Structural evolution, growth mechanism and photoluminescence properties of CuWO_4 nanocrystals


1. Introduction

Hydrous copper tungstate (CuWO_4·xH_2O) crystals can be naturally found as a mineral, presenting colors from bright yellowish to green [1]. This mineral, also known as “Cuprotungsite”, has been discovered and analyzed by Whitney T. Schaller in 1892. However, the same designation also is adopted for copper tungstate (CuWO_4), i.e., an oxide material belongs to wolframite sub-group [2]. Whitney T. Schaller verified that CuWO_4·xH_2O crystals are composed of two water molecules; therefore, it was posteriorly described as copper tungstate dihydrate (CuWO_4·2H_2O) [1,2]. In general, CuWO_4·2H_2O crystals are easily produced by the reaction between copper nitrate and sodium tungstate precursors in aqueous solutions, using specific pH and temperature conditions. Some published papers have reported on the structural features, morphological aspects and electronic properties of this tungstate [3–12]. Particularly, some of these studies [3–7] consider the CuWO_4·2H_2O as a raw or precursor precipitate formed during the initial synthesis stages due to its favorable thermodynamic condition [8–12].

In past years, CuWO_4 crystals were obtained by several traditional methods, mainly including oxide mixture or solid state reaction [13–17], flux growth technique [18,19], melting at a high temperature [20], and Czochralski process [21]. Generally, these techniques require high temperatures, long processing times and sophisticated equipment with high maintenance costs [22]. On the other hand, to overcome these drawbacks, simple methods were developed for the preparation of CuWO_4 micro- and nanocrystals, such as precipitation reaction [23–26], polyol-mediated at low-temperature [27], hydrothermal conventional [28,29], and microwave-assisted synthesis [30].
The wolframite-type monoclinic structure is commonly found in tungstates composed of transition metals belonging to the fourth period of the periodic table (MnWO₄ [31], FeWO₄ [32], CoWO₄ [33], NiWO₄ [34], and ZnWO₄ [35]). The only exception is CuWO₄, which crystallizes in a triclinic structure at room temperature [36–38]. In addition, CuWO₄ crystals exhibit a phase transition from triclinic structure at low-pressure to monoclinic structure at high-pressure (9.9 GPa) [39]. Therefore, when subjected to extreme pressure environments, the researchers [40–43] have reported that these crystals have a monoclinic structure characterized by space group (P2/c), point group symmetry (C₂h) and two molecular formula units per unit cell (Z = 2) [43, 44]. On the other hand, under low-pressure conditions at room temperature, these crystals exhibit a triclinic structure with space group (P1), point group symmetry (Ci) and two molecular formula units per unit cell (Z = 2) [45–47]. Moreover, CuWO₄ crystals with triclinic structure are influenced by Jahn–Teller effect due to the presence of Cu²⁺ ions, which promote distortions on octahedral [CuO₆] clusters. Consequently, this phenomenon gives rise to a d-orbital splitting, in which the degeneracy of σ-antibonding orbitals is broken [48, 49]. According to the literature [50, 51], the Pauli exclusion principle can provide that the Cu²⁺ ions have an electron with unpaired spin occupying the dₓ²−y² orbital, indicating that this electronic level could produce a mid-gap band state. The additional stabilization is greater in a Jahn–Teller-elongated Cu²⁺ ions (where 3dₓ²−y² contains two electrons) [52].

Currently, the scientific studies on the electronic properties of pure and doped CuWO₄ have been mainly focused on the photocatalytic (PC) degradation of organic dyes (Rhodamine B, eosin yellow dye and methylene blue) under ultraviolet and visible light [53–55], magnetic [56–59], photoelectrochemical water splitting [60–64], visible and solar-assisted water splitting [65, 66], photoanode for solar water oxidation [67, 68], electrical transport [69], and photoluminescence (PL) [24, 53, 70]. An important point to be considered is that the theoretical studies [16, 71–75], performed by means of ab initio calculations based on the density-functional theory (DFT) for the electronic structure of CuWO₄ crystals, have shown that the conduction band (CB) of this oxide is composed of 3d orbitals (Cu atoms) and 5d orbitals (W atoms), while the valence band (VB) is formed of 2p orbitals (O atoms).

