

# Photoluminescence properties of BaMoO<sub>4</sub> amorphous thin films

Ana Paula Azevedo Marques<sup>a,\*</sup>, Dulce M.A. de Melo<sup>a</sup>, Elson Longo<sup>b</sup>,  
Carlos A. Paskocimas<sup>a</sup>, Paulo S. Pizani<sup>c</sup>, Edson R. Leite<sup>b</sup>

<sup>a</sup>Laboratório de Análise Térmica e Materiais, Departamento de Química, Universidade Federal do Rio Grande do Norte, 59072-970, Natal, RN, Brazil

<sup>b</sup>Laboratório Interdisciplinar de Eletroquímica e Cerâmica, Centro Multidisciplinar de Desenvolvimento de Materiais Cerâmicos, Departamento de Química, Universidade Federal de São Carlos, C. Postal 676, 13565-905 São Carlos, SP, Brazil

<sup>c</sup>Laboratório de Semicondutores, Departamento de Física, Universidade Federal de São Carlos, C. Postal 676, 13565-905 São Carlos, SP, Brazil

Received 10 March 2005; received in revised form 14 May 2005; accepted 22 May 2005

## Abstract

BaMoO<sub>4</sub> amorphous and crystalline thin films were prepared from polymeric precursors. The BaMoO<sub>4</sub> was deposited onto Si wafers by means of the spinning technique. The structure and optical properties of the resulting films were characterized by FTIR reflectance spectra, X-ray diffraction (XRD), atomic force microscopy (AFM) and optical reflectance. The bond Mo–O present in BaMoO<sub>4</sub> was confirmed by FTIR reflectance spectra. XRD characterization showed that thin films heat-treated at 600 and 200 °C presented the scheelite-type crystalline phase and amorphous, respectively. AFM analyses showed a considerable variation in surface morphology by comparing samples heat-treated at 200 and 600 °C. The reflectivity spectra showed two bands, positioned at 3.38 and 4.37 eV that were attributed to the excitonic state of Ba<sup>2+</sup> and electronic transitions within MoO<sub>4</sub><sup>2-</sup>, respectively. The optical band gaps of BaMoO<sub>4</sub> were 3.38 and 2.19 eV, for crystalline (600 °C/2 h) and amorphous (200 °C/8 h) films, respectively. The room-temperature luminescence spectra revealed an intense single-emission band in the visible region. The PL intensity of these materials was increased upon heat-treatment. The excellent optical properties observed for BaMoO<sub>4</sub> amorphous thin films suggested that this material is a highly promising candidate for photoluminescent applications.

© 2005 Elsevier Inc. All rights reserved.

**Keywords:** BaMoO<sub>4</sub>; Photoluminescence; Thin films; Polymeric precursor method; Amorphous

## 1. Introduction

Scheelite-type crystalline structures, such as BaMoO<sub>4</sub>, where molybdenum atoms are arranged in tetrahedral coordination [1,2] have recently attracted great attention due to their approved usage as scintillating materials and in electro-optical applications including solid-state lasers and optical fibers [3]. In addition, numerous investigations on their luminescent properties have been carried out [2]. A variety of preparation techniques have been proposed to produce these materials including electrochemical methods, combustion synthesis, the Chochralski technique, co-precipitation and conven-

tional solid-state reaction [2–6]. Chang-Tai et al. [4], showed that BaMoO<sub>4</sub> thin films grown by an electrochemical method, consisted of an heterogeneous surface and grains with sizes varying from 2 to 10 μm. Using the polymeric precursor method, such drawbacks could be minimized because of the immobilization of metal-complexes in rigid organic polymeric networks. This reduces the segregation of particular metals, thus ensuring compositional homogeneity at a molecular scale. Such a characteristic is essentially important for the synthesis of multi-component oxides with complicated compositions, since the chemical homogeneity with respect to distribution of cations throughout the entire gel system often determines the compositional homogeneity of the final complex mixed oxides [7]. Cost-efficient compounds with strong photoluminescence

\*Corresponding author.

E-mail address: [apamarques@liec.ufscar.br](mailto:apamarques@liec.ufscar.br) (A.P.A. Marques).

(PL) at room temperature are technologically interesting materials for applications including solid-state optoelectronic devices. Much interest has been evinced in the study of PL in amorphous and nanostructured materials since visible PL at room temperature was first observed in porous silicon [8]. Several amorphous compounds based on different metal oxianions with intense PL at room temperature have been reported [9]. Nevertheless, data are scarce on  $\text{BaMoO}_4$  thin films prepared by soft chemical processing. Considering that the polymeric precursor method has been successful in preparing oxide thin films, this work reports on the preparation, characterization and photoluminescent properties of  $\text{BaMoO}_4$  thin films prepared from polymeric precursors.

## 2. Experimental procedure

$\text{BaMoO}_4$  thin films were deposited onto Si substrates by the polymeric precursor method. A flow-chart representing the synthesis of  $\text{BaMoO}_4$  used in this study is outlined in Fig. 1. Molybdenum citrate was formed by the dissolution of molybdic acid ( $\text{MoO}_3$ —molybdenum trioxide) in an aqueous solution of citric acid under constant stirring at 60–80 °C to homogenize the molybdenum citrate solution. After homogenization of this solution, barium carbonate was dissolved and a stoichiometric amount added to the molybdenum citrate solution. The complex was well stirred for several hours at 60–80 °C to produce a clear, homogeneous solution. After the solution was homogenized, ethylene glycol was added to promote the citrate polymerization by polyesterification. With continued heating of 80–90 °C, the viscosity of the solution increased, albeit devoid of any visible phase separation. The molar ratio between

barium and molybdenum cations was 1:1. The citric acid/ethylene glycol mass ratio was set to 60:40. The viscosity of the deposition solution was adjusted to 15 mPa/s by controlling the water content.

