Synthesis, growth process and photoluminescence properties of SrWO₄ powders


A R T I C L E   I N F O

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SrWO₄ powders were synthesized by the co-precipitation method and processed in a microwave-hydrothermal (MH) at 140 °C for different times. The obtained powders were analyzed by X-ray diffraction (XRD), micro-Raman (MR) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, field-emission gun scanning electron microscopy (FEG-SEM), ultraviolet-visible (UV–vis) absorption spectroscopy and photoluminescence (PL) measurements. XRD patterns and MR spectra showed that the SrWO₄ powders present a scheelite-type tetragonal structure without the presence of deleterious phases. FT-IR spectra exhibited a high absorption band situated at 831.57 cm⁻¹, which was ascribed to the W–O antisymmetric stretching vibrations into the [WO₄] tetrahedron groups. FEG-SEM micrographs suggested that the processing time is able to influence in the growth process and morphology of SrWO₄ powders. UV–vis absorption spectra revealed different optical band gap values for these powders. A green PL emission at room temperature was verified in SrWO₄ powders when excited with 488 nm wavelength.

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1. Introduction

At room temperature, the tungstates and molybdates present a scheelite-type tetragonal structure with general formula ABO₄ (A = Ba, Ca, Sr, Pb; B = W, Mo) and space group I₄₁/a [1–5]. In this type of structure, the B ions are within tetrahedral O-ion cages and isolated from each other, while the A ions are surrounded by eight oxygens [6,7]. Currently, these materials have been widely employed in several industrial applications, such as: optic fiber, humidity sensor, catalysts, scintillation detector, solid-state lasers, photoluminescent devices, photocatalysts, microwave applications and more [8–16]. In particular, SrWO₄ has attracted considerable attention to the development of new electrooptics devices due to its blue or green luminescence emissions at room temperature [17,18]. Moreover, SrWO₄ crystals allow the introduction of different lanthanide ions (Er³⁺, Nd³⁺, Yb³⁺, Tm³⁺), which can be used as matrices for laser active elements with non-linear self-conversion of radiation to a new spectral range [19–23].

Different preparation techniques have been employed to obtain this material, mainly including: pulsed laser deposition [24], spray pyrolysis [17], Czochralski [25,26] and polymeric precursor method [27]. Generally, these methods require expensive and sophisticated equipments, high temperatures with long processing times, expensive precursors and high consumption of electric energy [28]. Therefore, it is important to develop new processing material methods with low costs, environmentally friendly and with the possibility of formation of materials on micro and nanoscale with well-defined morphologies. For example, hydrothermal method [29,30], electrochemical method [31–34], simple chemical reaction [35] and chemical solution deposition (CSD) [36]. Morphology-controlled synthesis with well-defined shapes is technologically interesting due to the chemical and physical properties of nano- and microcrystals depend not only on its composition, but also on its structure, phase, shape, size and size distribution [37–40]. In this case, synthesis methods assisted by microwave radiation have received special attention due to its advantages in the formation of materials with different morphologies and high degree of crystallinity [41].

Recently, Thongten et al. [42] obtained SrWO₄ nanoparticles using a solvothermal method assisted by cyclic microwave radiation. These authors observed that the pH value, microwave power and prolonged synthesis times are able to influence the structural, morphologic and optical properties of this material. In another research, Thongten et al. [43] verified through the cyclic microwave radiation method that different mol fractions of cetyltrimethylammonium bromide result in the formation of SrWO₄ with different morphologies, such as: peach-like, dumb-bells and bundles.

Therefore, in this paper, SrWO₄ powders were synthesized by the co-precipitation method and processed in a microwave-hydrothermal at 140 °C for different times (30 min–8 h). The obtained powders were analyzed by X-ray diffraction (XRD), micro-Raman (MR) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy. The growth process was analyzed by field-emission gun scanning electron microscopy (FEG-SEM). The optical properties
were investigated by Ultraviolet-visible (UV–vis) absorption spectroscopy and photoluminescence (PL) measurements.

