



# White light emission from single-phase $Y_2MoO_6: xPr^{3+}$ ( $x = 1, 2, 3$ and $4$ mol%) phosphor



L.X. Lovisa<sup>a,\*</sup>, A.A.G. Santiago<sup>a</sup>, M.B. Farias<sup>a</sup>, B.S. Barros<sup>b</sup>, E. Longo<sup>c</sup>, M.S. Li<sup>d</sup>,  
C.A. Paskocimas<sup>a</sup>, M.R.D. Bomio<sup>a</sup>, F.V. Motta<sup>a</sup>

<sup>a</sup> LSQM—Laboratório de síntese química de materiais - DEMAT, UFRN, Campus Lagoa Nova, CEP 59078-900, Natal, RN, Brazil

<sup>b</sup> Universidade Federal de Pernambuco, Departamento de Engenharia Mecânica, Av. Prof. Moraes Rego-1235, Cidade Universitária, Recife, PE, Brazil

<sup>c</sup> LIEC—Laboratório interdisciplinar de eletroquímica e cerâmica, UFSCar, São Carlos Rua Francisco Degni s/n, CEP 14801-907 Araraquara, SP, Brazil

<sup>d</sup> IFSC—Instituto de Física de São Carlos, USP, São Paulo, Av. Trabalhador São-carlense, Centro, CEP 13566-590, São Carlos, SP, Brazil

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## ABSTRACT

A series of  $Pr^{3+}$  doped with  $Y_2MoO_6$  was synthesized using the co-precipitation method and the structural, photoluminescent and morphological properties of XRD, scanning electron microscopy (SEM) and photoluminescence spectrometry were investigated. The most intense absorption of its host matrix occurred between 200 and 340 nm due to a charge transfer in  $O \rightarrow Mo$ . The photoluminescence emission results of  $Y_2MoO_6: xPr^{3+}$  particles showed some white emission due to a strong contribution of the matrix and the  $Pr^{3+}$  dopant. All samples exhibited high color rendering index ( $>90\%$ ), indicating that the light source can reproduce colors. It was possible to obtain a white-emitting single-phase luminescent material from an easy route of production. The investigation indicated that  $Y_2MoO_6: xPr^{3+}$  is a potential candidate for applications with white light emitting diodes.

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## 1. Introduction

Constant efforts have been made in the research of new luminescent materials to be used in optical devices. This group of materials emerges as a very promising class of new solid state light sources for application in lighting and display devices [1–5]. Luminescent materials correspond to an order of materials that have aroused a growing industrial interest due to their wide range of applications such as WLEDs (white light emitting diodes), FEDs (field emission displays) and CRTs (cathode ray tubes) [6–8]. As a result, in the scientific environment, the aim is to obtain materials that meet the current market expectations in order to produce stable materials with high efficiency and reproducibility.

The first approach for WLED production was the combination of materials: YAG:  $Ce^{3+}$  (issued in yellow) with InGaN (issued in blue) [9], these phosphors became the most commercial and popular materials. However, yellow phosphors show some limitations such as low color rendering index (CRI) and low color temperature stability. In addition, the illumination color of this device is quite

sensitive to changes in transmission voltage and, therefore, stable WLEDs are difficult to produce [10].

WLEDs arise by combining excited red-green-blue (RGB) and phosphors in the ultraviolet region to optimize the color yield properties [11]. WLEDs with multiple emitting components may be questionable because the color balance is difficult to control. In this situation, single-phase phosphorus, which emerges as white emitters, presents luminous efficiency, excellent CRI, adjustable temperature and purity in its chromaticity coordinates [12].

Naresh et al. [13] used zinc borate matrix combined with  $Tm^{3+}$ ,  $Tb^{3+}$  and  $Eu^{3+}$  ions under ultraviolet light excitation to generate white light emission, obtaining satisfactory results regarding purity, reproducibility and proximity properties of the standard white light conditions. Their study was based on the evaluation of energy transfers among doping elements. Yang et al. [14] produced  $Sr_3Y-Na(PO_4)_3F: Dy^{3+}$  from solid state reaction and studied the thermal and chemical stability of the compound for photoluminescent use. It was verified that the high activation energy results in good thermal stability and that doping with the  $Dy^{3+}$  promoted simultaneous emitters in the violet (326–390 nm), blue (483 nm) and yellow regions (580 nm), allowing emitting white phosphor for white LEDs.

Grzyb et al. [15] studied the modification of color and time of life

\* Corresponding author.

E-mail address: [lauraengmat@hotmail.com](mailto:lauraengmat@hotmail.com) (L.X. Lovisa).

decay from the variation of the dopant concentration used in  $\text{Sr}_2\text{CeO}_4$ . The introduction of lanthanide ions ( $\text{Dy}^{3+}$  and  $\text{Eu}^{3+}$ ) into the  $\text{Sr}_2\text{CeO}_4$  structure turned the color of the matrix emission. The color emission can easily be adjusted by changing the dopant concentration.

Based on the results obtained by single-phase phosphors [16,17], researchers developed numerous surveys about the production of white emitters using single host matrix. Shang et al. [18] mentioned four possible methods to obtain white light in single-phase dies: (i) emission in white can be generated from the doping of only one type of rare earth in the matrix [14]; (ii) white light can be generated by combining multiple rare earth ions with simultaneous different emissions: red, green and blue; yellow and blue (such as  $\text{Ho}^{3+}/\text{Yb}^{3+}/\text{Tm}^{3+}$ ,  $\text{Tm}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ ) [19,20]; (iii) the emission of white light can be generated by the association of ions in pairs based on the energy transfer mechanism ( $\text{Eu}^{3+}/\text{Tb}^{3+}$ ,  $\text{Tm}^{3+}/\text{Er}^{3+}$ ,  $\text{Tm}^{3+}/\text{Ho}^{3+}$ ,  $\text{Dy}^{3+}/\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}/\text{Sm}^{3+}$ ) [21–27] and (iv) luminescent materials related to electronic defects may also emit white light [28].

Metallic molybdates ( $\text{AMoO}_4$  and/or  $\text{A}_2\text{MoO}_6$ , A = metal cation) are considered good hosts for luminescent materials due to their excellent chemical stability [29–32]. Another important feature is their extensive and intense ultraviolet charge transfer absorption bands, which make them good energy receptors [33]. The class of molybdates has attracted interest in numerous scientific and technological fields due to the innumerable industrial applications, including scintillation detectors, optical fibers, moisture sensors, solid state lasers, catalysts and photoluminescent devices [34–36]. Studies have been intensified to obtain new functionalities and behaviors in relation to their wide range of properties and applications [37].

The crystalline structure of  $\text{Y}_2\text{MoO}_6$  was detailed by Alonso et al. [38]. According to the authors, Y atoms occupy three non-equivalent crystallographic sites and are coordinated by eight O atoms. Mo atoms are coordinated to five O atoms, four of which, at short distance and the last one at long distance.  $\text{Y}_2\text{MoO}_6$  is an excellent matrix for trivalent rare earth doped due to its physical and chemical properties [39,40].