Si wafers were used as substrates. The substrates were spin-coated by dropping a small amount of the polymeric precursor solution onto them. Rotation speed and spin time were fixed at 700 rpm for 3 s and 7200 rpm for 30 s, using a commercial spinner (spin-coater KW-4B, Chemat Technology). After spinning onto the substrates, the films were heat-treated at 200 °C between 2 and 16 h or at 600 °C for 2 h in a resistive furnace under air or, alternatively, at 600 °C for 10 min in a microwave oven. A total of 4 layers were deposited. The procedure was repeated for each layer.

$\text{BaMoO}_4$  thin films were characterized by X-ray diffraction (XRD) using  $\text{CuK}\alpha$  radiation in order to determine the structural evolution of the thin films upon heat-treatment. The optical reflectance of the thin films was measured in the wavelength range from 200 to 800 nm, using a UV-Vis-NIR (Cary 5G spectrophotometer). FTIR reflectance spectra for  $\text{BaMoO}_4$  thin films deposited on Si substrates were gathered in the frequency range of 400–2100  $\text{cm}^{-1}$  at room temperature using an Equinox/55 (Bruker) spectrometer equipped with a 30° specular reflectance accessory. Atomic force microscopy (AFM) was used to obtain a 3D image reconstruction of the surface of the sample. These images allow for accurate analysis and quantification of highly relevant parameters such as roughness and grain size. A Multi-Mode Nanoscope IIIa from Digital Instruments was used.

Finally, PL spectra of  $\text{BaMoO}_4$  thin films were collected with a U1000 Jobin-Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon counting system. The 488.0 nm exciting wavelengths of an argon ion laser was used. The maximum output power of the laser was 20 mW. All measurements were taken at room temperature.

## 3. Results and discussion

Fig. 2 shows the FTIR absorption spectra of all  $\text{BaMoO}_4$  thin films deposited in Si(100) and heat-treated in a resistive furnace or in a microwave oven. Measurements were carried out in the reflection mode. Next Nakamoto [10] shows that the  $\nu(\text{CO})$  stretching occurs at 2375–1100  $\text{cm}^{-1}$  and the  $\nu(\text{OCO})$  if stretching occurs at 1100–550  $\text{cm}^{-1}$ . In Fig. 2a and b is clear that undecomposed organic ligands are still present in the film, the spectra present several bands ascribing to carbonates groups. Vibration of around 1755  $\text{cm}^{-1}$  associated to the  $\text{C}_4\text{O}$  stretching mode for ester ( $\text{R}-\text{COO}-\text{R}$ ) could also be observed. The vibration around of 1680  $\text{cm}^{-1}$  is attributed to the vibration

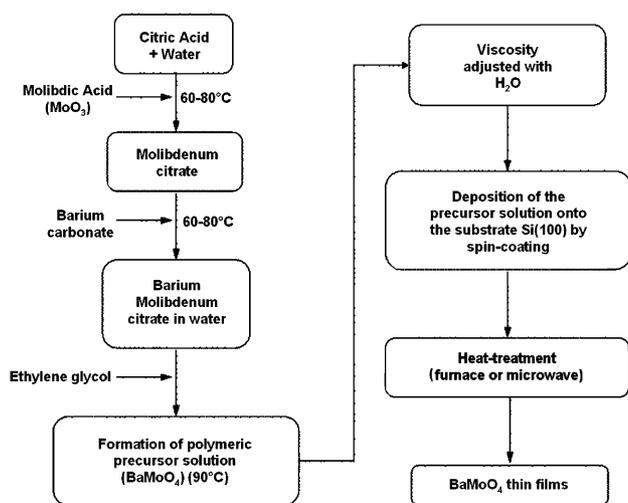


Fig. 1. Flow chart of the preparation of  $\text{BaMoO}_4$  thin films from polymeric precursors.

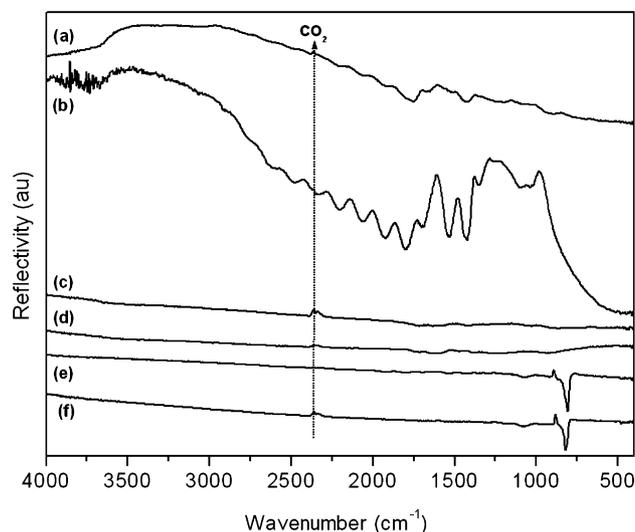


Fig. 2. FTIR absorption spectra of BaMoO<sub>4</sub> thin films deposited in Si(100) and heat-treated at 200 °C for 2 h (a), 4 h (b), 8 h (c) and 16 h (d) in a resistive furnace and heat-treated at 600 °C in a microwave for 10 min (e) and in a resistive furnace for 2 h (f).

