

Photoluminescent BaMoO₄ nanopowders prepared by complex polymerization method (CPM)

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Abstract

The BaMoO₄ nanopowders were prepared by the Complex Polymerization Method (CPM). The structure properties of the BaMoO₄ powders were characterized by FTIR transmittance spectra, X-ray diffraction (XRD), Raman spectra, photoluminescence spectra (PL) and high-resolution scanning electron microscopy (HR-SEM). The XRD, FTIR and Raman data showed that BaMoO₄ at 300 °C was disordered. At 400 °C and higher temperature, BaMoO₄ crystalline scheelite-type phases could be identified, without the presence of additional phases, according to the XRD, FTIR and Raman data. The calculated average crystallite sizes, calculated by XRD, around 40 nm, showed the tendency to increase with the temperature. The crystallite sizes, obtained by HR-SEM, were around of 40–50 nm. The sample that presented the highest intensity of the red emission band was the one heat treated at 400 °C for 2 h, and the sample that displayed the highest intensity of the green emission band was the one heat treated at 700 °C for 2 h. The CPM was shown to be a low cost route for the production of BaMoO₄ nanopowders, with the advantages of lower temperature, smaller time and reduced cost. The optical properties observed for BaMoO₄ nanopowders suggested that this material is a highly promising candidate for photoluminescent applications.

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1. Introduction

BaMoO₄ can have both structures, tetragonal distorted scheelite (β) and cubic (α), depending of temperature applied [1]. BaMoO₄ with a scheelite structure is an important material that presents a high application potential in various fields. Recently, crystal structures based on the scheelite type have attracted much interest because of their applications as a scintillating medium and in other electro-optical devices (i.e., solid-state laser and optical fibers) [2]. Aiming at a deeper understanding of the

luminescent properties of these type materials, numerous investigations have been carried out [3]. These materials have been synthesized by a variety of techniques, such as the Czochralski technique [1], spontaneous crystallization method [4] and calcinations method [5,6]. However, BaMoO₄ powders are relatively large and lack homogeneous morphology and composition. Such lack of homogeneity is due to the MoO₃ tendency to vaporize at high temperatures [7]. In the Complex Polymerization Method (CPM) this problem is reduced because the synthesis occurs at a low temperature and the immobilization of the metal complexes in such rigid organic polymeric networks can reduce the metal segregation, thus ensuring the compositional homogeneity at the molecular scale. This is of vital

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importance for the synthesis of multicomponent oxides with complicated compositions, since the chemical homogeneity, with respect to the cation distribution throughout the entire gel system, often determines the compositional homogeneity of the final multicomponent oxides [8]. Preparation of BaMoO₄ nanopowders by soft chemical process and displaying a high chemical homogeneity is very limited. Besides the successful synthesis of nanopowders by the CPM, this work also reports on the characterization and photoluminescent properties of BaMoO₄ nanopowders.

2. Experimental

BaMoO₄ was obtained by the CPM. A flow chart representing the synthesis of BaMoO₄ used in this study is outlined in Fig. 1. Molybdenum citrate was formed by the dissolution of MoO₃, molybdenum trioxide, in an aqueous solution of citric acid under constant stirring at 60–80 °C to homogenize the solution.

After the homogenization, barium carbonate was dissolved and the proper stoichiometric amount was 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 polyesterification. With continued heating at 80–90 °C, the viscosity of the solution increased, albeit devoid or any visible phase separation. The molar ratio between barium and molybdenum cations was 1:1, and the ratio between citric acid and the sum of metals was 6:1. The citric acid/ethylene glycol mass ratio was set at 60:40.

After partial evaporation of the water, the resin was heat treated at 300 °C for 2 h, in a static atmosphere, leading to the partial decomposition of the polymeric gel, forming an expanded resin, constituted of partially pyrolyzed material. The product was removed from the beaker and grinded.

The powders were annealed at 300, 350, 400, 450, 500, 550, 600, 700, 800 and 900 °C for 2 h in static atmosphere at a heating rate of 5 °C/min.

