Short communication

SrMoO₄ powders processed in microwave-hydrothermal: Synthesis, characterization and optical properties

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Abstract

In this work, we report on the synthesis of SrMoO₄ powders by co-precipitation method and processed in a microwave-hydrothermal at 413 K for 5 h. These powders were analyzed by X-ray diffraction (XRD), Fourier transform Raman (FT-Raman), ultraviolet–visible (UV–vis) absorption spectroscopy and photoluminescence (PL). XRD analyses revealed that the SrMoO₄ powders are free of secondary phases and crystallize in a tetragonal structure. FT-Raman investigations showed the presence of Raman-active vibration modes correspondent for this molybdate. UV–vis technique was employed to determine the optical band gap of this material. SrMoO₄ powders exhibit an intense PL emission at room temperature with maximum peak at 540 nm (green region) when excited by 488 nm wavelength of an argon ion laser.

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Keywords: Co-precipitation; Microwave-hydrothermal; SrMoO₄; Optical band gap; Photoluminescence

1. Introduction

In recent years, tungstates and molybdates are materials that have attracted the interest of many technological fields and scientific areas owing to their wide potential to industrial application, including optic fiber, humidity sensor, catalysts, scintillation detector, solid-state lasers, photoluminescent devices, microwave applications and so on [1–10]. These materials have been prepared in both powder and film forms by means of several technologies, such as spray pyrolysis, pulsed laser deposition, RF-magnetron sputtering and sol–gel method [11–15]. However, these methods generally require expensive and sophisticated equipments, high temperatures for a long time, expensive precursors and high consumption of electric energy [16]. A possible alternative for reduction of these factors can be the use of hydrothermal processing methods. The conventional hydrothermal process (CH) is an efficient low temperature method that allows the formation of powders with high degree of crystallinity and with easy dispersion in an aqueous medium [17]. In contrast, the main drawback of this technique is the slow reaction kinetic at any given temperature [18]. The use of microwave energy in conventional hydrothermal system promoted the development of a new technique able to allow a rapid heating to the required temperature with rapid rates of crystallization [19]. In microwave-hydrothermal (MH) processing the factor “acceleration of chemical reaction” is promoted by high-frequency electromagnetic radiation (2.45 GHz) that interacts with the permanent dipole of the liquid phase, which initiates 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 [19]. Therefore, MH process offer the following advantages over the CH, such as: (a) the kinetics of the reaction is enhanced by one to two orders of magnitude, (b) novel phases, especially layered ones can be obtained and (c) rapid heating to treatment temperature saves time and energy [20,21].

Recently, Thongtem et al. [22] has reported the use of a simple and attractive method by cyclic microwave radiation. They focused on the use of microwave in solutions for fast formation of several molybdates with scheelite-type structure. The obtained results for these authors revealed different morphologies for each molybdate using the same experimental conditions. Another interesting work, Thongtem et al. [23] mentioned the preparation of SrWO₄ using the same experimental technique by cyclic microwave radiation. The purpose of this work was...
investigate the influence of pH, microwave powers and prolonged times on the structural, morphologic and optical properties of SrWO4 powders.

In the present communication, we report on the preparation of SrMoO4 powders by co-precipitation method and processed in a microwave-hydrothermal at 413 K for 5 h. These powders were characterized by X-ray diffraction (XRD) and Fourier transform Raman (FT-Raman). Optical properties were investigated by ultraviolet–visible (UV–vis) absorption spectroscopy and photoluminescence (PL).

2. Experimental procedure

2.1. Synthesis and microwave-hydrothermal processing of SrMoO4 powders

SrMoO4 powders were obtained by co-precipitation and processed in a microwave-hydrothermal with the presence of polyethylene glycol (PEG). The typical synthesis procedure is described as follows: 5 × 10^-3 mol of molybdic acid (H2MoO4) (85% purity, Synth), 5 × 10^-3 mol of strontium acetate [(CH3CO2)2Sr] (99.5% purity, Aldrich) and 0.1 g of PEG (Mw 200) (99.9% purity, Aldrich) were dissolved in 150 mL of deionized water. Then 5 mL of ammonium hydroxide (NH4OH) (30% in NH3, Synth) was added in the solution until the pH value reached to 12. Afterwards, the aqueous solution was stirred for 30 min in ultrasound at room temperature. In the sequence, the mixture was transferred into a Teflon autoclave. The autoclave was then sealed and placed into a microwave-hydrothermal at 413 K for 5 h. The pressure into the autoclave was stabilized at 298 K/min. Fourier transform Raman (FT-Raman) spectroscopy measurements were performed at room temperature.

2.2. Characterizations

The obtained powders were structurally characterized by X-ray diffraction (XRD) using a Rigaku-DMax/2500PC with Cu Kα radiation (λ = 1.5406 Å) in the 2θ range from 10 to 75° with 0.02°/min. Fourier transform Raman (FT-Raman) spectroscopy measurements were performed using a Bruker-RFS/100. The 1064 nm line of an Nd:YAG ion laser was used as excitation source, the power was kept at 55 mW. Ultraviolet–visible (UV–vis) spectroscopy for the spectra of optical reflectance of SrMoO4 powders was taken using Cary 5G equipment. Photoluminescence (PL) measurements of the powders were taken with a U1000 Jobin-Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon counting system. The 488.0 nm excitation wavelength of an argon ion laser was used with the laser’s maximum output power kept at 30 mW. A cylindrical lens was used to prevent the sample from overheating. 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. 1 shows a typical XRD pattern of SrMoO4 powders processed in a microwave-hydrothermal at 413 K for 5 h.