asymmetric COO. The bands of around 1540 and 1430 cm<sup>-1</sup> are attributed to the vibration symmetric COO (Fig. 2a and b) [1]. The band at 2350 cm<sup>-1</sup> refers to the CO<sub>2</sub> atmospheric adsorbed. The spectra of Fig. 2c and d do not present these bands referent to carbonates groups, which prove that an treatment at 200 °C for 8 h is sufficient to eliminate the organic components and that the resulting phase is indeed a carbon-free intermediate inorganic amorphous phase. The spectrum of crystalline BaMoO<sub>4</sub> thin films (heat-treated at 600 °C) displays a very broad absorption band from 800 to 820 cm<sup>-1</sup> (Fig. 2e and f). This band is attributed to the Mo–O bonds of a solid oxide network [10]. The representation for the tetrahedral symmetry is  $\Gamma_{Td} = A_1(\nu_1) + E(\nu_2) + F_2(\nu_3) + F_2(\nu_4)$ , but only the  $F_2(\nu_3, \nu_4)$  modes are IR active. The  $F_2(\nu_3)$  vibrations are antisymmetric stretches, whereas the  $F_2(\nu_4)$  vibrations are bending modes. Therefore, the bands at 809 and 820 cm<sup>-1</sup> were assigned to  $F_2(\nu_3)$  antisymmetric stretching vibrations of BaMoO<sub>4</sub> thin films heat-treated at 600 °C in a resistive furnace or microwave, respectively. These bands have been reported to correspond to the Mo–O stretching vibration in the MoO<sub>4</sub><sup>2-</sup> tetrahedron [10].

Fig. 3 shows X-ray patterns of BaMoO<sub>4</sub> thin films deposited onto Si substrates after heat-treatment at 200 and 600 °C for different times. They correspond to the crystalline BaMoO<sub>4</sub> scheelite-type phase. In Fig. 3a–d, BaMoO<sub>4</sub> thin films heat-treated at 200 °C between 2 and 16 h were amorphous and no crystallized phases were observed. The diffraction peak (112) is the 100% peak, it is absent in Fig. 3a–d, indicating that these films were amorphous. Above 600 °C (Fig. 3e and f), the thin films consisted uniquely of BaMoO<sub>4</sub> phases, confirming

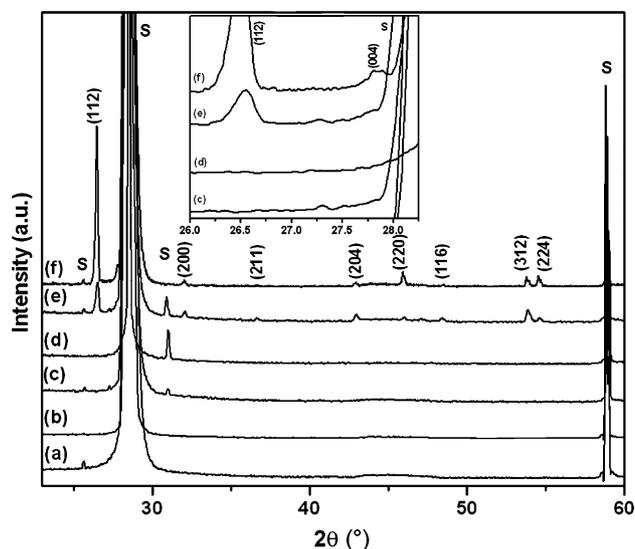


Fig. 3. X-ray diffraction patterns of BaMoO<sub>4</sub> thin films deposited in Si(100) and heat-treated at 200 °C for 2 h (a), 4 h (b), 8 h (c) and 16 h (d) in a resistive furnace and heat-treated at 600 °C in a microwave for 10 min (e) and in a resistive furnace for 2 h (f).

results published elsewhere [2,11]. The intensity of substrate peak changes according to thin film thickness: thin films with bigger thickness present minor substrate peak than thin films with smaller thickness. All diffraction peaks were indexed with the JCPDS database [12] and indicated the tetragonal symmetry. From the peak positions displayed in Fig. 3, the lattice parameters were calculated using a least-square refinement REDE93 program. The lattice parameters  $a$  and  $c$  for these BaMoO<sub>4</sub> thin films were found to be as  $a = 5.582(2)$  Å and  $c = 12.775(8)$  Å for the thin film heat-treated in a furnace and  $a = 5.581(2)$  Å and  $c = 12.805(13)$  Å heat-treated in microwave. These values are in good agreement with those corresponding to the structure of the bulk material ( $a = 5.5802$  Å and  $c = 12.821$  Å) [12].

Fig. 4 shows the transversal cross-section micrographs of the BaMoO<sub>4</sub> thin film on Si substrate by SEM. The BaMoO<sub>4</sub> thin films treated at 200 °C for 2, 4, 8 and 16 h have thicknesses of about 164, 308, 105 and 146 nm, respectively, and for thin films treated at 600 °C for 2 h in a furnace and 10 min in a microwave have of about 484 and 164, respectively, measured by transversal cross-section by SEM.