BaMoO₄ nanopowders were characterized by X-ray diffraction (XRD) using Cu K α radiation in order to determine the structural evolution and the unit cell volume of the nanopowders. The average crystallite diameter (D_{cryst}) of the heat-treated powders was determined by XRD, using from the (112) diffraction peak of the BaMoO₄ phase (2θ at around 26.5°), according to the Scherrer equation (Eq.(1)), as described by Suryanarayana [9],

$$B = k\lambda / (D_{\text{cryst}} \cos \theta), \quad (1)$$

where B is the full width at half maximum (FWHM), θ the Bragg angle, k is a constant and λ is the wavelength of the Cu K α radiation. The microstructure and surface morphology of the nanocrystalline powders of the BaMoO₄ heat treated at 700 °C were observed by high-resolution scanning electron microscopy (HR-SEM) using an Field Emission – Supra35 Gemini-Zeiss equipment.

The BaMoO₄ FTIR transmittance spectra were determined at the 400–2100 cm⁻¹ frequency range at room temperature, using an Equinox/55 (Bruker) spectrometer.

The Raman spectroscopy data were obtained at room temperature by a RFS/100/S Bruker FT-Raman equipment with spectral resolution of 4 cm⁻¹ attached to a Nd:YAG laser promoting an excitation light of 1064 nm, in the frequency range of 100–1000 cm⁻¹.

The photoluminescence (PL) spectra of the BaMoO₄ nanopowders were collected with a U1000 Jobin-Yvon double monochromator coupled to cooled GaAs photomultiplier and a conventional photon counting system. The 488.0 nm exciting wavelength of an argon ion laser was used. The maximum output power of the laser was 20 mW. All measurements were taken at room temperature.

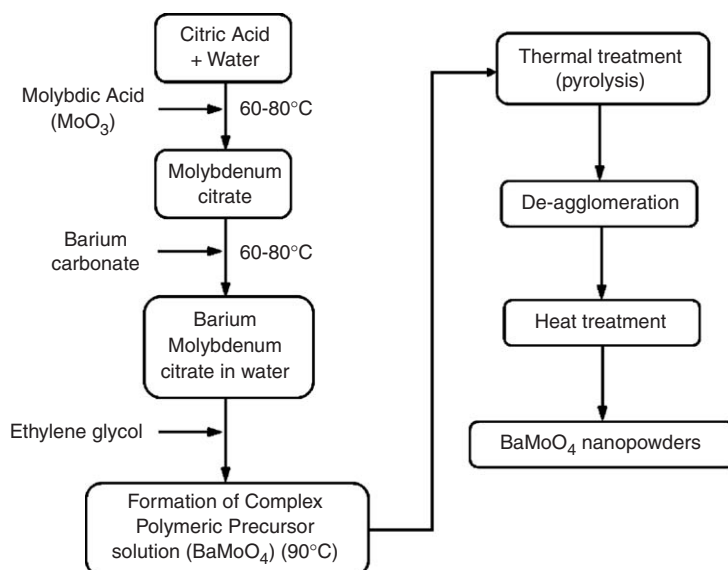


Fig. 1. Flowchart representing the procedure for the synthesis of BaMoO₄ nanopowders.

3. Results and discussion

BaMoO₄ has a scheelite crystal structure with tetragonal symmetry C_{4h}⁶ at room temperature. Its phase transition from tetragonal scheelite (β) to cubic structure (α) takes place at 1873 °C [1]. Experiments on heating and cooling BaMoO₄ crystals revealed that the above-mentioned $\beta \leftrightarrow \alpha$ phase transition was reversible. In the experimental methods which require high temperature reactions, the presence of this phase transition results in difficulties with growing BaMoO₄ single crystals from the melt.

Methods for the synthesis of BaMoO₄ are given in Table 1. In the Czochralski [1] method, the spontaneous crystallization method [4] and in the calcinations method reported by Hitoki [5], high temperatures and long reaction times are necessary for the production of binary oxide. The calcination method described by Hasan [6] utilizes lower temperature, around 450 °C, but the reaction products contain an additional phase, BaO₂·8H₂O. In the method used by Nassif [10] the temperature is of around 600 °C,

but high reaction times are required. In the present work, the temperature and reaction time used are low, respectively, around 500 °C and 2 h, and furthermore, the reaction products do not present any additional phase. Therefore, CPM was shown to be a low cost route for the production of BaMoO₄, at a lower temperature and reaction time.

