BaMoO₄ powders processed in domestic microwave-hydrothermal: Synthesis, characterization and photoluminescence at room temperature


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A R T I C L E   I N F O

Article history:
Received 19 December 2007
Received in revised form 17 May 2008
Accepted 17 June 2008

Keywords:
A. Optical materials
B. Chemical synthesis
C. Electron microscopy
D. Luminescence
D. Optical properties

A B S T R A C T

In this paper, BaMoO₄ powders were prepared by the coprecipitation method and processed in a domestic microwave-hydrothermal. The obtained powders were characterized by X-ray diffraction (XRD), Fourier transform Raman (FT-Raman) spectroscopy, ultraviolet–visible (UV–vis) absorption spectroscopy and photoluminescence (PL) measurements. The morphology of these powders were investigated by scanning electron microscopy (SEM). SEM micrographs showed that the BaMoO₄ powders present a polydisperse particle size distribution. XRD and FT-Raman analyses revealed that the BaMoO₄ powders are free of secondary phases and crystallize in a tetragonal structure. UV–vis was employed to determine the optical band gap of this material. PL measurements at room temperature exhibited a maximum emission around 542 nm (green emission) when excited with 488 nm wavelength. This PL behavior was attributed to the existence of intrinsic distortions into the [MoO₄] tetrahedron groups in the lattice.

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1. Introduction

Barium molybdate, BaMoO₄, presents at room temperature a scheelite-type tetragonal structure with general formula [AXO₄], where A = Ca, Sr, Ba and X = Mo [1,2]. This compound has been prepared by the conventional solid-state reaction between BaCO₃ and MoO₃ at high temperatures (> 1200 °C) [3]. BaMoO₄ obtained for this method presents several problems, such as: inhomogeneity, contamination by impurities and nonuniform particle size distribution [4]. Other methods also have been employed to prepare the BaMoO₄, including as flux crystallization [5], Czochralski technique [6] and spontaneous crystallization (SC) [7]. However, the main drawback of these techniques is the high processing temperature. To minimize these problems, wet chemical methods have been utilized, including polymerized complex [8], citrate complex method [9] and electrochemical method [10]. In addition, hydrothermal processing is considered an efficient and versatile method for the formation of several nanostructured materials with different morphologies and sizes. Recently, methods as solvothermal [11] and conventional hydrothermal (CHT) [12] have been used to process BaMoO₄ at temperatures in the range from 100 to 200 °C for times from 12 to 24 h. The microwave radiation has been employed in the citrate complex and solvothermal methods to accelerate the reaction process in the formation of molybdates with scheelite-type structure [13,14]. In the case of microwave-hydrothermal processing, the high frequency electromagnetic radiation interacts with the permanent dipole of the liquid (H₂O), which initiates a rapid heating from the resultant molecular rotation. Likewise, permanent or induced dipoles in the dispersed phase cause rapid heating of the particles. These result in a reaction temperature in excess of the surrounding liquid-localized superheating [15]. Thus, microwave radiation is able to promote the formation of materials with short processing time and reduced electric energy cost [16].

The literature has reported the formation of several amorphous compounds based on different metal oxianions with intense photoluminescence (PL) at room temperature [17–19]. In particular, an important material with scheelite-type structure is the BaMoO₄, which presents a high technological potential due to their blue photoluminescence (PL) property [20]. Recently, Marques et al. [8,21] reported the PL properties of amorphous BaMoO₄ in thin film and powders. PL properties were also verified in well-crystallized BaMoO₄ films [22]. Therefore, in this paper, we report on the preparation of BaMoO₄ powders by the coprecipitation method and processed in a domestic microwave-hydrothermal (DMW-HT) at 140 °C for 1 h. These powders were structurally characterized by X-ray diffraction (XRD) and Fourier transform Raman (FT-Raman) spectroscopy. The morphology was investigated by scanning electronic microscopy (SEM). The optical properties were analyzed by...
ultraviolet–visible (UV–vis) absorption spectroscopy and photoluminescence (PL) measurements at room temperature.