2. Materials and methods

2.1. Synthesis and microwave-hydrothermal processing of SrWO4 powders

SrWO4 powders were processed by microwave-hydrothermal (MH) in the presence of polyethylene glycol (PEG). The typical procedure is described as follows: 5 × 10^-3 mol of tungstic acid (H2WO4) (99% purity, Aldrich), 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 75 mL of deionized water. The solution pH was adjusted up to 12 by the addition of 5 mL of ammonium hydroxide (NH4OH) (30% in NH3, Synth). In the sequence, the aqueous solution was stirred for 20 min in ultrasonic at room temperature. After co-precipitation reaction, the solution was transferred into a Teflon autoclave, which was sealed and placed into a domestic MH (2.45 GHz, maximum power of 800 W). Each MH processing was performed at 140°C for 30 min, 1 h, 2 h, 5 h and 8 h, respectively. The heating rate in this system was fixed at 25°C/min and the pressure into the autoclave was stabilized at 294 kPa. After microwave-hydrothermal processing, the autoclave was cooled at room temperature naturally. The resulting solution was washed with deionized water several times to neutralize the solution pH (≈7). Finally, the white precipitates were collected and dried in a conventional furnace at 75°C for some hours.

2.2. Characterizations of SrWO4 powders

SrWO4 powders were structurally characterized by XRD using a Rigaku-DMax/2500PC (Japan) with CuKα radiation (λ = 1.5406 Å) in the 2θ range from 15° to 75° with 0.02°/min. MR spectrosopies were recorded using a T-64000 Jobin-Yvon triple monochromator coupled to a CCD detector. The spectra were obtained using a 514.5 nm wavelength of an argon ion laser, keeping its maximum output power at 8 mW. A 100 μm lens was used to prevent powder overheating. FT-IR spectroscopies were recorded using a T-64000 Jobin-Yvon triple spectrometer. The spectra were measured using a 514.5 nm wavelength of an argon ion laser, keeping its maximum output power at 25 mW. A cylindrical lens was used to avoid powder overheating. The slit width utilized was 100 μm. UV–vis and PL spectra were taken three times for each sample in order to ensure the reliability of the measurements. All measurements were performed at room temperature.

3. Results and discussion

3.1. X-ray diffraction analyses

Fig. 1 shows the XRD patterns of SrWO4 powders processed in MH at 140°C for different times. XRD patterns revealed that the SrWO4 powders can be indexed to the scheelite-type tetragonal structure with space group I41/a, in agreement with the respective JCPDS (Joint Committee on Powder Diffraction Standards) card No. 08-0490 [44]. Diffraction peaks corresponding to the secondary phases were not verified. According to the literature [45,46], XRD patterns are able to estimate the degree of structural order–disorder at long-range in the materials. Therefore, the strong and sharp peaks indicate that the SrWO4 powders processed in MH are highly crystallized and structurally ordered at long-range. This result shows that the MH system promotes the formation of crystalline SrWO4 powders with low heat treatment temperature and reduced processing time than the conventional methods [2,5]. The experimental lattice parameters and unit cell volume were calculated using the least square refinement from the UnitCell-97 program [47]. These obtained results are listed in Table 1.

As it can be seen in Table 1, the lattice parameters of SrWO4 powders are in agreement with the values reported in JCPDS card. The small deviations in the lattice parameter values can be mainly attributed to the effect of microwave radiation in the MH system. The microwave radiation when interacts with a permanent dipole of a liquid phase results in vibrations on the charged particles [42,48]. The heating promoted by these vibrations contributes to a rapid formation process of SrWO4 phase. As consequence, this mechanism is able to result in distortions and/or strains in the SrWO4 lattice. In this case, it can be verified through the non-linear variations on a, b and c lattice parameters and unit cell volume with the processing time in the MH system (Table 1).

3.2. Micro-Raman analyses

According to Basiev et al. [49], a typical SrWO4 primitive cell is characterized by the [WO4] molecular ionic groups and Sr2+ cations. The [WO4] molecular groups with strong covalent bond W–O are peculiar to the tungstates. Due to the weak coupling
between the [WO4] molecular groups and the Sr2+ cations, the vibrational modes observed in Raman spectra of SrWO4 can be classified into two groups, internal and external modes. The internal vibrations correspond to the vibrations within the [WO4] molecular group, considering a stationary mass center. The external vibrations or lattice phonons are associated to the motion of the Sr2+ cations and the rigid molecular unit. The [WO4] tetrahedrons present a Td-symmetry in the free space. When a [WO4] molecular group is placed into the scheelite structure, its symmetry point group is reduced to S4. The vibration of [WO4] tetrahedrons can be divided into four internal modes (ν1(A1), ν2(E), ν3(F2) and ν5(F2)), one free rotation mode (νη(F1)) and one translation mode (F1). At room temperature, SrWO4 belongs to symmetry. Thus, the irreducible representation for the symmetry C6h at the Γ point of the Brillouin zone for the lattice vibrations of SrWO4 crystal in an unit cell can be described by the following equation [25,49]:

\[ \Gamma = 3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u. \]