Therefore, the aim of the present study was to investigate the structural, morphological and optical properties of CuWO₄ crystals. These crystals were initially synthesized by the sonochemistry (SC) method (30 min), and then, heat treated in a conventional furnace at different temperatures for 1 h. A crystal growth mechanism was proposed in order to explain the evolution of particle shape/size with the increase of the heat treatment temperature. Finally, the optical properties of these crystals were investigated by Ultraviolet-Visible spectroscopy and PL measurements at room temperature.

2. Experimental details

2.1. Synthesis of CuWO₄ crystals

The synthesis of CuWO₄ crystals is described as follows: 1 × 10⁻³ mols of sodium tungstate trihydrate (Na₂WO₄·2H₂O; 99.5% purity, Sigma-Aldrich) and 1 × 10⁻³ mols of copper nitrate trihydrate [Cu(NO₃)₂·3H₂O; 99% purity, Sigma-Aldrich] were separately placed into two plastic tubes (Falcon – capacity of 50 mL) and dissolved with deionized water. The two solutions (pH = 6) were transferred into a beaker (250 mL) and ultrasonicated for 30 min by means of an ultrasonic cleaner (model CPX-1800H, Branson – USA) at frequency of 42 kHz. These suspensions containing bright green precipitates were seven times washed (water and acetone) and centrifuged (8500 rpm for 10 min), and then, dried in a single hot plate (60 °C for 30 min). Finally, the obtained CuWO₄·2H₂O precipitates were heat treated at different temperatures (100 °C, 200 °C, 300 °C, 400 °C, and 500 °C for 1 h), maintaining a heating rate of 5 °C/min⁻¹. The increase in the heat treatment temperature was employed to monitor the crystallization process of single CuWO₄ phase.

CuWO₄·2H₂O crystals were synthesized via chemical reaction between hexaquaocathode(II) complex ion ([Cu(H₂O)₆]²⁺) and tungstate ions (WO₄²⁻) in aqueous solution. These ions were originated by means of the complete dissolution of their respective chemical precursors [Na₂WO₄·2H₂O and Cu(NO₃)₂·3H₂O], as described in Eqs. (1)–(3):

\[
\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} (s) + 2\text{Na}^+ (aq) + \text{WO}_4^{2-} (aq) + 2\text{H}_2\text{O} \rightarrow 2\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} (s) + 2\text{H}_2\text{O}
\]

The heat treatment performed at low temperatures (from 100 °C to 200 °C) was responsible for the partial removal of water molecules belonging to CuWO₄·2H₂O structure, according to Eq. (4):

\[
\text{CuWO}_4 \cdot 2\text{H}_2\text{O} (s) \rightarrow \text{CuWO}_4 (s) + 2\text{H}_2\text{O} (g)
\]

The water removal (dehydration process) continues at low temperatures (=300 °C); however, there is a mixture of CuWO₄·xH₂O and CuWO₄ phases, as proposed in Eq. (5):

\[
\text{CuWO}_4 \cdot x\text{H}_2\text{O} (s) \rightarrow \text{CuWO}_4 (s) + x\text{H}_2\text{O} (g)
\]

The formation of single CuWO₄ crystals occurs at temperatures above 400 °C, according to Eq. (6):

\[
\text{CuWO}_4 \cdot x\text{H}_2\text{O} (s) \rightarrow \text{CuWO}_4 (s) + x\text{H}_2\text{O} (g)
\]