Fig. 2 shows the XRD patterns of the BaMoO₄ nanopowders heat treated at different temperatures. In Fig. 2a, the BaMoO₄ at 300 °C for 2 h was amorphous and no crystalline phases were observed. At 400 °C and higher temperatures (Fig. 2b–e), the nanopowders could be identified as crystalline BaMoO₄ displaying single scheelite-type phases [3,10–13]. All diffraction peaks were indexed according to the JCPDS database [13] and pointed to the tetragonal symmetry.

The CPM was shown to be efficient for the synthesis of BaMoO₄ nanopowders. From the peak positions displayed in Fig. 2, the lattice parameters were calculated using the least square refinement from the REDE93 program. The lattice parameters *a* and *c* for these BaMoO₄ powders are also close to the values reported for bulk material (*a* = 5.5802 Å and *c* = 12.821 Å) [13].

Table 2 presents the lattice parameters *a* and *c* and the mean crystallite sizes for the BaMoO₄ nanopowders heat treated at different temperatures, the values are near to 40 nm. The calculated mean crystallite sizes showed the tendency to increase with the heat treatment temperature.

Fig. 3 presents a HR-SEM micrograph of BaMoO₄ powders heat treated at 700 °C. This figure shows an agglomerate of individual BaMoO₄ particles, whose crystallite sizes are of around of 40–50 nm.

The spontaneous Raman spectra with the assignments of the Raman-active vibration modes of the BaMoO₄

Table 1
Barium molybdate synthesis methods

| Method | Temperature (°C) | Time (h) | Synthesis products |
|---|------------------|----------|---|
| Czochralski [1] | 1100–1200 | 30–40 | BaMoO ₄ |
| Spontaneous crystallization [4] | 950 | 72 | BaMoO ₄ |
| Calcination [5] | 900 | 24 | BaMoO ₄ |
| Calcination [6] | 450 | 3 | BaMoO ₄ , BaO ₂ ·8H ₂ O |
| BaCl ₂ + Na ₂ MoO ₄ [10] | 600 | 72 | BaMoO ₄ |
| CPM ^a | 400–500 | 2 | BaMoO ₄ |

^aThe present work.

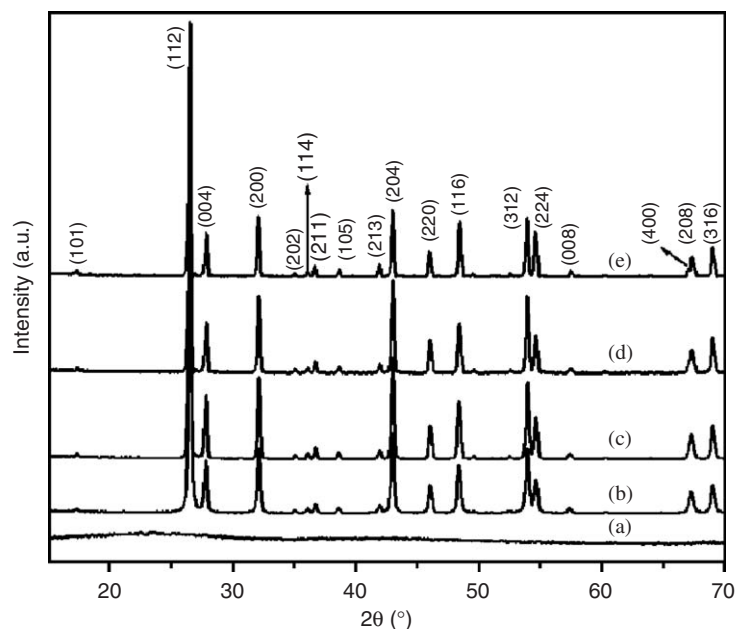


Fig. 2. X-ray diffraction patterns of BaMoO₄ nanopowders heat treated at (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C and (e) 700 °C.