2. Experimental details

2.1. Synthesis and processing of BaMoO₄ powders

BaMoO₄ powders were synthesized by the coprecipitation method [23] and processed in a DMW-HT at 140 °C for 1 h in the presence of polyethylene glycol (PEG). A typical experimental procedure to obtain BaMoO₄ powders is illustrated in Fig. 1.

About 5 × 10⁻³ mol of molybdic acid [H₂MoO₄] (85% purity, Synth), 5 × 10⁻³ mol of barium nitrate [Ba(NO₃)₂] (99.5% purity, Sigma-Aldrich), NH₄OH (30% in NH₃, Synth) and 0.1 g of PEG (Mw 200) (99.9% purity, Sigma-Aldrich) were used as raw materials. The solubilization of tungstic acid and barium salt in water can be observed in Fig. 1. The insert shows the precipitation reaction between H₂MoO₄ and Ba(NO₃)₂ for the formation of the first particles of BaMoO₄. This solution containing H₂MoO₄ and Ba(NO₃)₂ was stirred for 1 h. This procedure was employed to accelerate the coprecipitation rate of BaMoO₄. Then, the following, 5 mL of NH₄OH was added in this solution to intensify the hydrolysis rate between the metal acid and the salt in water. In this case, the Ba²⁺ cations are accept species of electron pairs (Lewis acid) while MoO₂⁻ are donor species of electron pairs (Lewis base). The reactions between these two species Ba²⁺ + MoO₂⁻ form a covalent bond. The covalent bond occurs due to the Lewis acid to occupy the lowest molecular orbital (LUMO), which interacts with the highest molecular orbital (HOMO) of the Lewis base. Afterwards 0.1 g of PEG was added into this solution to promote a interaction between the small particles. In the sequence, the chemical solution was stirred for 30 min in ultrasound at room temperature was transferred into a Teflon autoclave, which was sealed and placed into a DMW-HT (2.45 GHz, maximum power of 800 W). This system was kept at 140 °C for 1 h, using a heating rate fixed at 25 °C/min. The pressure into the autoclave was stabilized at 3.92 bar. After microwave-hydrothermal processing, the autoclave was cooled to room temperature naturally. The obtained powders were then collected and washed with deionized water several times and then slowly dried at 85 °C for some hours.

2.2. Characterizations

BaMoO₄ powders were characterized by XRD patterns recorded on a (Rigaku-DMax 2500PC, Japan) with Cu-Kz radiation in the 2θ range from 5° to 75° with 0.02°/min. FT-Raman spectroscopy was performed on Bruker-RFS 100, Germany. The spectra were obtained using a 1064 nm line of an Nd:YAG laser, keeping their maximum output power at 55 mW. The morphology of these powders was observed through an scanning electron microscopy (DSM940A, Carl Zeiss, Germany). UV–vis spectroscopy was taken using a (Cary 5G equipment, USA). PL spectra were taken with a (U1000 Jobin-Yvon, France) double monochromator coupled to a cooled GaAs photomultiplier with conventional photon counting system. The 488.0 nm excitation wavelength of an argon ion laser was used, keeping their maximum output power at 25 mW. A cylindrical lens was used to prevent overheating of the powders. The slit width used was 100 μm. All measurements were performed at room temperature.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 2 shows the XRD patterns of BaMoO₄ powders processed in DMW-HT at 140 °C for 1 h.

The presence of diffraction peaks can be used to evaluate the structural order at long-range or periodicity of the material. All diffraction peaks can be indexed to the scheelite-type tetragonal structure with space group I₄₁/a [24]. No additional phase peaks were observed. The lattice parameters were calculated using the least square refinement from the UNITCELL-97 program [25]. The obtained lattice parameters were a = b = 5.5696 Å and c = 12.7865 Å with an unit cell volume of 396.642(8) Å³. These values are in agreement with those reported in the literature and with the respective JCPDS (Joint Committee on Powder Diffraction Standards) card No. 29-0193 [26].
Table 1 shows a comparative between the lattice parameters values of BaMoO₄ obtained in this work with those reported in the literature by different methods.