2.2. Characterizations of CuWO₄ crystals

CuWO₄ nanocrystals were structurally characterized by X-ray diffraction (XRD) with a DMax2500PC diffractometer (Rigaku, Japan), using Cu-Kα radiation (λ = 0.15406 nm). Data were collected over 2θ ranging from 10° to 70°, employing a step scan of 2°min⁻¹. Rietveld analysis was performed over 2θ ranging from 5° to 120°, at a scan step and step size of 1°min⁻¹ and 0.02°, respectively. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out in a STA 409 thermal analyzer (Netzsch, Germany). These thermal measurements were performed from room temperature to 550 °C under synthetic air flow (15 cm³min⁻¹), maintaining a heating rate of 10 °C/min⁻¹. Micro Raman (M-Raman) spectra were recorded using a LabRAM HR 800 spectrometer (Horiba Jobin Yvon, France). These spectra were...
obtained from 50 cm⁻¹ to 1000 cm⁻¹ with an Ar⁺ laser of 514.5 nm (model CCD DU420AOE325), maintaining a maximum output power of 6 mW. A 50 μm lens was used to prevent sample overheating. Fourier Transform infrared (FT-IR) spectra were performed from 200 cm⁻¹ to 1000 cm⁻¹ with a Bomem–Michelson spectrophotometer operated in transmittance mode (model MB-102). Ultraviolet–Visible (UV–Vis) spectra were taken using a Cary 5G spectrophotometer (Varian, USA) operated in diffuse reflectance mode. The morphological features were examined by using a Supra 35-VP field-emission scanning electron microscope (FE-SEM) (Carl Zeiss, Germany) operated at 10 kV, and with a CM200 transmission electron microscope (TEM) (Philips/FEI, Netherlands) operated at 200 kV. The shape, average size and crystal growth directions of CuWO₄ crystals were determined using the selected-area electron diffraction (SAED) and high resolution (HR)-TEM, respectively. The samples for TEM and HR-TEM were prepared depositing (dropwise) dilute suspensions of CuWO₄ crystals in acetone on 300-mesh Cu grids. The photoluminescence (PL) spectra were conducted at room temperature by using a Monospec 27 monochromator (Thermal Jarrel Ash, USA) coupled to a R955 photomultiplier (Hamamatsu Photonics, Japan). A krypton-ion laser (Coherent Innova 90 K; λ = 350 nm) was used as an excitation source, maintaining a maximum output power at 500 mW. The laser beam passed through an optical chopper, so that the maximum power incident on the sample was maintained at 14 mW.

3. Results and discussions

3.1. Long-range structural analyses

Fig. 1(a, b) shows XRD patterns of CuWO₄·2H₂O and CuWO₄ crystals heat treated at different temperatures, respectively. According to the literature [76], the degree of structural order/disorder or periodicity of a crystalline lattice in oxide materials can be analyzed by means of X-ray diffraction. In Fig. 1(a), the precipitated crystals heat treated at 100 °C and 200 °C for 1 h revealed the presence of wide XRD peaks assigned to CuWO₄·2H₂O monoclinic structure. This widening can be due to the presence of water molecules bonded in this crystalline structure (TGA and DTA profiles in Support Information Fig. SI-1(a, b)) as well as because of effects of order–disorder [77], i.e., these crystals have not a complete long-range structural ordering. Increasing the heat treatment temperature up to 300 °C (Fig. 1(a)), XRD patterns revealed a mixture of CuWO₄·2H₂O and CuWO₄ phases. Therefore, in this temperature occurs a significant elimination of water molecules in CuWO₄·2H₂O. Chen and Xu [28] described the CuWO₄·2H₂O crystals as a crystalline phase with monoclinic structure referring to JCPDS card N°. 33-0503. When the heat treatment was performed at 400 °C and 500 °C for 1 h, all XRD patterns showed diffraction peaks ascribed to CuWO₄ triclinic structure, in agreement with the ICSD card N°. 16009 [78]. In order to confirm this triclinic structure, the structural refinement by means of Rietveld method [79] was performed for CuWO₄ crystals heat treated at 500 °C for 1 h. The Rietveld method is based on the construction of diffraction patterns calculated according to a structural model [80]. The calculated patterns are adjusted to the observed pattern, providing the structural parameters of the desired material and its diffraction profile. In the present study, the Rietveld method was applied to estimate the atomic positions, lattice parameters, and unit cell volume of CuWO₄ crystals. The Rietveld refinement was performed using the general structure analysis software (GSAS) program [81], in which the refined parameters were scale factor, background, shift lattice constants, profile half-width parameters (u, v, w), isotropic thermal parameters, lattice parameters, strain anisotropy factor, preferential orientation, factor occupancy, and atomic functional positions. The background was corrected using a Chebyshev polynomial of the first order. The peak profile function was modeled using a convolution of the Thompson–Cox–Hastings pseudo-Voigt (pV-TCH) function [82] with the asymmetry function described by Finger et al. [83] In order to explain the anisotropy in the half width of the reflections, the model by Stephens [84] was used.