The trivalent praseodymium ion ( $\text{Pr}^{3+}$ ) has configuration of energy levels represented by spectral emission lines in UV, visible and infrared range. In recent years, various materials have been extensively investigated in relation to their various potential applications, such as fiber laser amplifier [41], red-emitting phosphors [42,43] and laser up-conversion [44].  $\text{Pr}^{3+}$  ion presents the following specific  $^3\text{P}_J$  transitions ( $J = 0, 1, 2$ ) approximately located at 478, 459 and 428 nm, respectively [45].

In this sense, this study aimed to investigate the photoluminescent properties of  $\text{Y}_2\text{MoO}_6: x\%\text{Pr}^{3+}$  capable of emitting white light.  $\text{Y}_2\text{MoO}_6: x\%\text{Pr}^{3+}$  particles were characterized by the following techniques: X-Ray Diffraction, Uv–Visible Absorption Spectroscopy, Photoluminescence and Scanning Electron Microscopy.

## 2. Experimental

### 2.1. Materials

Sodium molybdate dihydrate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ), (Alfa Aesar), Yttrium Nitrate Hexahydrate ( $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) (Alfa Aesar), Praseodymium(III) nitrate ( $\text{Pr}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ) (Alfa Aesar), Ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) (Synth) and distilled water were used as soon as they were received to prepare  $\text{Y}_2\text{MoO}_6$  and  $\text{Y}_2\text{MoO}_6: x\%\text{Pr}^{3+}$  particles.

### 2.2. Experimental procedures

Two precursor solutions were prepared for the synthesis of  $\text{Y}_2\text{MoO}_6: x\%\text{Pr}^{3+}$  particles: one containing molybdenum (solution A) and the other containing yttrium (solution B). For both solutions, the starting reagent was dissolved in 40 ml of distilled water. After dissolution, solution B was added to solution A dropwise. After its complete dissolution, the dopant ( $\text{Pr}^{3+}$ ) was added to the system. Finally,  $\text{NH}_4\text{OH}$  was added to the solution to stabilize its pH at 8. The solution was centrifuged three times in distilled water and then left to dry in oven at temperature of  $80^\circ\text{C}$  for 24 h. Particles were calcined at  $1000^\circ\text{C}$  for 2 h at heating rate of  $10^\circ\text{C}/\text{min}$ .  $\text{Pr}^{3+}$  concentration varied from 1, 2, 3 and 4 mol%.

### 2.3. Characterization of $\text{Y}_2\text{MoO}_6: x\%\text{Pr}^{3+}$ particles

$\text{Y}_2\text{MoO}_6: x\%\text{Pr}^{3+}$  particles were structurally characterized by XRD using Shimadzu XRD 7000 instrument with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the  $2\theta$  range from  $10$  to  $80^\circ$  at scanning rate of  $0.02^\circ \text{ s}^{-1}$ . Lattice parameters and position were determined by means of the Rietveld refinement method [46] and were analyzed by the Structure Analysis System (GSAS) software with EXPGUI graphical interface software [47]. The lattice parameters and atomic positions obtained were used to model these unit cells using the Visualization for Electronic and Structural Analysis (VESTA) software [48], version 3.1.2. The morphologies and the dispersion of the atoms of samples were investigated by EDS spectroscopy using field-emission gun scanning electron microscopy (FEG-SEM; Carl Zeiss, Supra 35-VP Model, Germany) operated at 14 kV. The Uv–visible reflectance spectra of powders were performed using Shimadzu spectrophotometer, model UV-2600. The Photoluminescence (PL) spectra were acquired with Ash 27 monochromator Monospec (Thermal Jarrel, U.S.A.) and R4446 photomultiplier (Hamamatsu Photonics, U.S.A.). The 350 nm beam of a krypton ion laser (Coherent Innova 90K) was used as the excitation source while its maximum output power was kept at 200 mW. All measurements were performed at room temperature. Uv–Vis and PL spectra were performed three times for each sample to ensure reliability of measurements.

## 3. Results and discussion

### 3.1. X-Ray Diffraction of $\text{Y}_2\text{MoO}_6: x\%\text{Pr}^{3+}$

From XRD analysis, it was possible to identify that all diffraction peaks presented in Fig. 1 are indexed according to reference JCPDS 52–650, which represents the monoclinic crystal structure. No additional peaks of secondary phases are observed. It is reasonable to consider that  $\text{Y}^{3+}$  ions were successfully replaced by  $\text{Pr}^{3+}$  ions. The exchange of ions was favored because cations presented very similar characteristics: (i) approximate ionic radii:  $\text{Y}^{3+}$  (0.90 Å) and  $\text{Pr}^{3+}$  (1.00 Å) and (ii) have the same valence. A peak (221) displacement ( $\theta \approx 29^\circ$ ) was observed for the lowest angle region in the inset of Fig. 1 as the  $\text{Pr}^{3+}$  concentration increased. This behavior is explained by the disorder caused due to the  $\text{Y}^{3+} \rightarrow \text{Pr}^{3+}$  replacement, since the incorporation of  $\text{Pr}^{3+}$  ions into the  $\text{Y}_2\text{MoO}_6$  lattice induces local distortion in the crystal structure. The same behavior was verified in another work that used  $\text{Y}_2\text{MoO}_6$  as its host matrix [49]. The unit cell may undergo changes in its volume, contraction or expansion as its chemical composition changes.

The crystallite size and the microdeformation in the lattice are two properties that can be studied from the analysis of the half height of the diffraction peak (FWMH) and its intensity. Microdeformation can occur in several ways such as: contact or sinter stress, grain boundary, triple junction, stacking faults and

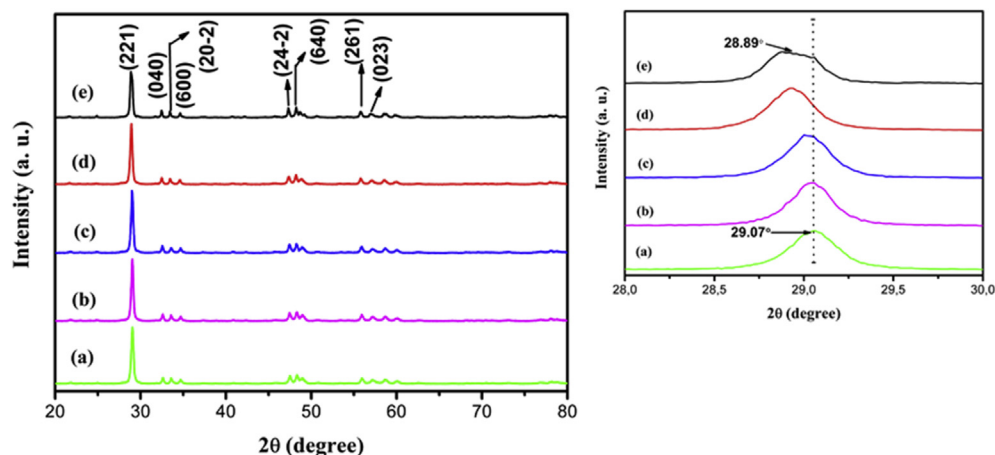


Fig. 1. XRD patterns of  $Y_2MoO_6: x\%Pr^{3+}$  (a = 0, b = 1, c = 2, d = 3 and e = 4 mol) particles.

coherency stress [50]. The mean crystallite size was estimated by the Scherrer equation (1).