As can be seen in Table 1, the preparation of BaMoO₄ powders in a DMW-HT system leads to a reduction of temperature and processing time. Compared with the usual methods, the microwave processing is able to promote the formation of materials with small particle sizes, narrow particle size distribution and high purity. Jansen et al. [27] reported that these advantages could be attributed to the fast homogeneous nucleation and easy dissolution of the particles in the sol–gel system.

3.2. Unit cell representation for BaMoO₄

Fig. 3 illustrates the schematic representation of BaMoO₄ tetragonal unit cell with \( \frac{1}{2} / C \) space group. The Java Structure Viewer Program (Version 1.08lite for Windows) [28] was used for modeling this unit cell.

For construction of \( \frac{1}{2} / C \) unit cell of BaMoO₄ as showed in Fig. 3, we employed the structural parameters and atomic coordinates listed in Table 2 [29,30]. Nassif et al. [31] showed that Ba\(^{2+}\) cations are coordinated to the eight oxygen atoms, forming a scalenohedra configuration. The oxygen coordination polyhedra of Mo\(^{6+}\) cations are slightly distorted tetrahedral, presenting the angles between oxygen of 108.3° and 111.83°. For visual effect, our unit cell shows only the coordination between Mo–O atoms.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Time (h)</th>
<th>( a = b ) (Å)</th>
<th>( c ) (Å)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>40</td>
<td>5.62</td>
<td>12.82</td>
<td>Czochralski</td>
<td>[6]</td>
</tr>
<tr>
<td>950</td>
<td>72</td>
<td>–</td>
<td>–</td>
<td>SC</td>
<td>[7]</td>
</tr>
<tr>
<td>700</td>
<td>2</td>
<td>5.579(1)</td>
<td>12.811(4)</td>
<td>CPM</td>
<td>[8]</td>
</tr>
<tr>
<td>1150</td>
<td>12</td>
<td>5.5479(9)</td>
<td>12.743(2)</td>
<td>Precipitation/calcination</td>
<td>[31]</td>
</tr>
<tr>
<td>550</td>
<td>12</td>
<td>–</td>
<td>–</td>
<td>Molten flux reaction</td>
<td>[37]</td>
</tr>
<tr>
<td>140</td>
<td>1</td>
<td>5.569(6)</td>
<td>12.786(5)</td>
<td>DMW-HT</td>
<td>[This work]</td>
</tr>
</tbody>
</table>

T, temperature; CPM, complex polymerization method; SC, spontaneous crystallization and DMW-HT, domestic microwave-hydrothermal.

Table 2 Atomic coordinates used to model the BaMoO₄ unit cell

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molybdenum</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Barium</td>
<td>4b</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>16f</td>
<td>0.76731</td>
<td>0.14013</td>
<td>0.08188</td>
</tr>
</tbody>
</table>

\( a = b = 5.5696 \text{ Å} \) and \( c = 12.7865 \text{ Å} \).

Fig. 3. \( 1 \times 1 \times 1 \) unit cell of BaMoO₄ tetragonal structure.

Fig. 4 shows the Raman spectrum in the range from 68 cm\(^{-1}\) to 1000 cm\(^{-1}\) for the BaMoO₄ powders processed in a DMW-HT at 140°C for 1 h.

3.3. FT-Raman spectroscopy analysis

Fig. 4 shows the Raman spectrum in the range from 68 cm\(^{-1}\) to 1000 cm\(^{-1}\) for the BaMoO₄ powders processed in a DMW-HT at 140°C for 1 h.