Table 2
Composition, crystallite sizes and comparison of tetragonal lattice constants of tetragonal structure^a of BaMoO₄ nanopowders prepared by the CPM method and heat treated at different temperatures

| Sample | Crystallite sizes ^b (nm) | Lattice constants (Å) | |
|----------------------------|--|-----------------------|-----------|
| | | <i>a</i> | <i>c</i> |
| BaMoO ₄ -400 °C | 35 ± 1.8 | 5.5725(5) | 12.833(2) |
| BaMoO ₄ -500 °C | 40 ± 2.1 | 5.5739(6) | 12.83(2) |
| BaMoO ₄ -600 °C | 44 ± 2.3 | 5.5770(7) | 12.813(3) |
| BaMoO ₄ -700 °C | 47 ± 2.4 | 5.579(1) | 12.811(4) |

^a*a* = 5.5802 Å and *c* = 12.821 Å [13].

^bCalculated using the (112), 100% diffraction peak.

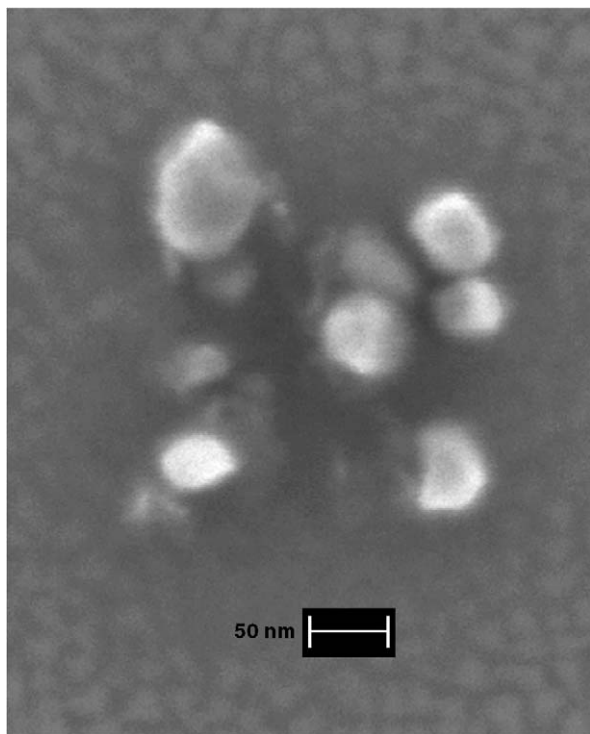


Fig. 3. HR-SEM micrograph of BaMoO₄ nanopowders heat treated at 700 °C for 2 h.

nanopowders are presented in Fig. 4 and detailed in Table 3. According to Basiev [1], the primitive cell of BaMoO₄ includes two formula units. The [MoO₄]²⁻ ionic group, with strong covalent Mo–O bonds, is peculiar to the BaMoO₄ scheelite structure. Due to weak coupling between the [MoO₄]²⁻ ionic group and the Ba²⁺ cations, the vibrational modes observed in the spontaneous Raman spectra of BaMoO₄ scheelite crystals can be divided into two groups, internal and external modes.

The internal vibrons correspond to the vibrations within the [MoO₄]²⁻ group, with an immovable mass center. The external or lattice phonons correspond to the motion of the Ba²⁺ cations and the rigid molecular unit. [MoO₄]²⁻ tetrahedral in free space have *T_d*-symmetry.

The scheelite primitive cell presents 26 different vibration modes: $\Gamma_{Td} = 3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u$, but only (*A_g*, *B_g* and *E_g*) are Raman-active, while the odd modes (*4A_u* and *4E_u*) can be registered only in the infrared spectra. The three *B_u* vibrations are silent modes; one *A_u* and one *E_u* modes are acoustic vibrations. The Raman spectra showed the well-resolved sharp peaks for the BaMoO₄ nanopowders treated at 500–700 °C, indicating that the synthesized powders were highly crystallized.

In the Raman spectra of BaMoO₄ nanopowders annealed at 300 °C it is clear that undecomposed organic ligands are still present. The Raman spectra of BaMoO₄ heat treated at 400 °C does not present such well-resolved sharp peaks, but its crystallization was observed by XRD. Probably, during the Raman experiment, the PL of the material overlapped with the peaks of the Raman spectra.

