{3+} cations with low $4f \rightarrow 4f$ absorption efficiency in the NUV region can be an activator of the red emitting phosphor and be excited by UV LEDs. Therefore, BMO matrix acts as an efficient host activator for the Eu^{3+} cations due to the energy transfer from the $[\text{MoO}_6]$ to the $[\text{EuO}_6]$ clusters.

Comparing the samples, BMO1Eu present the highest PL intensity, ascribing $1.0\text{ mol}\%$ Eu^{3+} cations as the quenching concentration for this matrix. Moreover, Eu^{3+} cations can be used as a site environmental probe due to the relative ratio of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (magnetic dipole) and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (electric dipole) transitions. It is clearly seen that the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition is more intense than the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ one, indicating that Eu^{3+} cations are located predominantly in a site without inversion of symmetry [63,95]. Fig. 3C shows a schematic energy level diagram and a proposed energy transfer mechanism under 290 nm excitation for the BMOxEu crystals. It is observed that under excitation at 290 nm , electrons are excited from valence band (VB) into the charge transfer state (CTS) of the $[\text{MoO}_6]$ clusters. Then, the excitation energy is transferred from the $[\text{MoO}_6]$ clusters to the ${}^5\text{D}_4$ level of Eu^{3+} cations. Finally, Eu^{3+} cations in the populated ${}^5\text{D}_4$ level undergo multiphonon relaxation to the luminescent ${}^5\text{D}_0$ level that radiatively relax to ${}^7\text{F}_J$ ($J = 1, 2, \text{ and } 4$) levels, resulting in the characteristic PL emissions of Eu^{3+} cations.

Measurement of color that the human eye perceives was evaluated by the *Commission internationale de l'éclairage* (CIE) chromaticity diagram. Fig. 4 shows the CIE diagram for the samples excited at 355 nm (Figs. 4A) and 290 nm (Fig. 4B), and the calculated values for the x and y coordinates are listed in Table 1. When the crystals are excited by 355 nm laser, blue region color is observed due to the predominant intense PL emission within $[\text{MoO}_6]$ clusters, whereas at 290 nm excitation, orange-red color intense PL emission is observed because of higher Eu^{3+} f-f transitions contribution. For BMO1Eu crystal, the values for the x and y coordinates are close to those published for the chromaticity coordinates of the international standards of commercial phosphorus. This result point out that $1.0\text{ mol}\%$ Eu^{3+} is the best concentration for phosphor application in the red emitting region of electromagnetic spectrum [77].

Field emission scanning electron microscopy (FE-SEM) images of BMOxEu crystals are shown in Fig. 5. The images confirm the *flake-like* morphology and smooth surfaces of the crystals, as similarly reported by Y. Zhu et al. and L. Xie et al. [46,53,69,96] BMO0.5, BMO1Eu, and BMO2Eu crystals show little variation in the organization patterns of the platelets, as well as in the width and length of the crystallites. For the BMO4Eu crystal, a decrease in the lateral dimensions of the crystallites is observed, while maintaining homogeneous thickness with values in the $15\text{--}45\text{ nm}$ range. Considering the Ostwald ripening model for crystal growth, it can be affirmed that the excess defect constituted by the addition of a high concentration of Eu^{3+} cations created a larger number of crystallite germination centers, therefore reducing the size of each one [53,61,62].

3. Conclusions

$\text{Bi}_{2-x}\text{MoO}_6:\text{xEu}^{3+}$ ($x = 0, 0.5, 1.0, 2.0, \text{ and } 4.0\text{ mol}\%$) materials were prepared via MAS method using ethylene glycol as a solvent. The orthorhombic structure was confirmed by XRD patterns without the presence of secondary phases, whereas the results for the Raman spectroscopy confirm structural short-range disorder as shown by the