BaMoO₄ presents a tetragonal structure with symmetry \( C_{6h} \) at room temperature. According to group theory calculation, the BaMoO₄ presents 26 different vibrations as described by the following equation:

\[
\Gamma = 3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u, \tag{1}
\]

where all the even vibrations (\( A_g \), \( B_g \) and \( E_g \)) are Raman-active modes, while the odd modes (\( 4A_u \) and \( 4E_u \)) can be only verified in the infrared spectra. The three \( B_u \) vibrations are silent modes. Eq. (1) also includes one \( A_g \) and one \( E_u \) acoustic vibrations [6]. According to Porto and Scott [32] the molybdates are classified into two groups, the external and internal modes. The first is
the SEM micrographs by the counting of approximately 102 particles for the formation of particles with octahedron-like morphology is small particles or seeds act as small nucleation centers during the coalescence process between small and large particles during the thermal can lead to the formation of possible defects in BaMoO₄. The differences verified in the optical band gap values can be related with the different preparation methods, shape, average crystal size and structural order–disorder degree in the lattice. As can be seen in Table 4, the E_g value is slightly lower than obtained by Marques et al. for BaMoO₄ thin films [21]. According to Eng et al. [38] the E_g values in material is dependent upon the electronegativity of the transition metal ion, connectivity of the polyhedra and deviations in the O–Mo–O bonds.

3.5. PL analysis

Fig. 8 shows the PL spectrum of BaMoO₄ powders processed in a DMW-HT at 140 °C for 1 h. The maximum (PL) emission was observed at around 542 nm (green emission). The average particle size of BaMoO₄ powders in the range from 0.7 μm to 3.1 μm present as tendency a regular lognormal distribution. The higher frequency (%) of particles was approximately 1.3 μm. This distribution is asymmetrical on the logarithmic scale of average particle size. This system presents the microcrystallites with an octahedron-like morphology and polydisperse particle size distribution.

Table 3

Comparative results between the Raman-active modes of BaMoO₄ obtained in this work with those reported in the literature by different methods

<table>
<thead>
<tr>
<th>M</th>
<th>T</th>
<th>t</th>
<th>B_g</th>
<th>E_g</th>
<th>B_g</th>
<th>E_g</th>
<th>A_g</th>
<th>B_g</th>
<th>E_g</th>
<th>B_g</th>
<th>A_g</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMW-HT</td>
<td>140</td>
<td>1</td>
<td>78</td>
<td>109</td>
<td>140</td>
<td>190</td>
<td>325</td>
<td>342</td>
<td>346</td>
<td>340</td>
<td>791</td>
<td>838</td>
</tr>
<tr>
<td>CZ</td>
<td>1200</td>
<td>40</td>
<td>76</td>
<td>110</td>
<td>137</td>
<td>188</td>
<td>234</td>
<td>324</td>
<td>345</td>
<td>358</td>
<td>791</td>
<td>837</td>
</tr>
<tr>
<td>CPM</td>
<td>700</td>
<td>2</td>
<td>78</td>
<td>107</td>
<td>141</td>
<td>190</td>
<td>325</td>
<td>326</td>
<td>346</td>
<td>359</td>
<td>791</td>
<td>838</td>
</tr>
<tr>
<td>MWS</td>
<td>165</td>
<td>½</td>
<td>--</td>
<td>--</td>
<td>184</td>
<td>--</td>
<td>325</td>
<td>--</td>
<td>780</td>
<td>829</td>
<td>871</td>
<td>--</td>
</tr>
</tbody>
</table>

M. method; T. temperature; t. time; assignments modes: , νMo=O-external modes MoO₄²⁻ and Ba²⁺ motions; , ν(MO₄) free rotation; , ν(MO₄); , ν(MO₄); , ν(MO₄); Methods of preparation: DMW-HT, domestic microwave-hydrothermal; CPM, complex polymerization method; CZ, Czochralski method and MWS, microwave-solvothermal process and Ref., references.

3.4. Scanning electron microscope analysis

BaMoO₄ powders with octahedral morphology was observed through the scanning electron microscope (SEM), as shown in Fig. 5.

The obtained result was similar to that reported by Afanasiev [37] and Eng et al. [38]. The fast processing in microwave-hydrothermal can lead to the formation of possible defects in BaMoO₄ lattice, thus promoting the appearance of intermediate electronic levels in the band gap. Table 4 shows a comparative between the Eg values of BaMoO₄ obtained in this work with those reported in the literature by different methods.