A detailed AFM analysis revealed differences in terms of surface morphology for BaMoO<sub>4</sub> thin films heat-treated at 200 °C and 600 °C (Fig. 5). The AFM analysis showed a considerable variation in the surface morphology between samples submitted to heat-treatment at 200 and 600 °C. It was clear from AFM analyses that the BaMoO<sub>4</sub> thin films heat-treated at 200 °C showed homogeneous surface morphology with very low roughness (2.2 nm). There was no evidence of granular

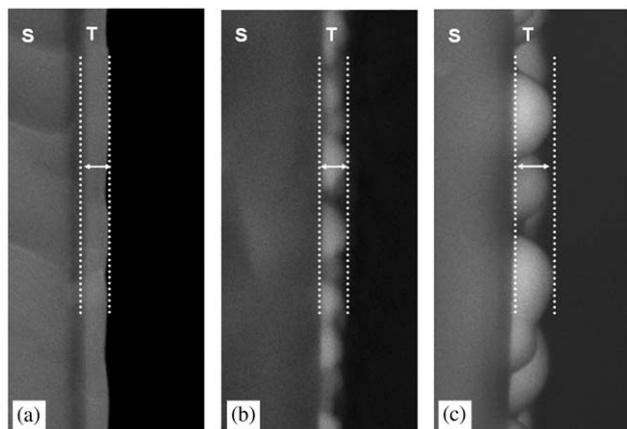


Fig. 4. SEM micrograph of BaMoO<sub>4</sub> thin films heat-treated at 200 °C for 4 h (a), heat-treated at 600 °C in a microwave for 10 min (b) and in a resistive furnace for 2 h (c), where *S* = substrate and *T* = thickness.

structure. Conversely, the surface morphology significantly changed upon heat-treatment at 600 °C. At this stage, nuclei coalescence took place accompanied by the formation of a granular structure thus increasing the roughness of the film (213.5 nm). This result was in good agreement with XRD data, which revealed significant crystallization after heat-treatment at 600 °C. The AFM analysis also showed that the BaMoO<sub>4</sub> thin films heat-treated at 600 °C presented homogeneous nucleation resulting in grain sizes between 280 and 320 nm.

Reflectivity spectra recorded in the 2.0–6.0 eV range for BaMoO<sub>4</sub> thin films are presented in Fig. 6. Two bands at 3.38 (367 nm) and 4.37 eV (284 nm) were observed for BaMoO<sub>4</sub> thin film crystalline treated at 600 °C. The band at 4.37 eV was attributed to electronic transitions within the MoO<sub>4</sub><sup>2-</sup> complex according to Spassky [13]. The band at 4.25 eV (292 nm) was attributed to electronic transitions within the MoO<sub>4</sub><sup>2-</sup>

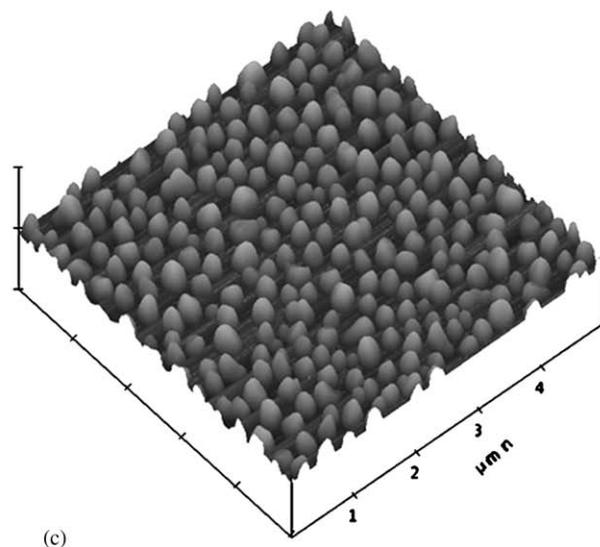
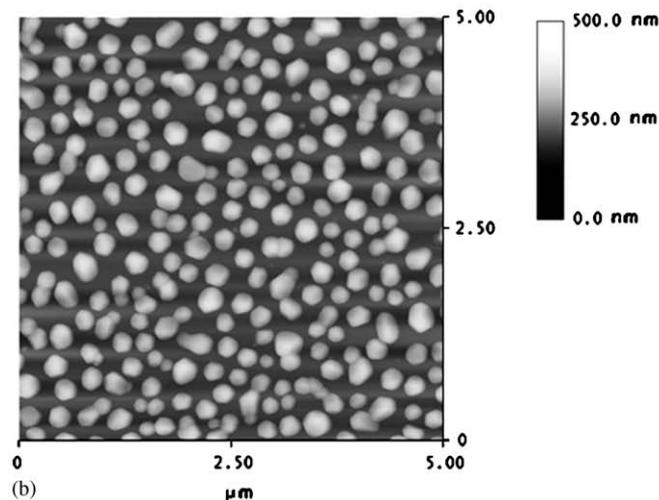
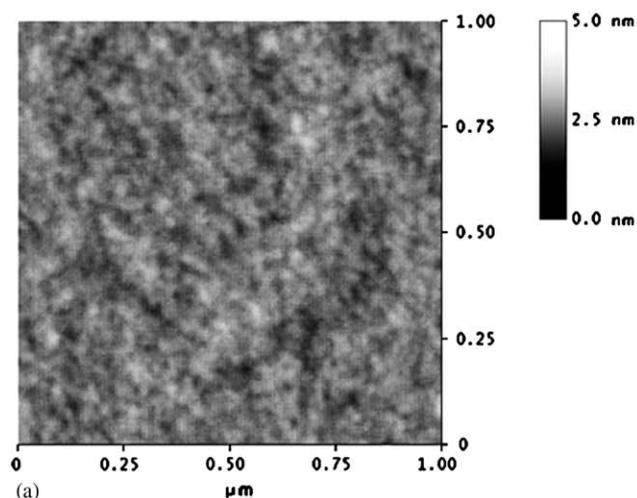