Fig. 5 shows the FTIR spectra of the BaMoO₄ nanopowders. Measurements were carried out in the transmittance mode. The representation for tetrahedral symmetry is $\Gamma_{Td} = A_1(\nu_1) + E(\nu_2) + F_2(\nu_3) + F_2(\nu_4)$, but only the *F₂*(*ν₃*, *ν₄*) modes are IR active. The *F₂*(*ν₃*) vibrations are the antisymmetric stretches, and the *F₂*(*ν₄*) vibrations are bending modes. From the spectrum of BaMoO₄ annealed at 300 °C (Fig. 5a), it is clear that undecomposed organic ligands are still present in the powders. This spectra present several bands ascribe to carbonates groups, second Nakamoto [14], the *ν*(CO) stretching occur at 2375–1100 cm⁻¹ and the *ν*(OCO) stretching occur at 1100–550 cm⁻¹. The spectra of the BaMoO₄ heat treated at 400–700 °C (Fig. 5b–e) display a very broad absorption band from 800 to 870 cm⁻¹. These bands for the BaMoO₄ nanopowders heat-treated at 400–700 °C are assigned to *F₂*(*ν₃*) antisymmetric stretch vibrations, which were reported to be ascribed to the Mo–O stretching vibration in MoO₄²⁻ tetrahedra [14]. After being submitted to the heat treatments at 400, 500, 600 and 700 °C (Fig. 5b–e), the BaMoO₄ samples present well-defined bands attributed to the Mo–O bonds. With the increase of the heat treatment temperature, the crystalline structure is increasingly ordered and the bands attributed to the Mo–O bonds showed a better definition, a characteristic confirmed by XRD and Raman spectroscopy.

Fig. 6 illustrates the PL spectra recorded at room temperature for the BaMoO₄ nanopowders heat treated at different temperatures, 300–900 °C, for 2 h. The samples were excited by the 488 nm line of an argon ion laser. The PL emission characteristics were broad and intense bands.

The BaMoO₄ emission bands peaked at a wavelength of about 2.15 eV for the amorphous nanopowders and around 2.26 eV for the crystalline nanopowders. The PL emission spectra could be decomposed into two Gaussian-shaped curves, ascribed to red and green emission bands.

The sample that presented the most intense red emission band was the one heat treated at 400 °C for 2 h (Fig. 6I, II). As for the most intense green emission band, it corresponded to the sample calcined at 700 °C for 2 h (Fig. 6III, IV). The intensity of the PL emission significantly increased

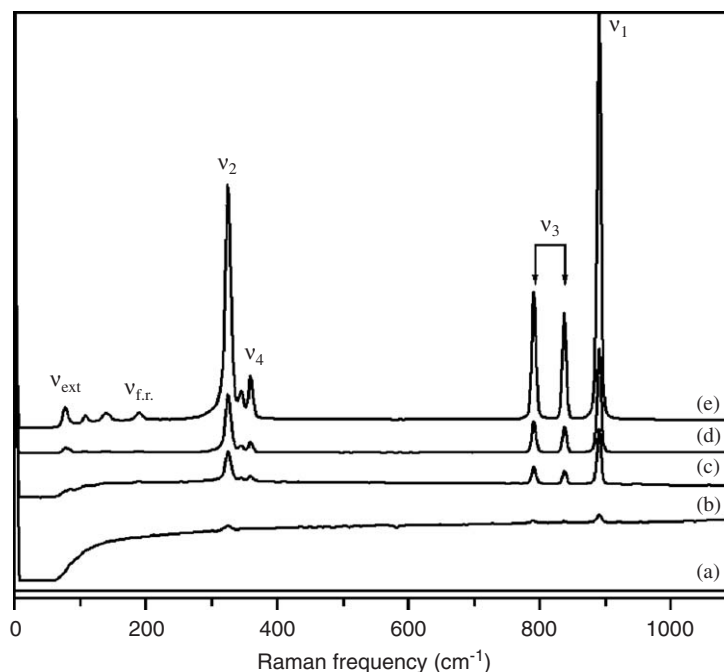


Fig. 4. Spontaneous Raman spectra of BaMoO₄ nanopowders heat treated at (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C and (e) 700 °C.