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where  $D$  is the mean crystallite size,  $\lambda$  is the wavelength,  $\theta$  is half the Bragg angle and  $\beta$  is the half height of the selected reflection (FWHM). For the  $D$  calculation, the average value of peaks (221), (040), (20-2), (600), (24-2), (640), (261), (023) was considered. Table 1 shows the crystallite size values, the microdeformation and the position of the diffraction peak in the plane (221).

Based on the XRD results, refinement was performed using the GSAS software Fig. 2 presents the results of Rietveld refinements, observing that the differences between experimentally observed diffraction patterns and theoretically calculated data (Obs-Calc line) are close to zero, showing that the diffraction patterns of samples are well adapted. The crystallographic and refinement quality parameters are recorded in Table 2; more details are provided in the Support Information (Table S1). The reliability parameters  $\chi^2$ ,  $R_{wp}$  and  $R_p$  indicate good quality of structural refinements and numerical results.

$Y_2MoO_6$  crystallizes into a monoclinic structure with  $C_{2/c}$  space group. The lattice parameters and unit cell volume of samples are in agreement with literature. Hou et al. [51] synthesized  $Y_2MoO_6$  using the solid state reaction and the lattice parameter values obtained were  $a = 16.3504 \text{ \AA}$ ,  $b = 11.0192 \text{ \AA}$ ,  $c = 5.3486 \text{ \AA}$ ,  $\beta = 108.49^\circ$  and unit cell volume equal to  $913.86 \text{ \AA}^3$ . Note that the unit cell volume of samples (Table 2) slightly increases with the replacement of  $Y^{3+}$  ions by  $Pr^{3+}$  ions, this is because  $Pr^{3+}$  ions present a slightly higher ionic radius than  $Y^{3+}$  ions ( $1.00 \text{ \AA}$  and  $0.90 \text{ \AA}$ , respectively), thus causing expansion and distortion in the lattice. According to the positions of Y, Mo and O atoms obtained by the structural analysis, the crystalline structures of samples  $Y_2MoO_6: x$

$\%Pr^{3+}$  ( $Pr = 0, 1, 2, 3$  and  $4$  mol) were plotted with the aid of the VESTA software as shown in Fig. 3.  $MoO_5$  clusters are highlighted.  $Y_2MoO_6$  crystallizes in the  $C_{2/c}$  space group, with 8 formula units in the unit cell. "The structure contains four zigzags, one-dimensional  $MoO_5$  polyhedral row per unit cell, running through the  $RO_8$  polyhedral framework along the [001] direction.  $MoO_5$  form discrete units (i.e. do not share common oxygen), with Mo–O distances ranging from 1.77 to 2.24  $\text{\AA}$ , although the oxygen coordination can be extended to distances of about 3.1  $\text{\AA}$ , giving rise to strongly distorted  $MoO_8$  scale. Thus,  $MoO_8$  and  $RO_8$  polyhedral are fully ordered in  $R_2MoO_6$  compounds, which, in fact, can be considered as fluorite superstructures ( $M_3O_6$ ), containing 24  $MO_2$  fluorite units per unit cell" [39]. Changes are observed in the distances between Mo–O bonds; these changes occur due to distortions caused in the  $Y_2MoO_6$  lattice introduced by the effect of  $Pr^{3+}$  doping and the tensions generated by the synthesis conditions that were applied. The values of Mo–O distances are in agreement with literature, Alonso et al. [38] analyzed the structure of  $Y_2MoO_6$  and obtained the distances of Mo–O bonds (Mo–O1 = 1.788  $\text{\AA}$ , Mo–O2 = 1.786  $\text{\AA}$ , Mo–O3 = 1.808  $\text{\AA}$ , Mo–O4 = 1.804  $\text{\AA}$  and Mo–O5 = 2.215  $\text{\AA}$ ), and the  $MoO_5$  polyhedral was formed by four short Mo–O bonds and one long Mo–O bond.

### 3.2. Uv–Vis absorbance spectra of $Y_2MoO_6: x\%Pr^{3+}$

Fig. 4 shows the Uv–Vis absorbance spectra of  $Y_2MoO_6$  and  $Y_2MoO_6: x\%Pr^{3+}$ . A high absorption band is observed up to 340 nm. This absorption band occurs mainly due to the absorption of the charge transfer (CT) within  $[MoO_4]^{2-}$  clusters [52]. It was verified that the presence of  $Pr^{3+}$  causes an increase in the absorption band for the green/yellow region in relation to the undoped sample, as well as the existence of a discrete band referring to the  $^3H_4 \rightarrow ^3P_0$  transition at 493 nm characteristic of  $Pr^{3+}$ .

The optical band gap of undoped, 1, 2, 3 and 4 mol%  $Pr^{3+}$

Table 1

Values of strain, crystallite size, FWHM (221) and Height of the plane (221) of  $Y_2MoO_6: x\%Pr$  ( $Pr = 0, 1, 2, 3$  and  $4$  mol %) particles.

Samples	Strain ( $\epsilon$ )	Crystallite size (nm)	Position of the diffraction peak (221)
		Scherrer's formula	
$Y_2MoO_6$	$1.0978 \times 10^{-4}$	22.68	$29.07^\circ$
$Y_2MoO_6:1\%Pr$	$8.0910 \times 10^{-4}$	30.57	$29.02^\circ$
$Y_2MoO_6:2\%Pr$	$1.1640 \times 10^{-3}$	21.45	$29.01^\circ$
$Y_2MoO_6:3\%Pr$	$1.1240 \times 10^{-3}$	22.21	$28.92^\circ$
$Y_2MoO_6:4\%Pr$	$1.1030 \times 10^{-3}$	22.63	$28.89^\circ$