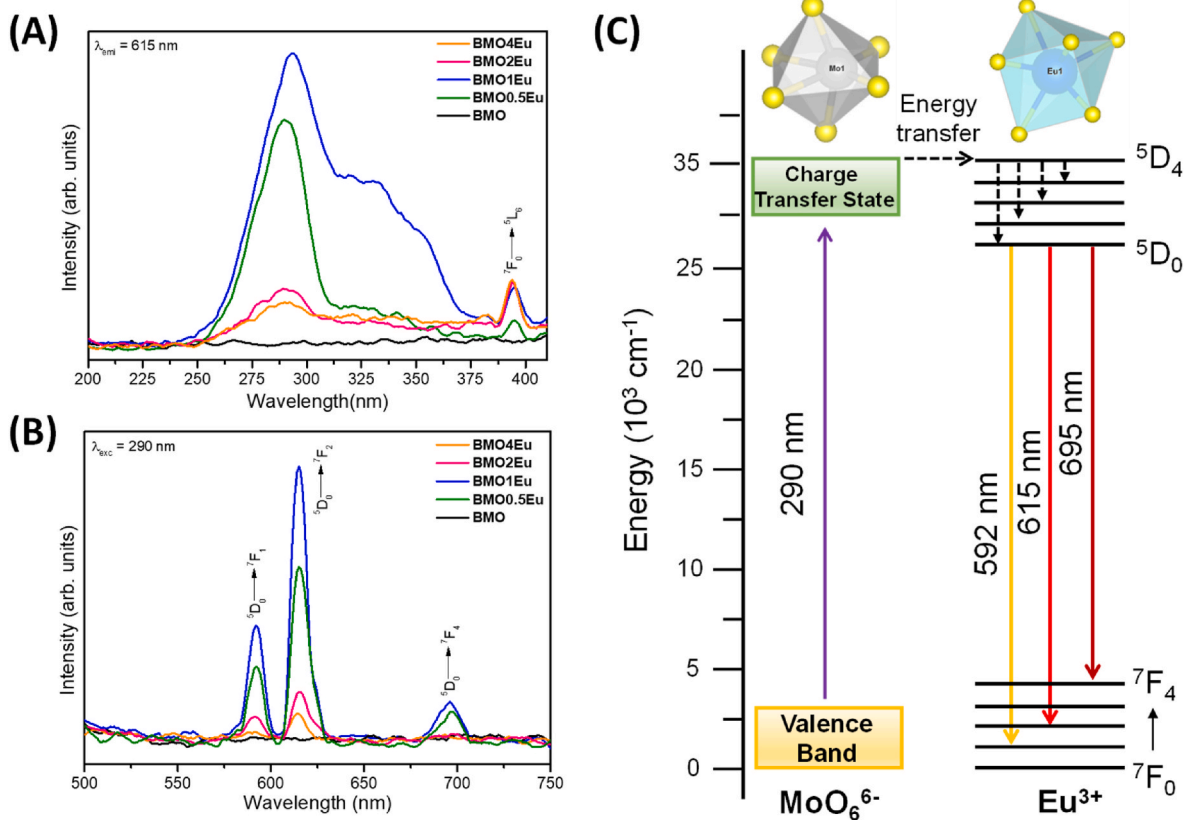


Fig. 3. (A) PL excitation spectra of the BMOxEu crystals monitoring emission at 615 nm, (B) PL emission spectra of the BMOxEu crystals excited at 290 nm, and (C) Schematic energy level diagram and a proposed energy transfer mechanism for the BMOxEu crystals.