All diffraction peaks can be indexed as a pure tetragonal structure with space group I41/a. The peaks indicate that the powders are well crystallized. The lattice parameters were calculated using the least square refinement from the UnitCell-97 program [24]. The obtained lattice parameters were a = b = 5.3796 Å and c = 11.9897 Å, with volume unit cell of 346.9920 Å³. These values are in agreement with the reported data in the respective JCPDS (Joint Committee on Powder Diffraction Standards) card N°08-0482 [25]. The average crystallite size was approximately estimated by the Scherrer’s equation using the full width at half maximum (FWHM) of the most intense peak (1 1 2). As reported in the literature [18], the Scherrer’s equation (Eq. (1)) is described as follows:

\[ D = \frac{0.9\lambda}{B\cos\theta} \]  

where λ is the wavelength of Cu-Kα (1.54059 Å), θ is the angle of Bragg diffraction and B is the FWHM. Based on this equation, the average crystallite size in the four samples of SrMoO4 powders was obtained in the range from 31.49 to 41.16 nm.

3.2. Unit cell representation for SrMoO4

SrMoO4 crystallizes in a tetragonal structure and belong to the materials group with scheelite-type structure with space
group I 41/a [26,27]. Chen et al. [27] described the primitive unit cell of this structure with two SrMoO4 units, each with an inversion center. The authors also mentioned that Sr and Mo sites present S4 point symmetry. Therefore, unit cell of SrMoO4 presents the molybdenum atoms surrounded by four oxygen atoms in a tetrahedral configuration and the strontium atoms are constituted by four ions surrounded by eight oxygen atoms [26,27]. Chen et al. [27] described the primitive [MO4]2− molecular group with a stationary mass center. The external vibrations or lattice phonons are associated to the free space [MO4]2− tetrahedrons presents T₄-symmetry. In this case, the vibrations of the [MO4]2− ions are constituted by four internal modes (ν₁ (A₁), ν₂ (E), ν₃ (F₂) and ν₄ (F₁)), one free rotation mode (ν₁(ν₁ν₃)) and one translation mode (F₂). When the [MO4]2− ions are present in a scheelite-type structure, its point symmetry reduce to S₄. Therefore, all degenerative vibrations are split due to the crystal field effect. For a tetragonal scheelite primitive cell with K = 0 wavevector, the results estimated by the group-theory show the presence of 26 different types of vibrations, represented by Eq. (2) [31]:

\[ \Gamma = 3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u \] (2)

All the vibrations A₇, B₇ and E₇ are Raman-active where 4 A₇ and 4 E₇ modes are active only in infrared frequencies. The system still includes the acoustic vibrations (1A_u and 1 E_u) and the silent modes (3 B_u).

The Raman modes obtained for SrMoO4 in the present work are shown in Fig. 3. As can be seen, just 10 different vibrations were detected. The internal modes ν₁ (A₉), ν₂ (E₉), ν₃ (E₉) and ν₄ (B₉) were observed at 885, 844, 795, 383, 387 and 326 cm⁻¹. The free rotation mode was detected at 180 cm⁻¹ and the external modes were localized at range 96–137 cm⁻¹. These results are in agreement with that reported in the literature [22,31,32].

3.4. Ultraviolet-visible absorption spectroscopy analysis

Fig. 4 shows the absorbance spectral dependence for SrMoO4 powders processed in a microwave-hydrothermal at 413 K for 5 h.

The equation proposed by Wood and Tauc [33] was used to estimate the optical band gap. According to these authors, the optical band gap energy is related with absorbance and photon energy by Eq. (3):

\[ h\nu \alpha \propto (h\nu - E_{g}^{\text{opt}})^{2} \] (3)

where \( \alpha \) is the absorbance, \( h \) is the Planck constant, \( \nu \) is the frequency and \( E_{g}^{\text{opt}} \) is the optical band gap.

Therefore, the optical band gap was determined by extrapolation of the linear portion of the curve or tail. The band gap in the materials is related with absorbance and photon energy. Therefore, the combination between absorbance and photoluminescence is useful for the determination of the optical band gap.

### Table 1

<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>Strontium</td>
<td>4b</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>16f</td>
<td>0.233</td>
<td>0.140</td>
<td>0.820</td>
</tr>
</tbody>
</table>

Fig. 2. 1 × 1 × 1 unit cell of SrMoO₄ tetragonal structure.