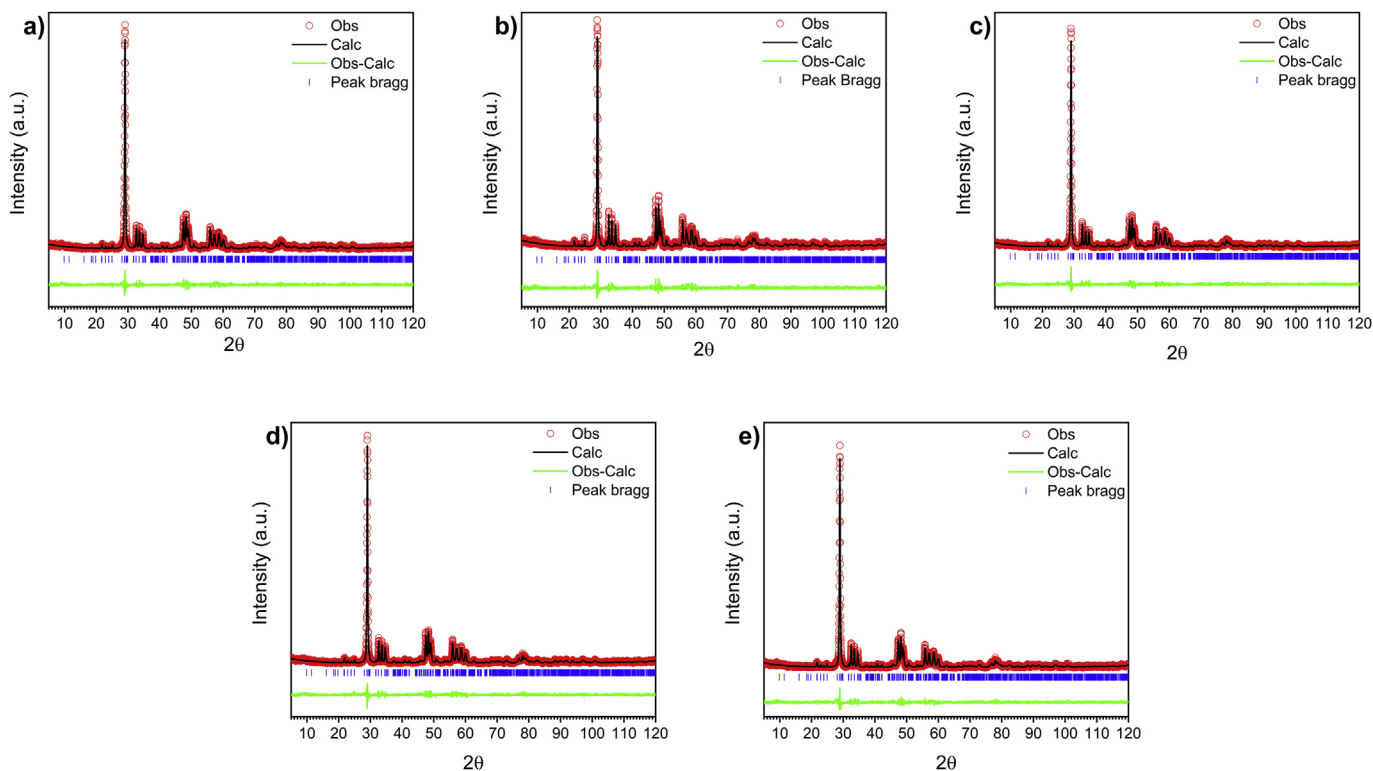


Fig. 2. Rietveld refinement of  $Y_2MoO_6: x\%Pr^{3+}$  ( $a = 0$ ,  $b = 1$ ,  $c = 2$ ,  $d = 3$  and  $e = 4$  mol) particles.

Table 2

Parameters of the Rietveld refinement of the particles  $Y_2MoO_6: x\%Pr$  ( $x = 0, 1, 2, 3$  and  $4$  mol %).

Samples	$Y_2MoO_6$	$Y_2MoO_6:1\%Pr$	$Y_2MoO_6:2\%Pr$	$Y_2MoO_6:3\%Pr$	$Y_2MoO_6:4\%Pr$	Ref [JCPDS 52–650]
<b>Crystal system</b>	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
<b>Space Group</b>	$C_{2/c}$	$C_{2/c}$	$C_{2/c}$	$C_{2/c}$	$C_{2/c}$	$C_{2/c}$
Lattice parameters (Å)						
$a$	16.4122	16.3826	16.4134	16.4213	16.4173	16.3538
$b$	11.0089	11.0227	11.0180	11.0152	11.0178	11.0183
$c$	5.3468	5.3531	5.3447	5.3472	5.3499	5.3506
$\beta$ (°)	108.66	108.57	108.69	108.71	108.69	108.52
$\alpha = \gamma$ (°)	90	90	90	90	90	90
$V(\text{Å})^3$	915.25	916.9	915.56	916.10	916.68	914.18
$\chi^2$	1.35	1.44	1.43	1.45	1.39	
Rwp (%)	17.59	18.76	17.80	18.04	17.60	
Rb (%)	12.78	14.02	13.00	13.10	13.90	

materials was evaluated from the absorption spectra. The absorption spectra  $F(R)$  were calculated from the reflection spectra using the Kubelka-Munk function [53]:

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{K}{S} \quad (2)$$

where  $R$  is the reflectance,  $K$  is the absorption coefficient, and  $S$  is the scattering coefficient. The bandgap value of  $Y_2MoO_6$  and  $Y_2MoO_6: x\%Pr^{3+}$  was evaluated by extrapolating the linear portion of the curve. The gap energy obtained for samples is between 3.41 and 3.46 eV.

### 3.3. Photoluminescence properties of $Y_2MoO_6: x\%Pr^{3+}$

Fig. 5 (a) shows the photoluminescent emission spectra of  $Y_2MoO_6$  and  $Y_2MoO_6: x\%Pr^{3+}$  particles. Samples were excited by a wavelength laser ( $\lambda$ ) of 350 nm at room temperature. The presence

of three broad bands centered at 440, 545 and 620 nm is observed in the spectrum of the pure sample in Fig. 5 (b). These bands are due to the electronic transitions in  $[MoO_4]^{2-}$  clusters [51,54,55]. According to Sczancoski et al. [56], the position that the electronic defects (h) occupy in the band gap can define different types of emissions. The energy states in molybdates are formed by the oxygen 2p orbital located just above the valence band (VB) and by the molybdenum orbital 4d located under the conduction band (CB). From the deconvolution of  $Y_2MoO_6$ , it is possible to estimate how each visible region contributes to the behavior in the whole. Mo (4d)  $\rightarrow$  O (2p $\sigma$ ) type transitions are associated to defects near the valence band, which corresponds to emissions in blue (21%). Mo (4d)  $\rightarrow$  O (2p $\pi$ ) type transitions are associated with distances far from the valence band [56], which correspond to emissions in green (33%) and red (46%).

PL emission is closely related to the crystal structure and distortions in the metal-oxygen polyhedra of molybdates. The distortion present in the  $Y_2MoO_6$  structure is justified by the substitution

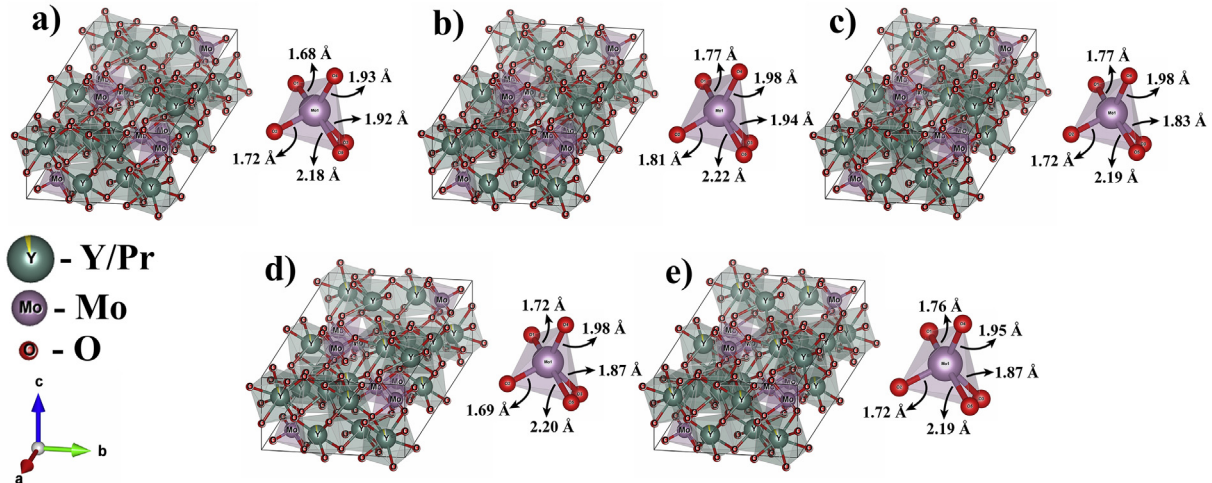


Fig. 3. Representation of the crystalline structure of  $\text{Y}_2\text{MoO}_6$ :  $x\%\text{Pr}^{3+}$  ( $a=0$ ,  $b=1$ ,  $c=2$ ,  $d=3$  and  $e=4$  mol) particles.