Fig. 2 shows the Rietveld refinement plot for CuWO₄ crystals synthesized by the SC method and heat treated at 500 °C for 1 h. All structural refinement results obtained by the Rietveld method [80] are consistent with ICSD N°. 16009 reported by Kluge and Gebert [78]. According to the literature [85], single CuWO₄ crystals have a triclinic structure, presenting a space group (P1), point group symmetry (C₁) and two molecular formula units per unit cell (Z = 2). The structural refinement confirmed the triclinic structure for CuWO₄ crystals (Fig. 2). In general, slight
differences in the intensity scale were identified between experimental and calculated XRD patterns, as described by the line \((Y_{\text{obs}} - Y_{\text{calc}})\). However, the quality of the structural refinement can be accurately determined by the \(R\)-values (\(R_{\text{wp}}\), \(R_{\text{Bragg}}\), \(R_p\), \(\chi^2\), and \(S\)). More details on the Rietveld refinement results are displayed in Table 1.

In this table, the fit parameters (\(R_{\text{Bragg}}, R_{\text{wp}}, R_p, \chi^2, \text{and } S\)) suggest that refinement results are very reliable. In general, small variations in atomic positions of O atoms were identified, while Cu and W atoms are fixed in their respective positions within the structure. In this case, the O atoms are able to induce distortions on both O–Cu–O or O–W–O bonds, resulting in distorted octahedral [CuO6] and [WO6] clusters.

3.2. Structural representation, and coordination of clusters in CuWO4

Fig. 3 shows a schematic representation of CuWO4 triclinic structure.

This triclinic structure was modeled through the visualization system for electronic and structural analysis (VESTA) software (version 3.4.0 for version of Windows 7-64-bit) [86,87], using the lattice parameters and atomic positions obtained from the Rietveld refinement data listed in Table 1. In Fig. 3, Cu and W atoms are both coordinated to six O atoms, forming distorted octahedral [CuO6] and [WO6] clusters, which are octahedron-type polyhedrons with 6-vertices, 8-faces and 12-edges [88]. In principle, these CuWO4 crystals heat treated at different temperatures are able to present variations in both (O–Cu–O)/(O–W–O) bond angles and lengths. This behavior implies in distortions on octahedral [CuO6] and [WO6] clusters with distinct degrees of order–disorder in the lattice.

![Fig. 3. Schematic representation of CuWO4 triclinic structure.](image)

3.3. Short-range structural analysis

Fig. 4(a–e) shows the M-Raman spectra of CuWO4 crystals heat treated at different temperatures.

The short-range structural ordering in the lattice of any material can be analyzed via Raman spectroscopy [89]. According to group theory calculations, tungstates with triclinic structure, space group \(\text{P}\bar{1}/C\bar{1}\) and point group symmetry \((C\bar{5})\) have 36 different

Table 1

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<th>Atoms</th>
<th>Wyckoff</th>
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<th>x</th>
<th>y</th>
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<tr>
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<tr>
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</table>

\(a = 4.7062(7)\) Å, \(b = 5.8432(8)\) Å, \(c = 4.8829(4)\) Å, \(\alpha = 91.6680(3)\)°, \(\beta = 92.4985(3)\)°, \(\gamma = 82.7871(3)\)°; \(V = 133.054(7)\) Å³, \(R_{\text{Bragg}} = 2.50\), \(R_{\text{wp}} = 8.84\), \(R_p = 6.89\), \(\chi^2 = 1.17\) and \(S = 0.8166\).

![Fig. 4. Micro-Raman spectra of CuWO4 crystals heat treated at (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C and (e) 500 °C for 1 h. Inset shows a typical symmetric stretching vibration of O–W–O bonds in octahedral [WO6] clusters. The vertical dotted lines with symbol (●) indicate the relative positions and intensities of Raman-active modes of CuWO4 crystals, while the symbol (*) show the presence of water molecules within these crystals, respectively.](image)
modes are expected for CuWO₄ crystal, shown in Eq. (8):

\[
\Gamma_{(\text{Raman} + \text{infrared})} = \{18A_g\} + \{18A_u\}
\]

where \(A_g\) are Raman-active vibrational modes, and \(A_u\) are infrared-active vibrational modes. Therefore, 18 Raman-active vibrational modes are only ascribed to CuWO₄ triclinic structure. In this table, there is a good agreement between our experimental Raman-active vibrational modes with the reported in other papers previously published [40–42,92]. The slight displacements in the positions of these vibrational modes can be related to variations in the degree of structural order-disorder in both octahedral [CuO₆] and [WO₆] clusters, as a consequence of the peculiarities of each synthesis condition (temperature, time) adopted for the formation of CuWO₄ phase.