According to Ling et al. [25], for the symmetry C6h, the Raman and infrared active optical modes at zero wave vector can be determined through the following equation:

\[ \Gamma = 3A_g + 5B_g + 5E_g + 4A_u + 4E_u. \]

All even vibrations A2, Bg and Eg are Raman-active modes, while the odd modes 4A2 and 4Eg are active only in infrared frequencies.

Fig. 2 shows the MR spectra in the range from 50 cm\(^{-1}\) to 1000 cm\(^{-1}\) for the SrWO4 powders processed in MH at 140 °C for different times.

The stronger Raman-active vibration modes indicate a strong interaction between the ions, which mainly arise from the stretching and bending vibrations of the shorter metal–oxygen bonds within the anionic groups [25]. Only nine Raman-active vibration modes were detected in the MR spectra, i.e., three A2 vibrations (921.55, 338.83 and 193.50 cm\(^{-1}\)) three Bg (839.87, 373.49 and 78.98 cm\(^{-1}\)) and three Eg (800.96, 136.34 and 103.50 cm\(^{-1}\)). These results are in agreement with the reported in the literature [50,51]. According to Marques et al. [45] and Rosa et al. [46], the Raman spectra are able to predict the degree of structural order–disorder at short-range in the materials. Therefore, the well-defined Raman-active modes indicate that the SrWO4 powders processed in MH are ordered at short-range (Fig. 2).

FT-IR spectra show the absorption bands of SrWO4 powders processed in MH at 140 °C for different times (Supporting information).

### 3.3. Field-emission gun scanning electron microscopy analyses

Fig. 3 shows the FEG-SEM micrographs of SrWO4 powders processed in MH at 140 °C for different times.

FEG-SEM micrographs revealed that the SrWO4 powders processed at 140 °C for 30 min in MH system exhibit a large quantity of particles with agglomerate and polydisperse nature (Fig. 3a). As it can be seen in this figure, the random aggregation process between the small particles resulted in the formation of a rice grain-like morphology. We believe that this aggregation process can be related to the increase of the effective collision rates between the small particles by the microwave radiation [52]. Fig. 3b shows that the processing of SrWO4 powders at 140 °C for 1 h initiates the growth process of aggregated particles by coalescence. This behavior can be associated with the influence of PEG-200 adsorbed on the surface of these particles. In this case, this polymer surfactant is able to promote a separation mechanism of the aggregated particles during the growth process. The increase of processing time for 2 h resulted in the formation of small quasi-octahedrons, as shown in Fig. 3c. This result suggests that the growth of the particles contributes to a higher adsorption rate of PEG on the crystal faces, which promotes interactions between the tails of surface-adsorbed surfactant molecules that possibly affect the growth of microcrystals [53]. Fig. 4d shows that the SrWO4 powders processed at 140 °C for 5 h resulted in the formation of faceted micro-octahedrons along the [110] direction [38, 54,55]. It is an indicative that the PEG favors an anisotropic growth caused by the differences in the surface energies on the different crystallographic faces [56]. In the final stage, the long processing time intensified the coalescence process between the small quasi-octahedrons and some faceted micro-octahedrons, resulting in the formation of large faceted micro-octahedrons. These micro-octahedrons can be observed in the SrWO4 powders processed at 140 °C for 8 h (Fig. 3e). FEG-SEM micrographs also allowed the estimation of the average particle size distribution (height and width) of SrWO4 powders processed at 140 °C for 8 h through the measure of approximately 100 particles. In this case, it was observed an average particle height distribution from 0.150 μm to 0.750 μm and average particle width distribution from 0.125 μm to 0.425 μm ( Insets in Figs. 3e and 3f). Possibly, the imperfections or differences between height and width of these micro-octahedrons can be associated with the influence of PEG during the growth process along the [001] direction.