The differences verified in the optical band gap values can be related with the different preparation methods, shape, average crystal size and structural order–disorder degree in the lattice. As can be seen in Table 4, the E_g value is slightly lower than obtained by Marques et al. for BaMoO₄ thin films [21]. According to Eng et al. [38] the E_g values in material is dependent upon the electronegativity of the transition metal ion, connectivity of the polyhedra and deviations in the O–Mo–O bonds.

3.6. PL analysis

Fig. 8 shows the PL spectrum of BaMoO₄ powders processed in a DMW-HT at 140 °C for 1 h. The maximum (PL) emission was observed at around 542 nm (green emission).

PL measurements were realized at room temperature because this optical property behavior can be influenced by the temperature. Moreover, PL measurements at different
temperatures generally require expensive and sophisticated equipments. Also, it is technologically more interesting the materials with PL emissions at room temperature for the development of electrooptic devices, including DVD player lasers, cell phone displays, photocopying lamps and so on. The literature has reported explanations on PL emissions of molybdates. Lan and Blasse [39] prepared BaMoO$_4$ using Ba(NO$_3$)$_2$ and Na$_2$MoO$_4$ solutions. These authors observed that BaMoO$_4$ exhibit a weak green emission (around 530 nm) at $268\,^\circ$C. This green emission was also verified by Spassky et al. [7], with the maximum emission around 520 nm at $263\,^\circ$C. Both authors attributed the green luminescence of BaMoO$_4$ with the intrinsic MoO$_2$ group. Ryu et al. [9] reported the great dependence of the PL properties on the morphology and crystallinity of the BaMoO$_4$ powders. Recently, Campos et al. [17] observed and reported the green PL emission in calcium molybdate and attributed this behavior to the intrinsic distortions into the [MoO$_4$] tetrahedron groups. In other work, Wu et al. [20] investigated the blue PL emission at room temperature of BaMoO$_4$ microcrystals and show that slightly distorted tetrahedral symmetry leads to an structured absorption band for the $A_1 \rightarrow T_{1u}$ transition. Marques et al. [40] attributed the green PL emission to structural disorder in the MoO$_4$ cluster for the BaMoO$_4$ powders obtained by the complex polymerization method. Liu et al. [41] attributed to the charge-transfer transitions within the [MoO$_4$]$^{2-}$ complex to mainly factor to green PL emission in barium molybdate. We believe that the green PL emission at room temperature in barium molybdate is linked a several factors, such as: distortions on the [MoO$_4$] tetrahedron groups caused by the different angles between O–Mo–O (108.3° and 111.8°), particle sizes, crystallinity degree, morphology and

Fig. 5. SEM micrographs: (a) BaMoO$_4$ powders processed in DMW-HT at 140 °C for 1 h, (b) selected region of an agglomerated of BaMoO$_4$ powders, (c) polydisperse particle size distribution, (d) nucleation process by small seeds, (e) coalescence process and (f) possible growth mechanism of BaMoO$_4$ powders in a domestic microwave-hydrothermal.
4. Conclusions

In summary, BaMoO$_4$ powders were obtained by the coprecipitation and processed at 140 °C for 1 h in a domestic microwave-hydrothermal system. XRD patterns and FT-Raman revealed that the BaMoO$_4$ powders present a scheelite-type tetragonal structure without the presence of secondary phases. UV-vis absorption spectroscopy revealed a characteristic optical band gap of 4.10 eV. SEM micrographs showed that the BaMoO$_4$ powders present a polydisperse particle size distribution. These micrographs also showed that the coalescence mechanism is responsible for the growth process of BaMoO$_4$ with octahedron-like morphology. Intense PL emission at room temperature was attributed to the distortions on the [MoO$_4$] tetrahedron groups, particle sizes, crystallinity degree, morphology and surface defects.

Acknowledgments

The authors thank the financial support of the Brazilian research financing institutions: CAPES, FAPESP, CNPq and also Prof. Dr. Davy Keyson-UFPB and Dr. Diogo P. Volanti by adaptation of the hydrothermal reactor in the domestic microwave.

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