Fig. 5. AFM 2D images for the surfaces of BaMoO<sub>4</sub> thin films heat-treatment at 200 °C for 8 h (a), at 600 °C for 10 min in a microwave (b) and AFM 3D image of BaMoO<sub>4</sub> thin films at 600 °C in a microwave (c).

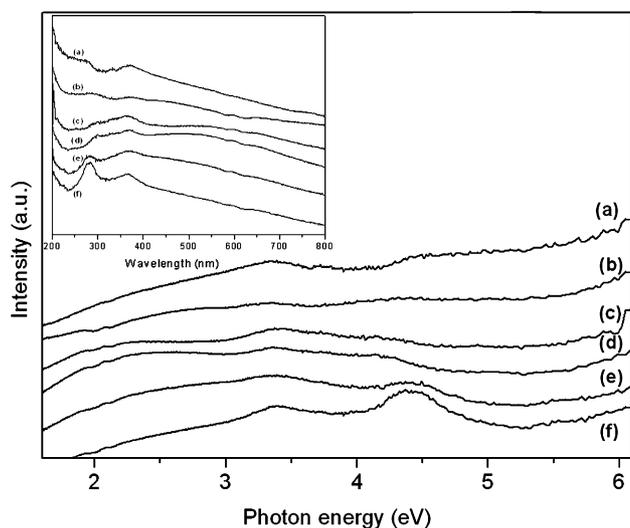


Fig. 6. Reflectivity spectra recorded in the 2.0–6.0 eV range of BaMoO<sub>4</sub> thin films heat-treated at 200 °C for 2 h (a), 4 h (b), 8 h (c) and 16 h (d) in a resistive furnace and heat-treated at 600 °C in a microwave for 10 min (e) and in resistive furnace for 2 h (f).

complex without noticeable contribution from cationic states by Spassky et al. [13]. A peak at 3.6 eV was observed in the PbMoO<sub>4</sub> but no in the CaMoO<sub>4</sub> and the BaMoO<sub>4</sub>. Kolobanov [14] observed similar situation for lead tungstate where at the edge of the fundamental absorption region reflectivity peak was observed that has no analogues in calcium and barium tungstates reflectivity spectra. Spassky et al. [13] showed that the dependence on sample orientation and comparison with excitons in lead halides was noticed after a study on the shift that peak as a function of the temperature. They were supposed that the peak at 3.6 eV in PbMoO<sub>4</sub> is also due to the creation of excitonic state in Pb<sup>2+</sup>. Therefore, although Spassky has not observed this peak in BaMoO<sub>4</sub> and the excitonic state between Pb<sup>2+</sup> and Ba<sup>2+</sup> were different, it is reasonable to assume that the peak observed at 3.38 eV in BaMoO<sub>4</sub> can also correspond to the creation of the excitonic state on Ba<sup>2+</sup>. One large band around 4.8 eV (258 nm) was observed for BaMoO<sub>4</sub> thin film amorphous treated at 200 °C for 2 and 4 h (Fig. 6a and b). This peak around 4.8 eV was attributed to organic ligands undecomposed present in the film [15].

The band gap ( $E_g$ ) was estimated by plotting  $(\alpha hv)^2$  as a function of  $(hv - E_g)$ , as it can be seen in Fig. 7. The optical absorption coefficient,  $\alpha$  may be obtained by  $\alpha = [1/d(\ln(1/T))]$ , where  $d$  is the thickness of the film and  $T$  the transmittance [16]. Zhang et al. [17] calculate the density-functional for CaMoO<sub>4</sub> using the linearized-augment-plane-wave method and the results indicate that CaMoO<sub>4</sub> have direct band gaps. The  $\alpha$  value obtained for BaMoO<sub>4</sub> was major at  $10^4$ , and Sian et al.

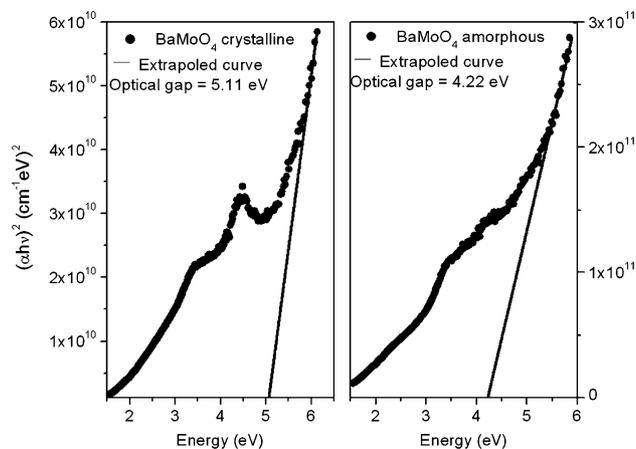


Fig. 7. Reflectivity spectra recorded in the 2.0–6.0 eV range of BaMoO<sub>4</sub> thin films heat-treated at 200 °C for 8 h (●) and 600 °C for 2 h in a resistive furnace (●) and plots of  $(\alpha hv)^2$  vs. photon energy  $hv$ . The band gap energy ( $E_g$ ) is deduced from extrapolation of the straight line up to  $(\alpha hv)^2 = 0$ .