### 3.4. Growth mechanism for the formation of SrWO4 particles with octahedron-like morphology

Fig. 4 shows a schematic representation of the synthesis and growth mechanism of SrWO4 particles by the MH processing.

Fig. 4a shows the initial formation stage of SrWO4 particles by the co-precipitation reaction. Firstly, the tungstic acid and the strontium salt were dissolved in water. The hydrolysis rate of this solution was intensified by the addition of 5 mL of NH4OH. As consequence, the electrostatic interaction between Sr2+ and WO42− ions resulted in the formation of SrWO4 particles. This solution was stirred for 20 min in ultrasound to accelerate the co-precipitation rate. 0.1 g of PEG was added into this solution to control the kinetics of crystal growth and determine the subsequent morphology of the products with the processing time [56]. Fig. 4b illustrates a schematic representation of a MH system employed in the processing of SrWO4 powders. This MH system was developed through adaptations performed on a domestic microwave oven (model NN-ST357WRPH, Panasonic) [57], including: temperature controller, thermocouple and Teflon autoclave. Fig. 4c shows a schematic representation of the processing of SrWO4 powders in
Fig. 3. FEG-SEM micrographs of SrWO₄ powders processed in MH at 140 °C for different times. (a) Rice grain-like morphology of SrWO₄ powders processed at 30 min, (b) growth of aggregated particles, (c) formation of small quasi-octahedrons, (d) presence of small quasi-octahedrons and faceted micro-octahedrons, (e) and (f) show the formation of large micro-octahedrons. The insets in Figs. 4e–4f show the average particle size distribution (height and width) of SrWO₄ micro-octahedrons formed after 8 h of processing.
MH system. Into the Teflon autoclave, the high-frequency electromagnetic radiation (2.45 GHz) interacts with the permanent dipole of the liquid phase [48]. This interaction leads to a vibration on the charged particles or molecules, which result in a rapid heating of the chemical solution and consequently of SrWO4 particles [42]. The increase of system temperature by the microwave radiation leads to a dissociation mechanism of some SrWO4 particles in Sr2+ and WO4−2 ions. However, the thermodynamic conditions and the electrostatic interaction between these ions favor the recrystallization process. Moreover, the microwave radiation is able to accelerate the solid particles to high velocities, leading to an increase of the interparticle collisions and inducing effective fusion at the point of collision [52] (Fig. 4c). We believe that these mechanisms are responsible for the fast nucleation of SrWO4 seeds and aggregation of several small particles. Also, during the initial stages of processing (140 °C for 30 min), the fast adsorption and absorption of PEG on the surface of the small particles and the high collision rates promoted by the microwave radiation favored the formation of a rice grain-like morphology (Fig. 4d—30 min). The increase of processing time contributed to a cooperative effect between coalescence process and adsorption of PEG. The coalescence promotes the growth of aggregated particles and consequently a high concentration of PEG can be adsorbed on the surface of these particles. When adsorbed, this polymer surfactant leads to a separation process of the aggregated particles and small spaces can be verified in the rice grain-like morphology of SrWO4 particles (Fig. 4e—1 h). The processing of SrWO4 powders at 140 °C for 2 h intensify the absorption of PEG on the crystal faces, which
Fig. 5. UV–vis absorbance spectra of SrWO$_4$ powders processed in MH at 140 °C for different times.

3.5. Ultraviolet–visible absorption spectroscopy analyses

Figs. 5a–5e show the UV–vis absorbance spectra SrWO$_4$ powders processed in MH at 140 °C for different times.

The optical band gap energy ($E_g$) was estimated by the method proposed by Wood and Tauc [58]. According to these authors the
optical band gap is associated with absorbance and photon energy by the following equation:

\[ h\nu \propto (h\nu - E_g)^{1/2}, \]

where \( \alpha \) is the absorbance, \( h \) is the Planck constant, \( \nu \) is the frequency and \( E_g \) is the optical band gap.

In this case, the \( E_g \) values of \( \text{SrWO}_4 \) powders were evaluated extrapolating the linear portion of the curve or tail. The obtained results are showed in Figs. 6a–6e and listed in Table 2. This table shows a comparative between \( E_g \) values of \( \text{SrWO}_4 \) obtained in this work with those reported in the literature by different methods.