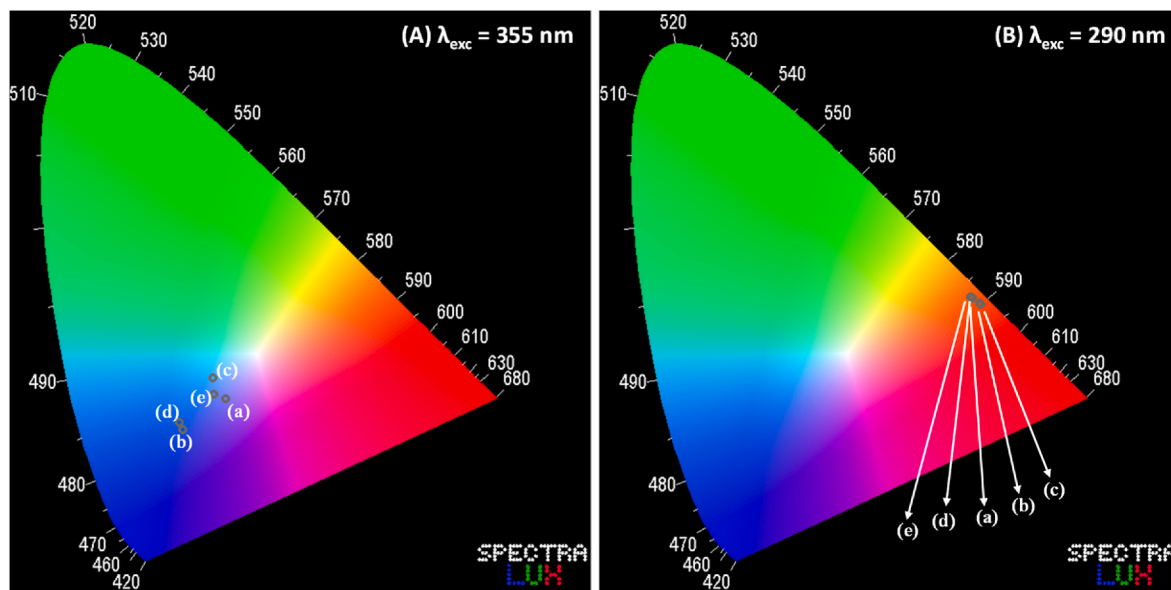


Fig. 4. CIE chromatic diagram of the PL emission spectra of BMOxEu crystals excited at (A) 355 nm, and (B) 290 nm. (a) BMO, (b) BMO0.5Eu, (c) BMO1Eu, (d) BMO2Eu, and (e) BMO4Eu.

enlargement of the vibrational modes. UV-vis spectroscopy results render that the substitution of Eu^{3+} cations favors the increase of the value of the direct band gap. The intensity of the PL emission intensity is enhanced as the Eu^{3+} concentration increases, and the optimal concentration is 1.0 mol% Eu^{3+} cations. In addition, it is quite clear that PL and photocatalysis in a semiconductor are closely related; in future

projects will study the substitution of Eu^{3+} cations in Bi_2MoO_6 as a promising strategy to investigate photocatalytic applications.

Credit author statement

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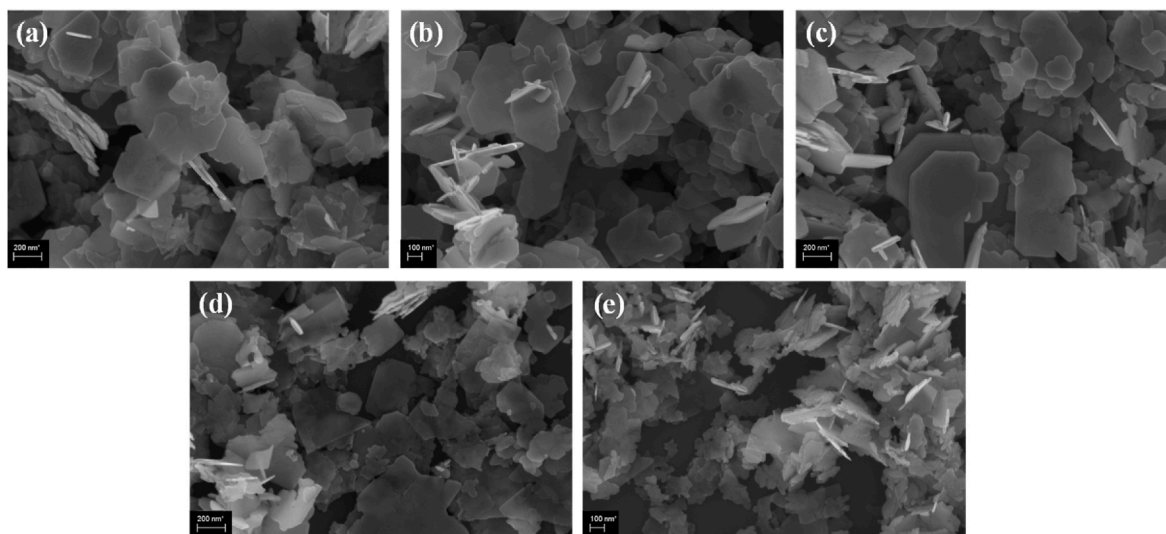


Fig. 5. FE-SEM images of (a) BMO, (b) BMO_{0.5}Eu, (c) BMO₁Eu, (d) BMO₂Eu, and (e) BMO₄Eu crystals.

and I.L.V.R., contributed equally to perform the required experiments, analyse the data and write the paper. All authors reviewed the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jlumin.2021.118675>.

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