Table 1  
 $E_g$  data of BaMoO<sub>4</sub> thin films

Samples	$E_g$ (eV)
BaMoO <sub>4</sub> —200 °C/2 h	4.77
BaMoO <sub>4</sub> —200 °C/4 h	4.73
BaMoO <sub>4</sub> —200 °C/8 h	4.22
BaMoO <sub>4</sub> —200 °C/16 h	4.82
BaMoO <sub>4</sub> —600 °C/2 h (furnace)	4.88
BaMoO <sub>4</sub> —600 °C/10 min (microwave)	5.11

[18] show the  $\alpha$  values major at  $10^4$ , confirm the existence of direct band gaps. One similarity between CaMoO<sub>4</sub> and BaMoO<sub>4</sub>; therefore, the same comportment is expected for both compounds. Zhang et al. [17] also showed that the valence and conduction bands near the band gap are dominated by molecular orbitals associated with the MoO<sub>4</sub><sup>2-</sup> ions, where  $\alpha \approx 2$ . The value for CaMoO<sub>4</sub> of band gap calculated for Zhang et al. [17] were underestimated and the value was 3.41 eV. In this work the calculated  $E_g$  values for BaMoO<sub>4</sub> starting from experimental dates were 4.22 and 5.11 eV for amorphous and crystalline films, respectively. In spite of differences in these values calculated experimentally and theoretically, this value obtained experimentally is acceptable because the value theoretically is one value underestimated [17]. The gap value for CaWO<sub>4</sub> obtained experimentally was 5.27 eV [7] and by calculated theoretically was 4.09 eV [17], showing that the difference between the value obtained by plotting  $(\alpha hv)^2$  as a function of  $(hv - E_g)$  starting from the experimental dates and the value theoretical using the linearized-augment-plane-wave method is acceptable. The band