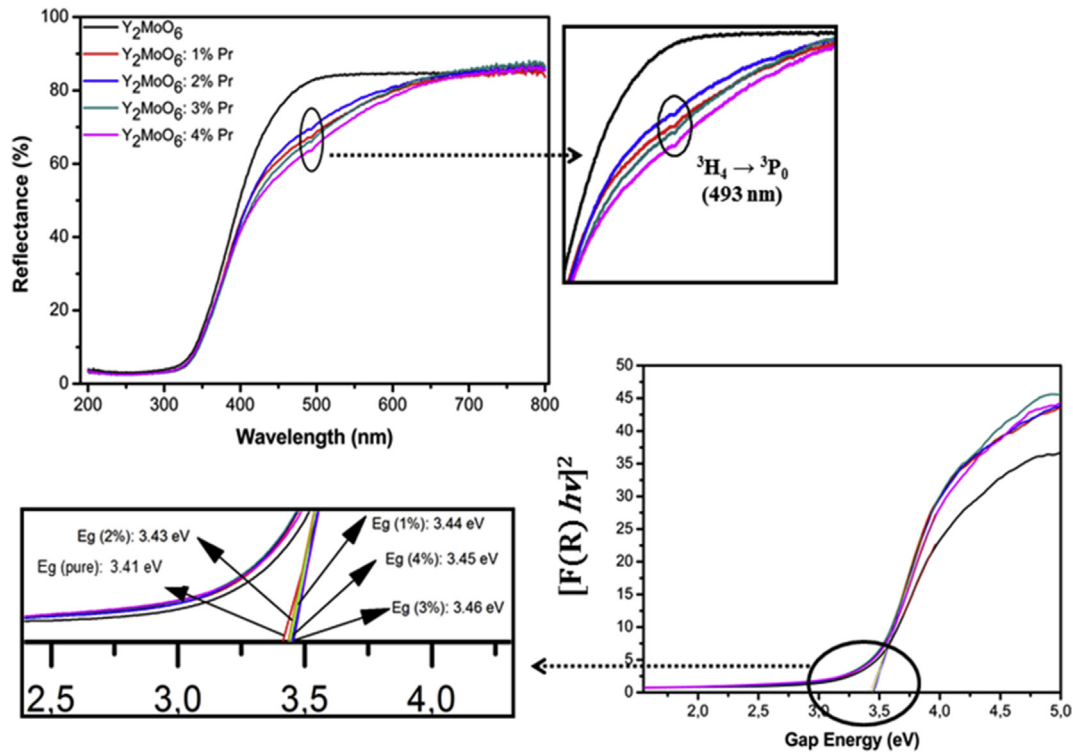


Fig. 4. UV-Vis absorbance spectra of  $\text{Y}_2\text{MoO}_6$  and  $\text{Y}_2\text{MoO}_6$ :  $x\%\text{Pr}^{3+}$  and gap energy determination.

of Y atoms for Pr. This exchange is responsible for one of the crucial components that lead to the formation of structural defects in the crystalline lattice of the matrix, that is, oxygen vacancies [57]. These oxygen vacancies were reported to be an important factor in obtaining luminescent materials that exhibit long-acting phosphorescence [58,59]. Oxygen vacancies act as centers of electron trapping. They capture electrons and gradually release them to the luminescent centers [60] and in the electron-hole recombination, luminescence with long response is observed in Refs. [61,62]. These factors probably result in a distortion process on  $[\text{MoO}_5]$  and  $[\text{YO}_8]$  (or  $[\text{PrO}_8]$ ) clusters, favoring the formation of intermediate energy levels within the band gap of this material. These energy levels are composed of oxygen 2p states (near the valence band) and

praseodymium 5d levels (below the conduction band). During the excitation process with 350 nm wavelength, some electrons are promoted from the oxygen 2p states to praseodymium 5d levels through the absorption of photons ( $h\nu$ ). This mechanism results in the formation of self-trapped excitons (STEs), i.e., trapping of electrons ( $e^-$ ) by holes ( $h$ ). The emission process of photons ( $h\nu$ ) occurs when an electron localized in a praseodymium 5d levels decays into an empty oxygen 2p state. Consequently, this mechanism is responsible for the PL emission of  $\text{Y}_2\text{MoO}_6$  nanoparticles. The proposed mechanism is based on the distortion  $[\text{MoO}_5]$  and  $[\text{YO}_8]$  (or  $[\text{PrO}_8]$ ) clusters.

For the  $\text{Y}_2\text{MoO}_6$ :  $x\%\text{Pr}^{3+}$  series ( $x=1, 2, 3$  and  $4$  mol), the presence of  $f \rightarrow f$  characteristic transitions of  $\text{Pr}^{3+}$  was observed.

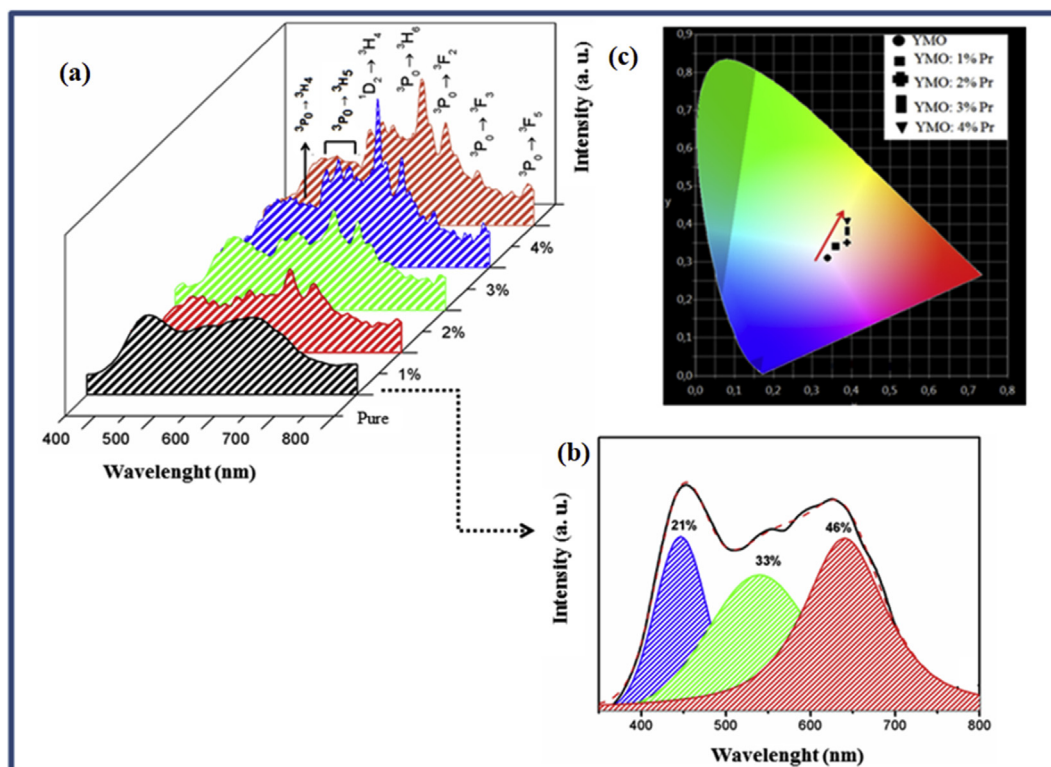


Fig. 5. (a) Emission spectra of Y<sub>2</sub>MoO<sub>6</sub>: x%Pr<sup>3+</sup> (x = 0, 1, 2, 3 and 4 mol); (b) deconvolution curve of Y<sub>2</sub>MoO<sub>6</sub> and (c) chromaticity diagram.