Fig. 3. Raman spectra of SrMoO₄ powders excited with a 1064 nm line of an Nd:YAG ion laser at room temperature. The symbols represent the assignments, Raman modes: (♦) external modes MoO₄²⁻ and Sr²⁺ motions, (□) fr(F₁) free rotation, (●)ν₁(E), (■)ν₂(F₂), (▲)ν₃(F₂) and (●)ν₅(A₁).
nescence measurements allows to discover the energy levels in the materials and the optical band gap value. UV–vis measure-
ments on the four samples showed a typical value of 3.98 eV.
The observed behavior can be associated with the energy dif-
fERENCE BETWEEN the valence band and conduction band for this material.

3.5. Photoluminescence emission at room temperature analysis

Fig. 5 shows the PL spectrum at room temperature of SrMoO4 powders using an exciting wavelength of 488.0 nm. As can be seen in this figure, the general aspect of the PL curve is a broad band covering a large part of the visible spectrum with a maximum situated at 540 nm (green emission). Possibly, the emission profile of this sample can be associated with the contribution of various components. Therefore, to estimate the contribution of each individual component was necessary to deconvolute the PL spectrum.

The deconvolution of the PL spectrum was performed by the PeakFit program (4.05 version) using the Gauss area shape function [34]. The deconvolution results show that the PL profile was better adjusted by adding three peaks. The P1 peak is situated in the green visible region, the P2 peak is positioned in the yellow and the P3 peak is centered in the red wavelength region. Each component represents a different type of electronic transition, which can be linked with the structural arrangement or surface defects. Table 2 shows the obtained parameters in the fit, including position, area and amplitude of each peak individ-

Table 2

Results obtained by the deconvolution of the PL curves of SrMoO4 powders obtained by microwave processing at 413 K for 2 h

<table>
<thead>
<tr>
<th>Sample</th>
<th>Center of PL maximum emission (nm)</th>
<th>Peak-P1 center (nm)</th>
<th>Area of peak-P1 (%)</th>
<th>Amplitude of peak-P1 (arb. units)</th>
<th>Peak-P2 center (nm)</th>
<th>Area of peak-P2 (%)</th>
<th>Amplitude of peak-P2 (arb. units)</th>
<th>Peak-P3 center (nm)</th>
<th>Area of peak-P3 (%)</th>
<th>Amplitude of peak-P3 (arb. units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrMoO4</td>
<td>540</td>
<td>529</td>
<td>37.08</td>
<td>4121.22</td>
<td>571</td>
<td>39.60</td>
<td>3255.44</td>
<td>627</td>
<td>23.32</td>
<td>1277.52</td>
</tr>
</tbody>
</table>

The maximum emission of the PL spectra for the sample SrMoO4 occurs in the P1 peak position (green region). As can be seen, area and amplitude of this component corresponds a 4121.22 (arb. units) and 37.08% of the experimental PL curve, respectively.

Many valid hypotheses are put forward in the literature to explain the possible mechanisms responsible by the emission process of the SrMoO4. Recently, Chen and Gao [35] argued that the green emission is a result of the intrinsic luminescent behavior of the MoO42− group. These authors mentioned that the transition of the green luminescence is due 3T1g,3T2g→1A1g transition in the tetrahedral molybdates group. Liu et al. [36] using the microemulsion method showed that PL behavior of SrMoO4 can be modified by the crystallites morphology.

Table 3

Comparative results for SrMoO4 powders obtained by different methods reported in the literature

<table>
<thead>
<tr>
<th>Method</th>
<th>Form</th>
<th>Temperature (K)</th>
<th>Time (min)</th>
<th>Excitation line (nm)</th>
<th>PL maximum emission (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galvanic cell</td>
<td>Film</td>
<td>298</td>
<td>9000</td>
<td>290</td>
<td>485</td>
<td>[16]</td>
</tr>
<tr>
<td>Cell electrochemical</td>
<td>Film</td>
<td>286–338</td>
<td>0.13–0.21</td>
<td>230</td>
<td>520</td>
<td>[35]</td>
</tr>
<tr>
<td>Microemulsion</td>
<td>Powder</td>
<td>298</td>
<td>60–900</td>
<td>330</td>
<td>390</td>
<td>[36]</td>
</tr>
<tr>
<td>Microwave hydrothermal</td>
<td>Powder</td>
<td>413</td>
<td>300</td>
<td>488</td>
<td>540</td>
<td>[This work]</td>
</tr>
</tbody>
</table>
Table 3 presents a comparative of the PL maximum emission of SrMoO₄ obtained by different methods reported in the literature.

As can be seen in Table 3, the differences observed in the position of the maximum PL emission in SrMoO₄ probably can be associated with the structural organization levels, preparation methods, form and thermal treatment conditions. These factors can be responsible for generating visible color centers in the SrMoO₄ lattice and contribute to the PL emission. Moreover, another important factor can be associated with the different excitation wavelengths, which are able to excite different populations of electrons localized in additional energy levels into the band gap.

4. Conclusions

SrMoO₄ powders were synthesized by the co-precipitation method and processed in a domestic microwave-hydrothermal. XRD patterns and FT-Raman analyses revealed that obtained powders after MH processing are free of secondary phases and also Prof. Dr. Dawy Keyson-UFPB for adaptation of the microwave-hydrothermal process and its photoluminescence property, J. Alloy Compd. 325 (2001) 245–249.

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References


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