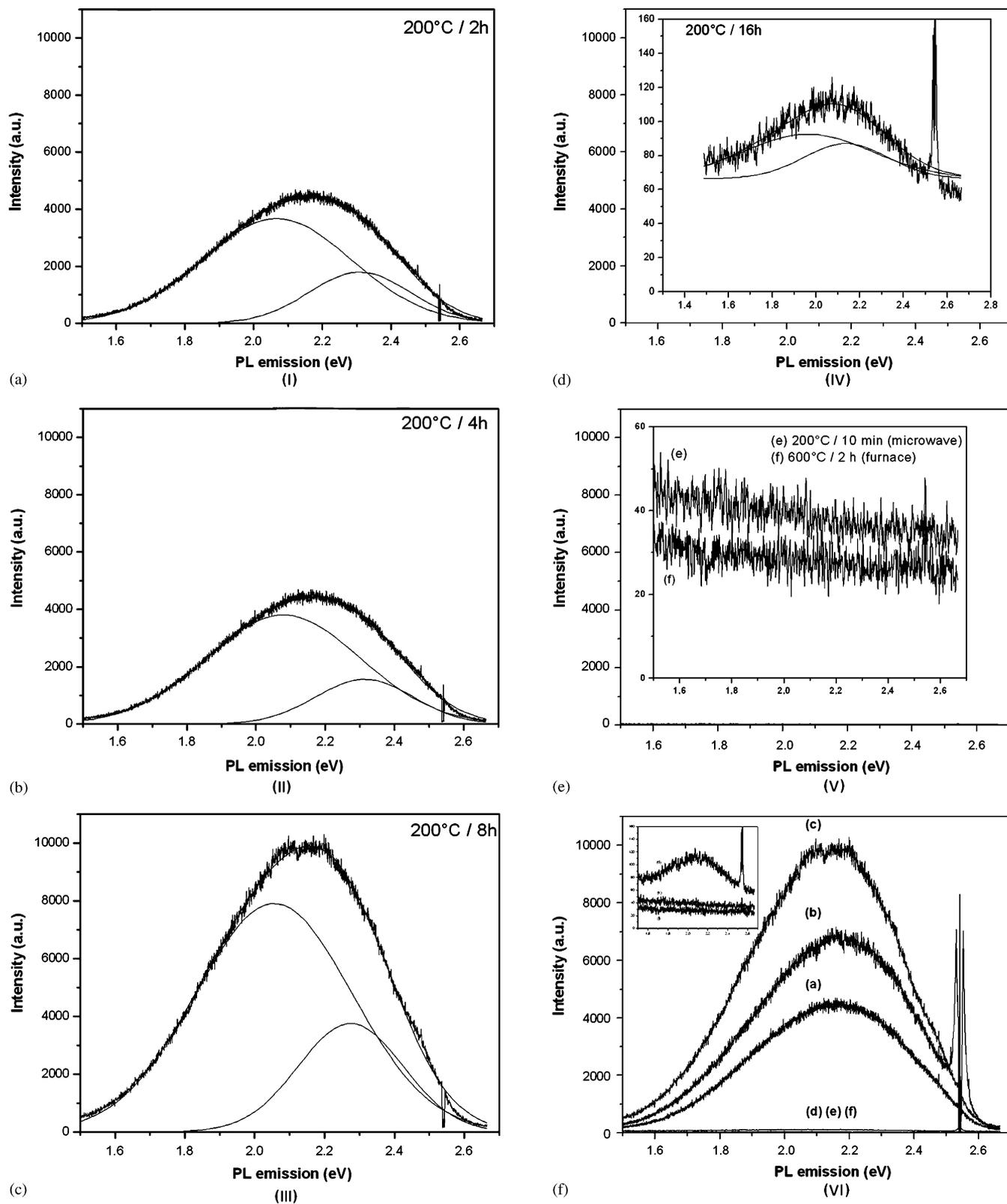


Fig. 8. Room-temperature PL spectra of BaMoO<sub>4</sub> thin films excited with the 488 nm line of an argon ion laser: I—heat-treated at 200 °C for 2 h (a), II—heat-treated at 200 °C for 4 h (b), III—heat-treated at 200 °C for 8 h (c), IV—heat-treated at 200 °C for 16 h (d), V—heat-treated at 600 °C in a microwave for 10 min (e) and in a resistive furnace for 2 h (f) and VI—PL spectra of all BaMoO<sub>4</sub> thin films.

gap decreases in the amorphous material with relation of the crystalline because the amorphous materials have the crystal orbital not degenerated due which there has been a loss of symmetry that is crystalline. In the crystal orbital of the amorphous material were formed new levels of energy, and this new levels were responsible for the band gap change. The cause of band gap change will be studied more deeply in a new paper that is being prepared. Fig. 7 showed for the BaMoO<sub>4</sub> thin film crystalline two bands around of 3.4 and 4.4 eV, this band are the same presented for this material in the reflectivity spectra. The  $E_g$  data of the BaMoO<sub>4</sub> thin films are given in Table 1.

Fig. 8 illustrates PL spectra recorded at room temperature for BaMoO<sub>4</sub> thin films heat-treated at 200 or 600 °C for different periods of time. The samples were excited by the 488 nm line of an argon ion laser. The band emission wavelength of BaMoO<sub>4</sub> thin films was around 2.13 eV. The bands were broad and intense, mostly for the amorphous thin film heat-treated at 200 °C for 8 h (Fig. 8c). The intensity of the PL emission significantly increased (about 660 times) comparing the film heat-treated at 200 °C for 8 h with that heat-treated at 600 °C. The PL emission of BaMoO<sub>4</sub> crystalline thin films heat-treated in a resistive furnace or microwave oven was virtually null comparing to that of amorphous films heat-treated at 200 °C/8 h (Fig. 8c). The PL intensity of the thin film heat-treated at 200 °C for 8 h was 1.4, 2.2 and 93.5 times higher comparing to the intensity of films heat-treated at 200 °C for 4, 2 and 16 h, respectively. The PL intensity is linked to the thermal treatment history of the films, and therefore, to their structural disorder. The best PL emission was obtained from the structure that was neither completely amorphous (200 °C/2 h) nor fully ordered (600 °C). Although crystalline samples are not photoluminescent under excitation by the 488 nm line of an argon ion laser used in this study, similar compounds exhibit luminescence with different light sources [13].

Orhan et al. [19] showed that the emission bands from SrWO<sub>4</sub> can be decomposed into two components, two broadbands. In this case, molybdenum is similar to tungsten, therefore your emission bands also are decomposed in two components with their maxima around 2.07 eV (600 nm) (orange-red), peak 1, and 2.34 eV (530 nm) (green), peak 2, as illustrated on Fig. 8 I–IV. The orange-red band represents 75%, 76%, 79% and 66% of the total PL band area for the thin films heat-treated at 200 °C for 2, 4, 8 and 16 h, respectively (see Table 2). This decomposition of the broad PL emission band indicates that with the degree of structural disorder, the fraction of the red emission band increases. The thin film treated at 200 °C/8 h possesses the biggest red area because it is a transition between completely amorphous structures and completely ordered one, similar to SrWO<sub>4</sub> showed for Orhan

Table 2  
Evolution of the PL red fraction with the structural disorder

Samples	Peak 1 (eV)	Peak 2 (eV)	RA/FA
BaMoO <sub>4</sub> —200 °C/2 h	2.06	2.31	0.75
BaMoO <sub>4</sub> —200 °C/4 h	2.07	2.31	0.76
BaMoO <sub>4</sub> —200 °C/8 h	2.05	2.28	0.79
BaMoO <sub>4</sub> —200 °C/16 h	1.96	2.14	0.66

RA, FA are areas of the red decomposed band and fitted band, respectively.

[19]. The components of the PL emission bands are probably linked to specific atomic arrangements. Similar to SrWO<sub>4</sub>, as studied by Orhan [19], the structural transformations of the BaMoO<sub>4</sub> occurring from disordered to ordered phases start from the early stage of the polyesterification of the citrate solution contain the molybdenum and barium ions. The molybdenum, who is the lattice former, tends ideally to bond with four oxygens, but before it reaches this ideal configuration there exist various coordination numbers for Mo in the structure. When the crystallization is reached, only MoO<sub>4</sub> clusters exist and the PL vanishes, showing that a complete order is not suitable for a good PL emission. Before the crystallization, the structure is a mixture of MoO<sub>x</sub> clusters ( $x =$  mostly 3 and 4) intercalated by Ba atoms. The higher the heat treatment temperature, the more frequent the MoO<sub>4</sub> conformation and the more ordered the structure, confirmed by FTIR and reflectivity spectra. The PL spectra show that a complete disorder is not favorable for a high PL emission, as the spectrum of the 200 °C/8 h sample is much higher than one of the 200 °C/2 h sample.