Pr<sup>3+</sup> emission in the emission spectrum of PL in Fig. 5(a) is: <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>4</sub>, <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>5</sub>, <sup>1</sup>D<sub>2</sub> → <sup>3</sup>H<sub>4</sub>, <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>6</sub>, <sup>3</sup>P<sub>0</sub> → <sup>3</sup>F<sub>2</sub>, <sup>3</sup>P<sub>0</sub> → <sup>3</sup>F<sub>3</sub> and <sup>3</sup>P<sub>0</sub> → <sup>3</sup>F<sub>5</sub>, respectively located in, 491, 531–567, 612, 629, 654, 706 and 790 nm [63,64]. It was observed that with the addition of Pr<sup>3+</sup>, the photoluminescence intensity is favored. However, for sample doped with 4 mol% Pr<sup>3+</sup>, there is a drop in photoluminescence. This behavior can be justified due to a critical concentration of the dopant in the matrix lattice, known as quenching concentration. What actually occurs in this case is that Pr<sup>3+</sup> ions are at a very close distance, and in this condition, the appearance of non-radioactive

transitions occurs more effectively [65]. Non-radioactive transitions are expressed in phonon forms, which result in vibrations within the crystal lattice. The concentration of dopants determines the average distance between the two neighboring activating cations, as well as the photoluminescence efficiency of RE<sup>3+</sup> in doped systems [66]. Fig. 6 shows the relationship between the photoluminescence intensity and the Pr<sup>3+</sup> concentration (mol%).

A decrease in the emission intensity shows that the energy migrates among Pr<sup>3+</sup> cations in different sites in the lattice, resulting in concentration quenching. Thus, optimum Pr<sup>3+</sup> concentration is found to be 3 mol% (X<sub>c</sub> = 0.03). Concentration quenching occurs by the non-radioactive migration of energy among Pr<sup>3+</sup> cations. The migration of non-radioactive energy can take place from two distinct mechanisms: i. e (i) Forster resonance energy transfer (multipole-multipole interaction) and (ii) Dexter mechanism (exchange interaction) [67].

The critical energy transfer distance (R<sub>c</sub>) for Y<sub>2</sub>MoO<sub>6</sub>:Pr<sup>3+</sup> was estimated by equation (3) suggested by Blasse [68] from the structure parameters, namely the unit cell volume (V), the number of units of the molecular formula per unit cell (Z) and the quenching concentration (X<sub>c</sub>).

$$R_c \cong 2 \left( \frac{3V}{4X_c \pi Z} \right)^{1/3} \quad (3)$$

For the Y<sub>2</sub>MoO<sub>6</sub>: 3%Pr<sup>3+</sup> system, the following values were considered: Z = 8, V = 916.10 Å<sup>3</sup> and X<sub>c</sub> = 0.03, the calculated R<sub>c</sub> was 19.40 Å. Normally, the exchange interaction is preferably in an energy transfer process when the R<sub>c</sub> value is between 5 and 10 Å [69]. In case of values higher than 10 Å, there is no indication of exchange interaction in this mechanism. Consequently, other multipolar electrical interactions are responsible for the quenching effect between two more activating ions (Pr<sup>3+</sup>).

[MoO<sub>4</sub>]<sup>2-</sup> clusters act as sensitizers for Pr<sup>3+</sup>. They are able to

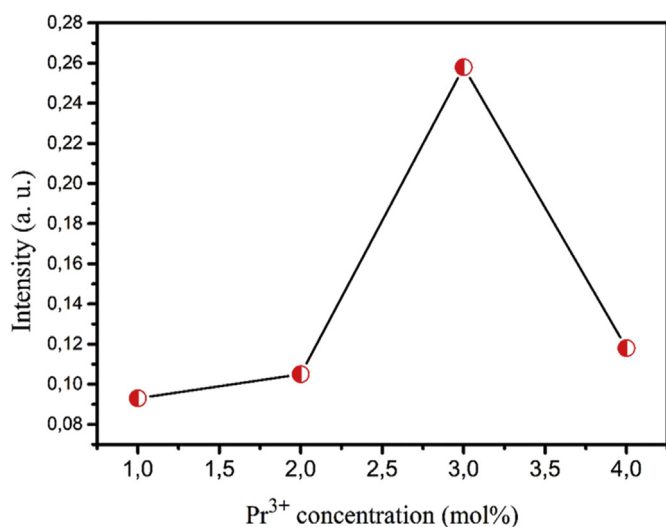


Fig. 6. Relationship between photoluminescence intensity and Pr<sup>3+</sup> concentration (mol%).

absorb the excitation energy ( $\lambda_{exc} = 350$  nm) more efficiently, as can be seen in the UV–Vis absorption spectrum result indicated in Fig. 4. This result is in agreement with other works reported in literature [70]. A strong absorption in the ultraviolet occurs due to the charge transfer in  $[\text{MoO}_4]^{2-}$  groups, and part of this energy is transferred to  $\text{Pr}^{3+}$  ions. To clearly demonstrate the luminescence process, a schematic diagram is shown in Fig. 7.

According to Brenier and Kityk [71], the main reason for the low cross-relaxation in the photoluminescent processes is the specific influence of 2p-type potential ligands (oxygen) in the transition moments of dipoles, determining the probabilities of particular level occupations. Another possibility of level occupation is connected with the multiphonic decay for  $^1\text{D}_2$  of  $\text{Pr}^{3+}$  level. According to the authors, it was evaluated that the multiphonic contribution to the  $^1\text{D}_2$  emission corresponds to about 12%, being, therefore, twice as large as the particular processes of cross relaxation.

According to the spectra distribution, the chromaticity coordinates (Xc, Yc) were calculated. Fig. 5(c) represents the CIE diagram, identifying all samples emitted in the white region. It was observed that as the  $\text{Pr}^{3+}$  concentration increases, there is a tendency of yellow emission. The correlative color temperature (CCT) and the color rendering index (CRI) were calculated. All samples presented CRI levels higher than 90%, indicating that samples exhibited behavior close to natural light. The National Institute of Standard and Technology (NIST) evaluated the quality of colors from CRI measurements, and that closer to 100% presents a degree of precision in the reproduction of colors of a certain object. Table 3 shows the values of chromaticity coordinates, CCT, CRI and the color of the light emitted.