The literature [5,27] has reported that the \( E_g \) is associated with the presence of intermediary energy levels within the band gap of the materials. These energy levels are dependent of the degree of structural order–disorder in the lattice. Therefore, the increase of structural organization in the lattice leads to a reduction of these intermediary energy levels and consequently increases the \( E_g \) value. We believe that the \( E_g \) also can be related with other factors, such as: preparation method, shape (thin film or powder), particle morphology, heat treatment temperature and processing time [62]. These factors result in different structural defects (oxygen vacancies, bond distortions), which are able to promote the formation of intermediary energy levels within the band gap. Probably, the differences verified for the \( E_g \) of \( \text{SrWO}_4 \) in Table 2 can be associated with these factors. Our results indicate that the \( \text{SrWO}_4 \) powders processed in MH system are structurally ordered at long and short-range, in agreement with XRD and MR analyses (Figs. 1 and 2). In this case, the \( E_g \) values are not related to the degree of structural order–disorder in the lattice. We believe that the \( E_g \) can be associated with the formation of intermediary energy levels due to the distortions on the \([\text{WO}_4]\) tetrahedrons during the MH processing. These distortions are arising from the vibration process on the charged particles by the microwave radiation. Also, the \( E_g \) of these powders can be related with the morphology modifications caused by the growth mechanism and/or superficial defects arising from the high collision rates between the particles by the microwave radiation. An important factor is that the equation proposed by Wood and Tauc [58] no reports the influence of the morphology on \( E_g \) of the materials. In this case, the \( E_g \) values obtained by this equation can be considered qualitative. Therefore, future investigations will be necessary to a better understanding.

Table 2
Comparative results between \( E_g \) values of \( \text{SrWO}_4 \) obtained in this work with those reported in the literature by different methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Shape</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>( E_g ) (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPM</td>
<td>Powder</td>
<td>600</td>
<td>2</td>
<td>4.50</td>
<td>[5]</td>
</tr>
<tr>
<td>PPM</td>
<td>Powder</td>
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<td>2</td>
<td>4.70</td>
<td>[5]</td>
</tr>
<tr>
<td>PPM</td>
<td>Thin film</td>
<td>400</td>
<td>2</td>
<td>5.78</td>
<td>[27]</td>
</tr>
<tr>
<td>PPM</td>
<td>Thin film</td>
<td>400</td>
<td>4</td>
<td>4.61</td>
<td>[27]</td>
</tr>
<tr>
<td>SP</td>
<td>Thin film</td>
<td>600</td>
<td>4</td>
<td>5.76</td>
<td>[27]</td>
</tr>
<tr>
<td>CSSM</td>
<td>Powder</td>
<td>1300</td>
<td>12</td>
<td>3.90</td>
<td>[59]</td>
</tr>
<tr>
<td>DDFR</td>
<td>Crystal</td>
<td>900</td>
<td>2</td>
<td>4.49</td>
<td>[60]</td>
</tr>
<tr>
<td>CZM</td>
<td>Crystal</td>
<td>1000</td>
<td>24</td>
<td>5.08</td>
<td>[61]</td>
</tr>
<tr>
<td>MH</td>
<td>Powder</td>
<td>140</td>
<td>0.50</td>
<td>4.36</td>
<td>[★]</td>
</tr>
<tr>
<td>MH</td>
<td>Powder</td>
<td>140</td>
<td>1</td>
<td>4.49</td>
<td>[★]</td>
</tr>
<tr>
<td>MH</td>
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<td>140</td>
<td>2</td>
<td>4.59</td>
<td>[★]</td>
</tr>
<tr>
<td>MH</td>
<td>Powder</td>
<td>140</td>
<td>5</td>
<td>4.68</td>
<td>[★]</td>
</tr>
<tr>
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<td>Powder</td>
<td>140</td>
<td>8</td>
<td>4.43</td>
<td>[★]</td>
</tr>
</tbody>
</table>

\( E_g = \) optical band gap energy; Ref. = reference; PPM = polymeric precursor method; SP = spray pyrolysis; CSSM = conventional solid state method; DDFR = double decomposition flux reaction; CZM = Czochralski method; MH = microwave-hydrothermal; ★ = this work.