Table 3
Raman mode frequencies in BaMoO₄ nanopowders heat treated at different temperatures

| Lattice mode symmetry C _{4h} ⁶ | BaMoO ₄ | | | Assignments |
|--|-------------------------|---------------------------|-------------------------------|---|
| | 500–700 °C ^a | 1100–1200 °C ^b | Room temperature ^c | |
| A _g | 891 | 892 | 888 | v ₁ (A ₁) |
| B _g | 838 | 837 | 835 | v ₃ (F ₂) |
| E _g | 791 | 791 | 789 | |
| E _g | 359 | 358 | 361 | v ₄ (F ₂) |
| B _g | 346 | 345 | 348 | |
| B _g | 326 | 324 | 323 | v ₂ (E) |
| A _g | 325 | 324 | 323 | |
| E _g | 190 | 188 | 187 | v _{f.r.} (F ₁) free rotation |
| B _g | 141 | 137 | 133 | v _{ext.} —external modes MoO ₄ ²⁻ and Ba ²⁺ motions |
| E _g | 107 | 110 | 107 | |
| B _g | 78 | 76 | — | |
| E _g | 76 | 74 | — | |

^aThe present work.

^bCzocharalski method [1].

^cElectrochemical preparation of BaMoO₄ solid solution films at room temperature [11].

(about 18 times) comparing the powders heat treated at 400 °C for 2 h with the sample heat treated at 600 °C. The PL intensity of the nanopowders heat treated at 400 °C for 2 h was 1.6, 1.8, 11.9, 9.1, 10.2, 18.3, 3.1, 4.3 and 3.9 times higher than the intensity of the samples heat treated at 300, 350, 450, 500, 550, 600, 700, 800 and 900 °C for 2 h, respectively.

The PL intensity and the band emission wavelength depend on the thermal treatment history of the powders, and therefore, to their structural disorder or order. Fig. 6 showed that the most intense PL intensity for the red and green emission correspond to the samples heat 400 and

700 °C, respectively. The highest red emission PL was obtained from the structure that was neither completely amorphous (300 °C) nor fully ordered (600 °C). The most crystalline sample (700 °C) presented the highest green emission PL.

In this work, it was observed that the BaMoO₄ samples with the most intense PL in the red region possess the biggest red area (0.65) and the samples with the highest PL intensity in the green region display the biggest green area (0.74). These results are in agreement with the work of Marques et al. [15], in which the BaMoO₄ thin film with the highest PL intensity possessed the biggest red area. The

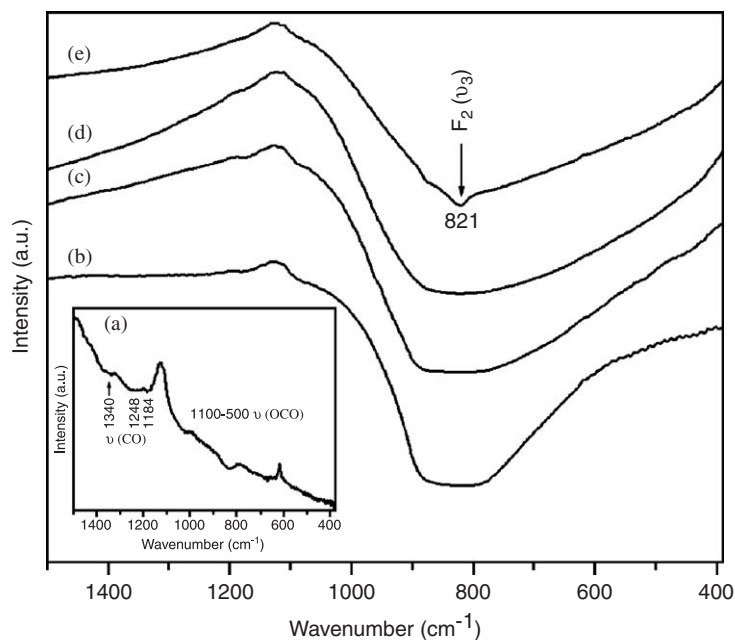


Fig. 5. FTIR absorption spectra of BaMoO₄ nanopowders heat treated at (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C and (e) 700 °C.