### 3.4. Decay profiles of $\text{Y}_2\text{MoO}_6: x\%\text{Pr}^{3+}$

Decay was recorded for  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  transition of  $\text{Pr}^{3+}$  at 612 nm emission. The decay curves of all  $\text{Y}_2\text{MoO}_6: x\%\text{Pr}^{3+}$  samples exhibited bi-exponential decay as shown in Fig. 8 and were fitted into

**Table 3**  
CIE coordinate values, color temperature and color rendering index.

Samples	(Xc)	(Yc)	CCT (K)	CRI (%)	Region
$\text{Y}_2\text{MoO}_6$	0.34	0.32	5073	91	White
$\text{Y}_2\text{MoO}_6: 1\% \text{Pr}$	0.36	0.34	4373	95	
$\text{Y}_2\text{MoO}_6: 2\% \text{Pr}$	0.39	0.35	3503	94	
$\text{Y}_2\text{MoO}_6: 3\% \text{Pr}$	0.39	0.38	3774	94	
$\text{Y}_2\text{MoO}_6: 4\% \text{Pr}$	0.39	0.41	3988	94	

exponential equation (4). The average lifetime for the bi-exponential decay was calculated from the following formula (5). The calculated decay parameters are listed in Table 4.

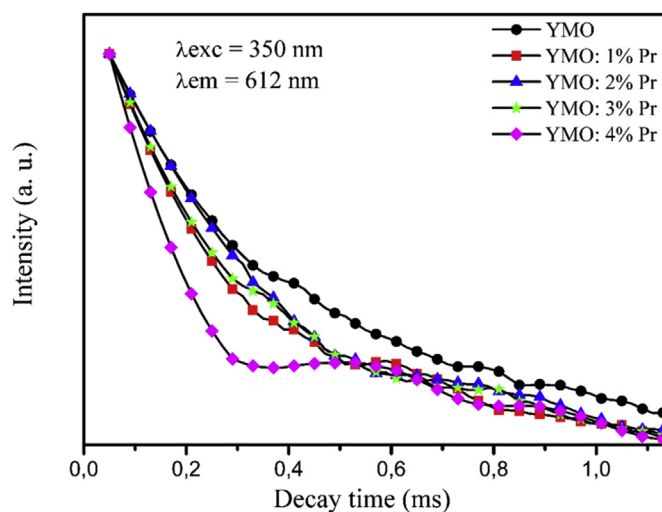


Fig. 8. Decay Curves of  $\text{Y}_2\text{MoO}_6: x\%\text{Pr}^{3+}$ .

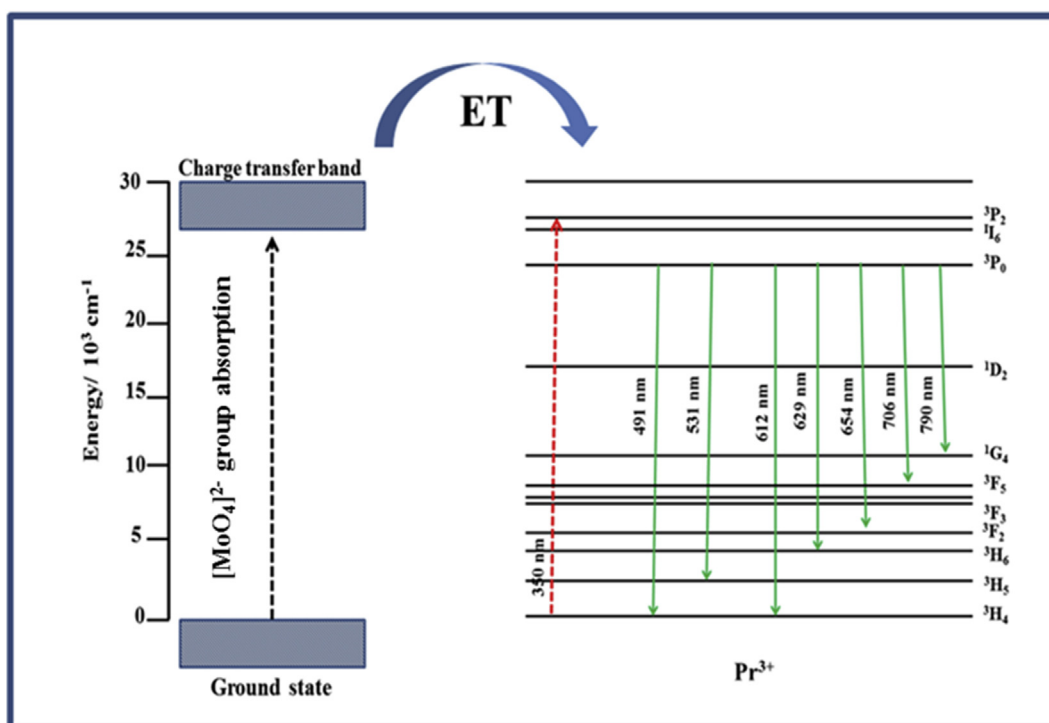


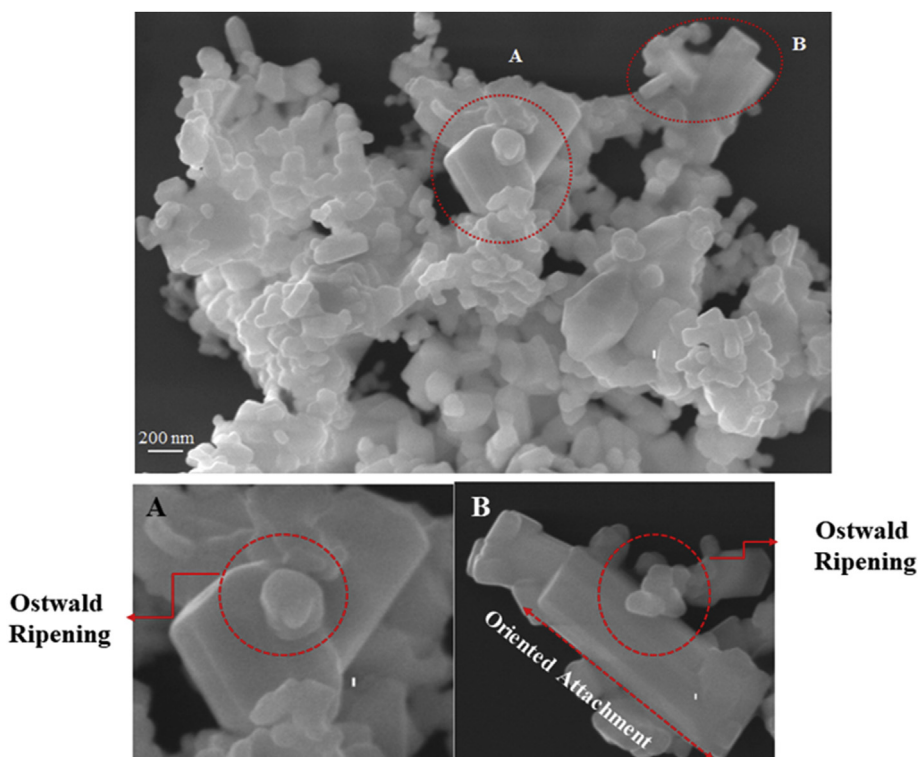
Fig. 7. Schematic representation of the energy transfer between  $[\text{MoO}_4]^{2-}$  cluster and  $\text{Pr}^{3+}$  ion.