![Fig. 6. PL spectra at room temperature of SrWO4 powders processed in MH at 140 °C for different times.](image-url)
3.6. Photoluminescence analyses and model based in distortions

Fig. 6 shows the photoluminescence (PL) spectra at room temperature of SrWO4 powders processed in MH at 140 °C for different times.

Blasse and Grabmaier [63] reported that the PL emission arises from the radiative return to the ground state, phenomenon that is in concurrence with the non-radiative return to the ground state. In the non-radiative process, the energy of the excited state is used to excite the vibrations of the host lattice, i.e., heat the lattice. The radiative emission process occurs more easily if there are trapped holes or trapped electrons within the band gap [27]. PL emission of tungstates with scheelite-type tetragonal structure is not completely understood. In particular, the literature has reported several hypotheses to explain the mechanisms responsible by the PL emission of SrWO4. Orhan et al. [27] performed theoretical studies on the PL emission of SrWO4 thin films through structural order–disorder. These authors reported the existence of WO3 and distorted WO4 clusters in the SrWO4 lattice, which are able to induce the formation of intermediary energy levels within band gap. These energy levels are composed of oxygen 2p states (near the valence band) and tungsten 5d states (below the conduction band).

In this case, the polarization induced by the symmetry break and the existence of these localized energy levels are favorable conditions for the formation of trapped holes and trapped electrons. The influence of structural order–disorder on the PL properties was also reported by Anicete-Santos et al. [5] for SrWO4 powders prepared by the polymeric precursor method and heat treated at 500 °C, 600 °C and 700 °C for 2 h. Lou et al. [17] mentioned that the luminescence of SrWO4 thin films formed by spray pyrolysis is due to the intrinsic transitions within the [WO4]2– complex. Thongtem et al. [42,43] attributed the PL emission of SrWO4 powders with the 1T2 → 1A1 transition of electrons within [WO4] tetrahedron groups, which can be treated as excitons. These authors also verified the presence of some shoulders on the PL profile and interpreted them as extrinsic transitions caused by the defects and/or impurities in the material. Sun et al. [1] showed that PL emission of SrWO4 can be modified by the morphology. These authors observed that different morphologies contribute to the formation of surface defects (roughness) that influence in the PL behavior. Yu et al. [64] verified a green emission in PbWO4 micro-crystals, which was attributed to the existence of Frenkel defects structure (oxygen ion shifted to the inter-site position with simultaneous creation of vacancy) in the surface layers.

In Fig. 6, the PL profiles of SrWO4 powders suggest an emission mechanism by multilevel process i.e., a system in which the relaxation occurs by means of several paths, involving the participation of several energy states within the band gap of the material [27]. Therefore, in order to estimate the contribution of each individual component it was necessary to deconvolute the PL spectra. The deconvolution was performed through the PeakFit program (4.05 version) [65] using the Voigh area function. As it can be seen in Table 3.

### Table 3

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>PT (h)</th>
<th>ME (nm)</th>
<th>P1 peak</th>
<th>P2 peak</th>
<th>P3 peak</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Center</td>
<td>Center</td>
<td>Center</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(nm)</td>
<td>(nm)</td>
<td>(nm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Area (%)</td>
<td>Area (%)</td>
<td>Area (%)</td>
</tr>
<tr>
<td>140</td>
<td>0.5</td>
<td>553.48</td>
<td>523.243</td>
<td>19.37</td>
<td>564.356</td>
</tr>
<tr>
<td>140</td>
<td>1</td>
<td>555.48</td>
<td>523.243</td>
<td>17.71</td>
<td>564.356</td>
</tr>
<tr>
<td>140</td>
<td>2</td>
<td>557.36</td>
<td>523.243</td>
<td>17.80</td>
<td>564.356</td>
</tr>
<tr>
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<td>5</td>
<td>549.61</td>
<td>523.243</td>
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<td>564.356</td>
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<td>552.54</td>
<td>523.243</td>
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<td>564.356</td>
</tr>
</tbody>
</table>

a T = temperature.
b PT = processing time.
c ME = maximum emission.
Figs. 6a–6e, the PL profiles were better adjusted by the addition of three peaks. In order to ensure a better analyze of the PL behavior, the peaks were positioned on a same position for all SrWO4 powders. The P1 and P2 peaks localized at 523.243 nm and 564.356 nm correspond to the green emission components. The P3 peak situated at 619.966 nm is ascribed to the orange emission component. Table 3 shows the contribution of each individual component (P1, P2 and P3 peaks) on the PL profile.