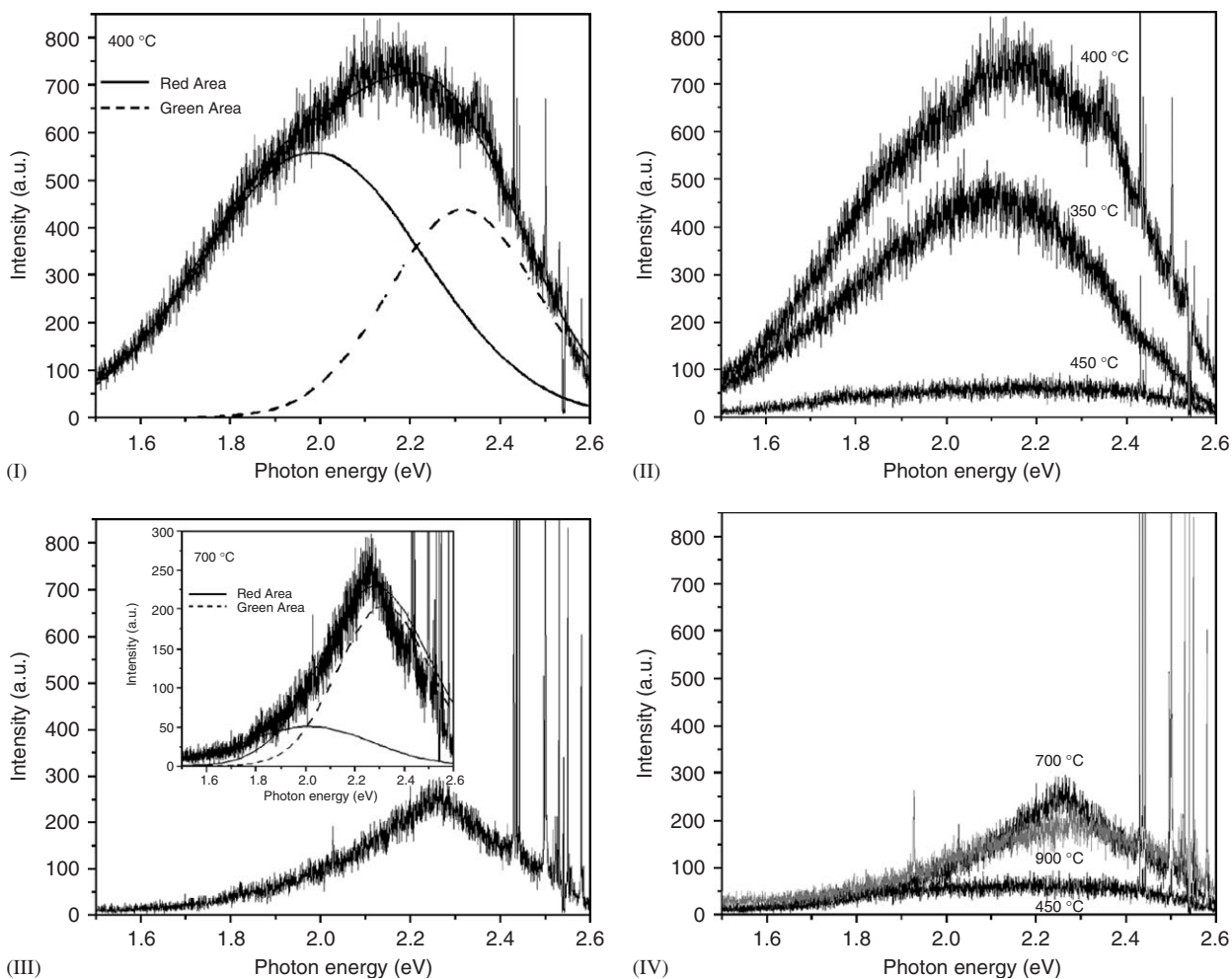


Fig. 6. Room-temperature PL spectra of BaMoO₄ nanopowders excited with the 488 nm line of an argon ion laser: (I) heat treated at 400 °C for 2 h, (II) heat treated at 300, 400 and 450 °C for 2 h, (III) heat treated at 700 °C for 2 h, (IV) heat-treated at 450, 700 and 900 °C for 2 h.

nanopowder sample in this work that presented the smallest PL intensity was the one heat treated at 600 °C for 2 h. Its PL emission area distributed with 49% in the red region and 51% in the green region, practically half for each emission, indicating that different emissions compete for the PL intensity.

Marques et al. [15] showed that the emission bands from BaMoO₄ thin films can be decomposed into two components, two broad bands with their maxima at around 2.07 eV (600 nm) (orange-red), peak 1, and 2.34 eV (530 nm) (green), peak 2. In this work, the red band (peak 1) represents, respectively, 59%, 65%, 54%, 49%, 26%, 47% and 43% of the total PL band area for nanopowders heat treated at 300, 400, 500, 600, 700, 800 and 900 °C for 2 h, respectively (see Table 4).