3.4. FT-IR spectroscopy analyses

In this figure, the FT-IR spectra of CuWO₄ crystals heat treated at different temperatures.

![FT-IR spectra of CuWO₄ crystals heat treated at different temperatures.](image)

Table 2

<table>
<thead>
<tr>
<th>M</th>
<th>THEO</th>
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<th>SC-C</th>
<th>SC-C</th>
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<tr>
<td>v</td>
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<tr>
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<tr>
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<td>479</td>
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<td>472.1</td>
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<tr>
<td>o</td>
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<td>550</td>
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</tr>
<tr>
<td>d</td>
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<tr>
<td>Ref.</td>
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<td>854.4</td>
<td>906</td>
<td>905</td>
<td>900.9</td>
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</tbody>
</table>

M = Method; ⎯ = time; Raman modes = (cm⁻¹); THEO = Theoretical, TSSG = top-seeded solution growth; SC-C = Sonochemical-Calcination; [Æ] = This work and Ref. = References.
According to the literature [93], IR spectra also is able to provide information on the degree of structural order-disorder in atomic bonds of ABO₅ materials. Eq. (7) shows that the CuWO₄ crystals with triclinic structure have 18 Raman-active vibrational modes and 18 IR-active vibrational modes, as indicated by Eq. (9) [94]:

\[ \Gamma_{\text{IR}} = 18 \delta_u \]  
(9)

As illustrated in Fig. 5(a–e), only eleven IR-active vibrational bands [\( \delta_u \) modes] were detected in our IR spectra. This behavior is explained by the low symmetry of CuWO₄ lattice and phonon pattern associated with each mode that is in general complex and involves the whole unit cell [94]. However, the atom dynamics associated to highest energy modes can be understood on the basis of the main atomic shifts [94,95]. The band located at around 910 cm\(^{-1}\) is related to symmetric stretching vibrations (\( \delta(O=W=O) \)) in distorted octahedral [WO\(_6\)] clusters. It was noted a smaller band at 812 cm\(^{-1}\) is explained by the low symmetry of CuWO₄ lattice and phonon interaction at zone center [94]. Another band of low intensity at 558 cm\(^{-1}\) is related to anti-symmetric stretching vibrations (\( \delta(O=W=O) \)) between [WO\(_6\)]–[WO\(_6\)] clusters [Inset Fig. 5]. Also, it was noted a shoulder at 631 cm\(^{-1}\) [\( \delta_u \) mode], which cannot be attributed to optical modes [94]. The symmetric stretching vibrations (\( \delta(O=W=O=W=O) \)) between [WO\(_6\)]–[WO\(_6\)] clusters were verified at 558 cm\(^{-1}\). On the other hand, the symmetric stretching vibrations (\( \delta(O=Cu=O) \)) of distorted octahedral [CuO\(_6\)] clusters were detected at 478 cm\(^{-1}\). The small band at 417 cm\(^{-1}\) is arising from symmetric bending vibrations (\( \gamma(O=W/O) \) in [WO\(_6\)] clusters [94]. Finally, the last four modes (from 275 cm\(^{-1}\) to 377 cm\(^{-1}\)) are assigned to anti-symmetric (\( \gamma(O=Cu=O) \)), symmetric (\( \gamma(O=Cu=O) \)) and symmetric bending vibrations (\( \gamma(O=Cu=O) \) in [CuO\(_6\)] clusters, respectively. A comparison between the respective positions of IR-active vibrational modes of CuWO₄ nanocrystals are listed in Table 3. As expected in this table, our experimental IR-active vibrational modes are in good agreement with the results verified in other papers [41,94–97]. In addition, we have noted that some of these infrared vibrational modes of CuWO₄ nanocrystals are similar to isostructural CuMoO₄ crystals [98].