According to Pontes et al. [20], if the photoluminescent signal is related to the amorphous structure, as the system is organized, the signal fades away as confirmed by Fig. 8d. This conclusion is a good indication that the PL of BaMoO<sub>4</sub> thin films obtained by the polymeric precursor method originates from inorganic amorphous phases with photoluminescent properties.

#### 4. Conclusions

Intense visible PL at room temperature was observed in highly amorphous BaMoO<sub>4</sub> thin films prepared by the polymeric precursor method and heat-treated at relatively low temperatures (200 °C/8 h). Processing thin films in such a manner does not require expensive equipment or reagents, deposition in high vacuum chambers or special atmospheric control. The results revealed that BaMoO<sub>4</sub> is a highly promising candidate material for PL applications.

## Acknowledgments

The authors gratefully acknowledge the financial support granted by the Brazilian Research Financing Institutions FAPERN, CEPID, CNPq and PRONEX. The authors gratefully acknowledge the Miryam R. Joya, of Departamento de Física—Universidade Federal de São Carlos for the collaboration in the article accomplishing the measures of PL.

## References

- [1] F.M. Pontes, M.A.M.A. Maurera, A.G. Souza, E. Longo, E.R. Leite, R. Magnani, M.A.C. Machado, P.S. Pizani, J.A. Varela, *J. Eur. Ceram. Soc.* 23 (2003) 3001.
- [2] J.H. Ryu, J.W. Yoon, C.S. Lim, W.C. Oh, K.B. Shim, *J. Alloys Comp.* 390 (1–2) (2005) 245.
- [3] W.S. Cho, M. Yoshimura, *Solid State Ionics* 100 (1–2) (1997) 143.
- [4] C.T. Xia, V.M. Fuenzalida, R.A. Zarate, *J. Alloys Comp.* 316 (1–2) (2001) 250.
- [5] P. Yang, G.Q. Yao, J.H. Lin, *Inorg. Chem. Commun.* 7 (3) (2004) 389.
- [6] S.B. Mikhlin, A.N. Mishin, A.S. Potapov, P.A. Rodnyi, A.S. Voloshinovskii, *Nucl. Instrum. Methods A* 486 (1–2) (2002) 295.
- [7] M.A.M.A. Maurera, A.G. Souza, L.E.B. Soledade, F.M. Pontes, E. Longo, E.R. Leite, J.A. Varela, *Mater. Lett.* 58 (5) (2004) 727.
- [8] L.T. Canham, *J. Appl. Phys. Lett.* 57 (1990) 1046.
- [9] E.R. Leite, F.M. Pontes, E.J.H. Lee, R. Aguiar, E. Longo, D.S.L. Pontes, M.S.J. Nunes, P.S. Pizani, F. Lanciotti Jr., et al., *J. Mol. Struct.-THEOCHEM* 668 (2–3) (2004) 87.
- [10] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, fourth ed, Wiley, New York, 1986.
- [11] V. Thangadurai, C. Knittlmayer, W. Weppner, *Mater. Sci. Eng. B-Solid* 106 (2004) 228.
- [12] JCPDS No. 29-0193.
- [13] D.A. Spassky, S.N. Ivanov, V.N. Kolobanov, V.V. Mikhailin, V.N. Zemskov, B.I. Zadneprovski, L.I. Potkin, *Radiat. Meas.* 38 (2004) 607.
- [14] V.N. Kolobanov, I.A. Kamenskikh, V.V. Mikhailin, I.N. Shpinkov, D.A. Spassky, B.I. Zadneprovsky, L.I. Potkin, G. Zimmerer, *Nucl. Instrum. Meth. A* 486 (1–2) (2002) 496.
- [15] R.M. Silverstein, G.C. Bassler, T.C. Morrill, *Identificação Espectrométrica de Compostos Orgânicos*, 5th ed, Tradução de R. B. Alencastro, Rio de Janeiro, Guanabara Koogan, 1994.
- [16] M. Sreemany, S. Sem, *Mater. Chem. Phys.* 83 (2004) 169.
- [17] Y. Zhang, N.A.W. Holzwarth, R.T. Williams, *Phys. Rev.* 57 (20) (1998) 12738.
- [18] T.S. Sian, G.B. Reddy, *Solar Energy Mater. Solar Cells* 82 (2004) 375.
- [19] E. Orhan, M. Anicete-Santos, M.A.M.A. Maurera, F.M. Pontes, C.O. Paiva-Santos, A.G. Souza, J.A. Varela, P.S. Pizani, E. Longo, *Chem. Phys.* 312 (1–3) (2005) 1.
- [20] F.M. Pontes, C.D. Pinheiro, E. Longo, E.R. Leite, S.R. de Lazaro, R. Magnani, P.S. Pizani, T.M. Boschi, F. Lanciotti, *J. Lumin.* 104 (3) (2003) 175.