The decomposition of the overall PL emission spectra indicates that the fraction of overall PL emission ascribed to the red emission band increases with the degree of structural disorder. In the most crystalline structure, the fraction of the green emission band is bigger than the fraction of the red emission band. Both observations agree with the works of Marques et al. [15] and Orhan et al. [16].

The nanopowder sample heat treated at 400 °C possesses the biggest red area because it is a transition between a completely amorphous structure and a completely ordered structure, similarly to BaMoO₄ thin film reported by Marques et al. [15] and the SrWO₄ reported by Orhan et al. [16]. The nanopowders heat treated at 700 °C display the biggest green area because it is a completely ordered structure [15,16].

The components of the PL emission bands are probably linked to specific atomic arrangements. In the polyesterification stage of the citrate solution containing the molybdenum and barium ions occurs the structural transformations from disordered to ordered phases [15]. Molybdenum, the lattice former, ideally has the tendency to bond with four oxygen atoms, but before it reaches this ideal configuration there are various coordination numbers for Mo in the structure. Before the crystallization, the structure is a mixture of MoO_x clusters (*x* = mostly 3 and 4) intercalated by Ba atoms. This mixture of the clusters is responsible for the PL in the red region. When the crystallization is reached, only MoO₄ clusters exist, the

PL in the red region practically vanishes and the PL in the green region appears. It is agreed that the MoO₄ clusters are responsible for the green luminescence of molybdates. The PL spectra show that the transition between the completely amorphous structure and the completely ordered structure is suitable for a good PL emission in the red region, and, that a complete order is suitable for a good PL emission in the green region.

4. Conclusions

A simple method to prepare scheelite BaMoO₄ nanopowders is presented. The XRD, IR and Raman spectroscopy showed that the BaMoO₄ at 300 and 350 °C were disordered. At 400 °C and higher temperatures, crystalline BaMoO₄ scheelite-type phases could be identified, without the presence of additional phases. The lattice parameters values are also close to values reported for the bulk material. The calculated mean crystallite sizes was around 40 nm. The Raman spectra showed that the synthesized powders were highly crystalline for the BaMoO₄ nanopowders treated at 500–700 °C, whereas at 400 °C the main Raman peaks are only barely seen. The FTIR spectra of BaMoO₄ annealed at 400–700 °C presented a very broad absorption band from 800 to 870 cm⁻¹, related to the Mo–O stretching vibration in MoO₄²⁻ tetrahedra. Higher heat treatment temperature of the materials showed more order in the FTIR spectra, confirmed by XRD and Raman spectroscopy. Intense visible PL at room temperature was observed in amorphous and crystalline BaMoO₄ nanopowder samples. The BaMoO₄ nanopowder sample that presented the most intense red emission band was the one heat treated at 400 °C for 2 h. The sample that presented the most intense green emission band was the one heat treated at 700 °C for 2 h. The optical properties observed for BaMoO₄ nanopowders suggested that this material is a highly promising candidate for photoluminescent applications. The CPM method was shown to be a low cost route for the production of BaMoO₄, at a lower temperature and at a smaller time and a reduced cost.

Acknowledgments

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Table 4
Evolution of the red PL fraction with the structural order

| Samples | Peak 1 (eV) | Peak 2 (eV) | RA/FA |
|--------------------------------|-------------|-------------|-------|
| BaMoO ₄ -300 °C/2 h | 1.93 | 2.21 | 0.59 |
| BaMoO ₄ -400 °C/2 h | 1.99 | 2.32 | 0.65 |
| BaMoO ₄ -500 °C/2 h | 1.92 | 2.34 | 0.54 |
| BaMoO ₄ -600 °C/2 h | 1.90 | 2.44 | 0.49 |
| BaMoO ₄ -700 °C/2 h | 2.01 | 2.32 | 0.26 |
| BaMoO ₄ -800 °C/2 h | 2.09 | 2.33 | 0.47 |
| BaMoO ₄ -900 °C/2 h | 2.02 | 2.38 | 0.43 |

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

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