### 3.5. FE-SEM images analyses

Fig. 6(a–e) shows FE-SEM images of CuWO₄ crystals heat treated at different temperatures.

FE-SEM micrographs can be used as a powerful tool to accompany the particle shape evolution and growth process of CuWO₄ nanocrystals. Fig. 6(a) shows that the CuWO₄·2H\(_2\)O microcrystals obtained at 100 °C have a similar aspect of irregular flowers, which are formed by aggregated assemblies of several crystals (as “petals”). These “petals” show many imperfections and surface defects, as a direct result of both uncontrollable formation and interaction of nanocrystals caused by the chemical synthesis employed, solvent nature or intrinsic morphological feature of CuWO₄·2H\(_2\)O microcrystals [64]. These final structures similar to flowers have an average size of 4.7 μm, while their petals have an average size of 860 nm (Support Information Fig. SI-2(a, b)).

When the heat treatment was performed at 200 °C, both shape and size of these crystals were modified. This morphological change can be due to the initial stage of elimination of water molecules in CuWO₄·2H\(_2\)O, resulting in irregular stone-like microcrystals with average crystal size of 3.3 μm (Fig. 6(b)). These microcrystals are composed of several aggregated nanocrystals with average size of approximately 7.7 nm (Support Information Fig. SI-2(c, d)). In Fig. 6(c), the increase of heat treatment temperature up to 300 °C was able to maintain the morphological feature of stone-like microcrystals in the samples. In this case, it was estimated for these microcrystals an average size of approximately 6.6 μm, in which their aggregated nanocrystals presented an average crystal size of 11 nm (Support Information Fig. SI-2(e, f)). In Fig. 6(d), the presence of a large number of small crystals was verified on the surface of stone-like microcrystals heat treated at 400 °C for 1 h. As detected by XRD patterns (Fig. 1(b)), in this temperature occurs only the presence of CuWO₄ triclinic structure. Therefore, the counting of these stone-like CuWO₄ microcrystals revealed an average size at around 9.3 μm, which are formation by irregular nanocrystals with average size of 18.3 nm (Support Information Fig. SI-2(g, h)). Finally, for the temperature of 500 °C, it was possible to prove that these large stone-like microcrystals are composed of several flake-like CuWO₄ nanocrystals. For these

### Table 3

<table>
<thead>
<tr>
<th>M</th>
<th>THEO</th>
<th>TSSG</th>
<th>CP-C</th>
<th>CP-C</th>
<th>SSR</th>
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<tr>
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<td>8</td>
<td>36</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
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M = method; T = temperature; t = time; IR-active modes = (cm\(^{-1}\)); TSSG = Top-seeded solution growth; CP-C = Co-precipitation-Calcination; SSR = Solid state reaction; SC-C = Sonochemical-Calcination; THEO = Theoretical; and |\( \phi \) = this work.
nanocrystals was found an average size of approximately 41 nm (Support Information Fig. SI-2(i)). All results on the average size distribution of CuWO₄ crystals are summarized in Table 4 and (Support Information Fig. SI-2(a–i)).

All experimental results obtained in our study are good agreement with the literature [99–103]. In addition, all statistical data obtained through the counting of particle sizes using FESEM and TEM images were well-described by the log-normal distribution [104].

3.6. TEM and HR-TEM images analyses

Fig. 7(a–j) show TEM and HR-TEM images of CuWO₄ crystals heat treated at different temperatures.