**Table 4**  
Comparison of emission lifetimes of  $Y_2MoO_6: x\%Pr^{3+}$ .

Samples	$\lambda_{exc}$ (nm)	$\lambda_{em}$ (nm)	$A_1$	$\tau_1$ (ms)	$A_2$	$\tau_2$ (ms)	$\tau$ (ms)
$Y_2MoO_6$	350	612	35.53	0.14	82.56	0.50	0.64
$Y_2MoO_6: 1\% Pr$	350	612	88.88	0.53	61.64	0.07	0.6
$Y_2MoO_6: 2\% Pr$	350	612	90.84	0.32	90.84	0.32	0.64
$Y_2MoO_6: 3\% Pr$	350	612	78.20	0.48	33.41	0.06	0.55
$Y_2MoO_6: 4\% Pr$	350	612	55.44	0.26	20.30	0.06	0.32

$$I = A_1 \exp\left(\frac{-\tau}{\tau_1}\right) + A_2 \exp\left(\frac{-\tau}{\tau_2}\right) \quad (4)$$

Where  $I$  is the emission intensity at any time “ $\tau$ ” after switching off the excitation illumination,  $A_1$ ,  $A_2$  are constant.  $\tau_1$ ,  $\tau_2$  are the bi-



**Fig. 9.** SEM image of  $Y_2MoO_6: 1\% Pr^{3+}$  particles.

exponential component of the decay time. The average lifetime for 612 nm emission can be determined by the following formula (5):

$$\tau = \frac{(A_1 \cdot \tau_1^2) + (A_2 \cdot \tau_2^2)}{(A_1 \cdot \tau_1 + A_2 \cdot \tau_2)} \quad (5)$$

And the energy transfer efficiency from host to  $Pr^{3+}$  can be calculated according to equation (6) [72]:

$$n = \left(1 - \frac{\tau}{\tau_0}\right) \times 100\% \quad (6)$$

Where  $\tau$  and  $\tau_0$  are the corresponding emission lifetime of the donor in the presence and absence of acceptor ( $Pr^{3+}$ ) for the same donor concentration, respectively. The energy transfer efficiency from host to  $Pr^{3+}$  in  $Y_2MoO_6$  is 50% for the  $Y_2MoO_6: 3\%Pr^{3+}$  sample.

### 3.5. Scanning electron microscopy of $Y_2MoO_6: x\% Pr^{3+}$ particles

**Fig. 9** shows the high resolution SEM image of  $Y_2MoO_6: x\% Pr^{3+}$  particles. The microscopic characterization allowed the comprehension of the process of particle morphology formation as a function of the route synthesis and thermal treatment used in particles. In the crystallization processes, the solute is transferred from liquid to a solid phase due to the difference in the chemical potential between phases. Crystallization is described by combining the following mechanisms: nucleation, crystal growth and side effects such as agglomeration [73]. The fit among these mechanisms defines the particle size distribution until the end of the crystal growth. Particle agglomerates of nanometric sizes are observed in the image. The size of these particles depends on the nucleation rate of the precipitate and its dependence over time

[74]. The nucleation step is predominant at the beginning of the process when the chemical potential difference between solution and the solid phase is typically high. Smaller particles exhibit great thermodynamic instability due to the large surface area/volume ratio. A spontaneous process shown in **Fig. 9(A)** shows that smaller particles adhere to the surface of larger particles, which phenomenon is known as Ostwald Ripening (**OR**) and is thermodynamically favored due to the decrease of the surface energy of particles [75]. The **OR** process occurs naturally since larger particles are energetically favored by smaller ones, resulting in coalescence.

The presence of some particles with regular sides and with cube-type morphology was verified. It was observed that these crystals are made up of a series of smaller particles and have a preferred orientation, as can be seen in **Fig. 9(B)**. This type of growth mechanism well reported in literature [76] is known as Oriented Attachment. This process consists of an aligned growth of particles in a certain crystallographic direction, and consequently coalescence of neighboring particles, eliminating the common



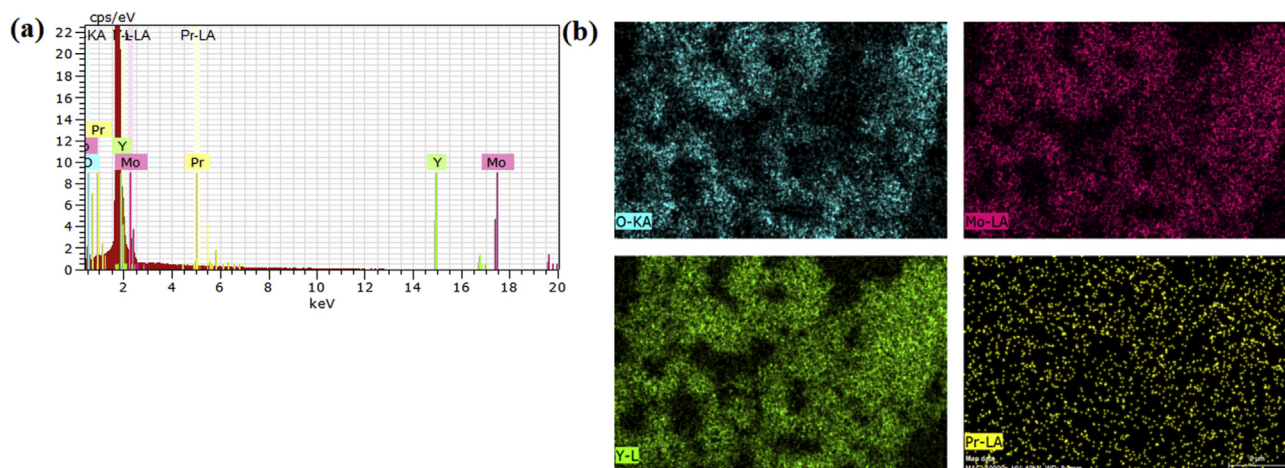


Fig. 10. EDS spectrum and mapping of atoms of  $\text{Y}_2\text{MoO}_6: 3\%\text{Pr}^{3+}$  phosphor.

interface among particles, while other particles have a disoriented growth. This preferential growth can be justified by the reduction of the surface energy in a given plane that is adjusted by a specific arrangement and coordination of atoms [77,78]. Thus, it is possible to verify that some particles presented anisotropic behavior.

Fig. 10 shows the EDS spectrum and the mapping of the distribution of atoms of  $\text{Y}_2\text{MoO}_6: 3\%\text{Pr}^{3+}$  phosphor to prove the chemical composition of the material produced as well as to verify the homogeneity of Zn, Mo, O and Pr throughout the sample.

#### 4. Conclusions

$\text{Y}_2\text{MoO}_6$  and  $\text{Y}_2\text{MoO}_6:\text{x}\%\text{Pr}^{3+}$  particles were successfully obtained by the co-precipitation method. It was shown that in  $\text{Y}_2\text{MoO}_6$ -based phosphor, the energy transfer from  $[\text{MoO}_4]^{2-}$  anion to  $\text{Pr}^{3+}$  leads to visible emission. Samples showed emission in white, with chromaticity coordinate values very close to the ideal white (0.33, 0.33). The color rendering index presented levels exceeding 90%. The energy levels of  $\text{Pr}^{3+}$  ions in each site were identified from the emission spectra and their lifetime was discussed. It could be concluded that  $\text{Y}_2\text{MoO}_6: \text{Pr}^{3+}$  phosphor is a potential candidate as phosphor for application in white LEDs.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jallcom.2018.07.339>.

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