In this table, it was verified that the maximum PL emission of SrWO4 powders presents small deviations. Also, small changes were observed in the area (%) between the three components. These results indicate that the PL emission is probably dependent of the specific atomic arrangements. In this case, the modifications in the atomic arrangement can be associated with the formation of distortions on the [WO4] tetrahedron groups of SrWO4 powders by the microwave-radiation.

In Fig. 6f, it was observed that the PL intensity can be influenced by the processing time in a MH system. This behavior is not associated to the band-to-band emission process due to the wavelength’s energy (2.54 eV) to be smaller than the Eg of SrWO4 powders. Probably, the PL of these powders is arising from the contribution of different intermediary energy levels within the band gap. Our results indicate that the SrWO4 powders processed in MH are highly crystalline and structurally ordered at long and short-range in agreement with XRD patterns (Fig. 1) and MR spectra (Fig. 2). Therefore, PL of these powders is not due to the structural order–disorder in the lattice. As previously described, we believe that the behavior of this physical property is related to the influence of microwave radiation on the [WO4] tetrahedron groups.

Fig. 7 shows a simple mechanism to explain the PL behavior of SrWO4 powders processed in MH at 140 °C for different times. In this figure, the 1 × 1 × 1 unit cell of SrWO4 with $I4_1/a$ space was modeled using the Java Structure Viewer Program (Version 1.08Lite for Windows) and VRML-View (Version 3.0 for Windows) [66,67].

The literature reports that the tungsten atoms are considered good microwave absorbers [68]. Thus, we believe that the interaction between microwave radiation and tungsten groups (network formers) results in a rapid heating of SrWO4 powders and leads to a vibration on the charged particles (Fig. 7a). These factors probably result in a distortion process on the [WO4] tetrahedron groups, favoring the formation of intermediary energy levels within the band gap of this material (Figs. 7b and 7c). These energy levels are composed of oxygen 2p states (near the valence band) and tungsten 5d states (below the conduction band). During the excitation process with 488 nm wavelength, some electrons are promoted from the oxygen 2p states to tungsten 5d states 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 ($h^+$) (Fig. 7d). The emission process of photons ($h\nu$) occurs when an electron localized in a tungsten 5d state decays into an empty oxygen 2p state (Fig. 7e). Consequently, this mechanism is responsible for the PL emission of SrWO4 powders (Fig. 7f).

This proposed mechanism based on the distortion process of [WO4] tetrahedron groups, consequently can be related with the non-linear variations on the PL intensity of SrWO4 powders with the processing time in MH (Fig. 7f). Also, this behavior can be associated with the formation of superficial defects caused by the modifications on the morphology of these powders [69]. These defects are arising from rapid heating, high effective collision rates between the small particles and growth processes during the processing of SrWO4 powders. However, future investigations will be necessary in order to understand the effect of microwave-radiation on the PL properties.

4. Summary

SrWO4 powders were synthesized by the co-precipitation method and processed at 140 °C for different times in a MH system. XRD patterns revealed that these powders crystallize in a scheelite-type tetragonal structure with space group $I4_1/a$. The small deviations in the lattice parameter values were associated with the effect of microwave radiation. MR and FT-IR spectra showed characteristic modes of these powders. XRD patterns and MR spectra indicated that independent of the processing time in a MH system, SrWO4 powders are ordered at long and short-range. FEG-SEM micrographs showed that the processing time is an important factor in the growth mechanism of SrWO4 powders. These micrographs also indicated that the PEG is a surfactant that favors the growth of SrWO4 micro-octahedrons along the [001] direction. A possible growth mechanism for the formation of SrWO4 micro-octahedrons was proposed. UV–vis absorption spectra showed different optical band gap values, which were associated with the presence of intermediary energy levels within the band gap. PL behavior was explained through distortions on the [WO4] tetrahedron groups by the microwave radiation.

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Supporting information

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References