Fig. 6. FE-SEM images of CuWO₄ crystals heat treated at different temperatures: (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C and (e) 500 °C for 1 h, respectively.
orientation. HR-TEM image presented in Fig. 7(b) shows the presence of nanocrystals with diameters of approximately 4 nm. The interplanar distance for these nanocrystals was estimated in approximately 0.23 nm, which correspond to (200) crystallographic plane of CuWO 4 triclinic phase, which is present in small points locally in the hydrated global lattice. The selected area electron diffraction (SAED) image (inset in Fig. 7(b)) was indexed also as CuWO 4 phase. In this case, it is important to emphasize that both TEM and SAED focused on some nanocrystals locally indicate the CuWO 4 phase, while X-ray patterns, due to be a long-range technique, indicated the CuWO 4·2H 2O phase. The low resolution TEM image for the sample obtained at 200 °C showed several aggregated nanoparticles (Fig. 7(c)). SAED (not shown here) indicated the presence of low intensity rings related to nanocrystalline particles, which is supported by HR-TEM image in Fig. 7(d). The materials heat treated at 300 °C are illustrated in Fig. 7(e, f). Again, the micrographs revealed that the stone-like CuWO 4 microcrystals are clearly formed by randomly distributed aggregated nanoparticles, as confirmed by low intensity rings in SAED (Inset in Fig. 7(f)). HR-TEM image also revealed the same interplanar distance (0.23 nm), as observed in Fig. 7(b), i.e., proving the CuWO 4 triclinic phase. Exactly, this same behavior was also identified for the materials obtained at 400 °C (Fig. 7(g, h)). For the material heat treated at 500 °C, the existence of larger particles was identified, in which some of them are well-faceted (high degree of crystallinity). TEM images also showed these particles are agglomerated instead of aggregated, presenting an interplanar distance of 0.31 nm related to (111) plane of CuWO 4 triclinic phase. The other TEM and HR-TEM images can support the explanations above as found in Support Information Figs. S1-3(a–j). All experimental results obtained in this study are in good agreement with the literature and presented in Table 4 [99–103]. Therefore, TEM images provides some advantages over SEM images, specially confirming that larger particles for samples obtained from 200 °C to 400 °C are composed of smaller nanoparticles. On the other hand, the particles observed at 500 °C are single-crystalline. SAED agrees with XRD results, in which the synthesis method allowed the formation of crystalline nanoparticles of CuWO 4.

### 3.7 Crystal growth mechanism

Fig. 8(a–k) shows a schematic representation of all stages involved in the synthesis and growth of CuWO 4 nanocrystals synthesized by the SC method and heat treated at different temperatures for 1 h.

Initially, there is the coulomb interaction between [Cu(H 2O) 6] 2+ and WO 4 2− complex ions in aqueous solution, promoting the formation of first CuWO 4·2H 2O nuclei (Fig. 8(a, b)). These nuclei control the kinetics of nucleation and growth of CuWO 4 nanocrystals. In the next growth stage (Fig. 8(c, d)), the crystals in the aqueous medium are able to rotate and align to find a common crystallographic plane via self-assembly process. As this process is uncontrollable, there is the random and spontaneous aggregation of nanocrystals, resulting in petal-like CuWO 4·2H 2O microcrystals (Fig. 8(e)). After heat treatment performed at 100 °C for 1 h, flower-like CuWO 4·2H 2O microcrystals are formed, which are composed of several petal-like crystals (Fig. 8(f)). The initial stage of elimination of water molecules in CuWO 4·2H 2O due to the heat treatment temperature at 200 °C resulted in irregular stone-like microcrystals (Fig. 8(g)). The progressive removal of these water molecules in the lattice with the increase of heat treatment promoted a phase transition from CuWO 4·xH 2O (monoclinic structure) to CuWO 4 crystals (triclinic structure). However, for temperatures of 300 °C and 400 °C, the morphological aspect of irregular stone-like microcrystals is maintained (Fig. 8(i, j)). Finally, when the materials were heat treated at 500 °C, CuWO 4 crystals grew by means of nanocrystals. These results can be proved through FESEM, TEM and HR-TEM images (Figs. 6(e) and 7(i, j)).

### 3.8 Uv–vis spectra and optical band gap energy

The optical band gap energy (E band gap) was calculated using the method proposed by Kubelka and Munk [105]. This methodology is based on the transformation of diffuse reflectance measurements to estimate E band gap values of semiconductors with good accuracy [106]. The Kubelka–Munk Eq. (10) for any wavelength is defined as:

\[
F(R_\infty) = \frac{(1 - R_\infty)}{2R_\infty} = \frac{k}{s} \quad \text{(10)}
\]

where \(F(R_\infty)\) is the Kubelka–Munk function or absolute reflectance of the sample. In our case, magnesium oxide (MgO) was adopted as standard in reflectance measurements. \(R_\infty = \frac{R_{\text{sample}}}{R_{\text{MgO}}}\). Where \(R_\infty\) is the reflectance, \(k\) is the molar absorption coefficient, and \(s\) is the scattering coefficient. The optical band gap and absorption coefficient of semiconductor oxides [107] can be calculated using the following Eq. (11):

\[
x\hbar v = C_1(hv - E_{\text{band \ gap}})^n \quad \text{(11)}
\]

where \(x\) is the linear absorption coefficient of the material, \(hv\) is the photon energy, \(C_1\) is a proportionality constant, and \(n\) is a constant associated to the type of electronic transition (\(n \approx 0.5, 2, 1.5, \) and 3 for direct allowed, indirect allowed, direct forbidden, and indirect forbidden transitions, respectively). According to Lalic et al. [72] and Lacomba-Peral et al. [108] CuWO 4 crystals have an optical absorption spectrum governed by indirect electronic transitions.
Fig. 7. TEM/HR-TEM images and SAED of CuWO$_4$ crystals heat treated at different temperatures: (a, b) 100°C, (c, d) 200°C, (e, f) 300°C, (g, h) 400°C and (i, j) 500°C for 1 h, respectively.
between the valence band (VB) and conduction band (CB). After the electronic absorption process, the electrons located in the maximum-energy states in VB return indirectly to minimum-energy states in CB (different points in the Brillouin zone) [109]. Based on this information, $E_{\text{gap}}$ values of CuWO$_4$ crystals were calculated using $n = 2$ in Eq. (11). Finally, using the remission function described in Eq. (10) with the term $k = 2a$ and $C_2$ as a proportionality constant, the modified Kubelka–Munk equation can be obtained, as indicated by Eq. (12):

$$\left[ F(R_a) \right]^{1/2} = C_2 (h\nu - E_{\text{gap}})$$

By finding the $F(R_a)$ value from Eq. (12) and plotting $[F(R_a)]^{1/2}$ against $h\nu$, the $E_{\text{gap}}$ value of CuWO$_4$ crystals was determined.

Fig. 9(a–f) shows the UV–vis diffuse reflectance spectra of CuWO$_4$ crystals heat treated at (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C, and (e) 500 °C for 1 h, (f) optical band gap values as a function of temperature.

In this figure, a slight decrease in $E_{\text{gap}}$ values with the increase in the heat treatment temperature was detected. This behavior, for samples heat treated from 100 °C to 300 °C, is related to removal of water molecules (dehydration process) in the lattice, resulting in a phase transition from CuWO$_4$·$x$H$_2$O to CuWO$_4$, modifying the number and organization of intermediary energy levels between the VB and CB (Fig. 9(a–c)). Moreover, the exponential optical absorption profile as well as $E_{\text{gap}}$ are controlled by the degree of structural order-disorder in the lattice [110]. For samples heat treated at 400 °C and 500 °C, there is only single CuWO$_4$ triclinic phase; therefore, the decrease in $E_{\text{gap}}$ values (2.24 and 2.19 eV) can be explained by the presence of low symmetry and distortions on both octahedral [CuO$_6$] and [WO$_6$] clusters in the lattice. However, the contributions of electronic levels in these crystals can be achieved only by means of theoretical calculations, which will be perforated in a future study.

3.9. Photoluminescence properties

Fig. 10(a–e) illustrates PL spectra at room temperature of CuWO$_4$ crystals heat treated at different temperatures.

In the last years, the experimental results previously reported in the literature [26,53,70] have explained the key factors or variables responsible for PL properties of CuWO$_4$ crystals. Pourmortazavi et al. [26,70] and ReddyPrasad and Naidoo [53] described the PL emission of these crystals with the electronic transitions within complex structure of WO$_4^{2-}$ anion molecular as well as by the trap-
Moreover, the increase of temperature at 200°C with a narrower profile in relation to other samples.

Samples heat treated at 100°C for CuWO₄ crystals published in these papers were related to pro-spectral-like crystals; (f) formation of flower-like CuWO₄ crystals; (g) crystal growth via heat treatment; (h) irregular stone-like CuWO₄ crystals; (i) stone-like CuWO₄·xH₂O microcrystals and flake-like CuWO₄ nanocrystals; (j) formation of aggregated CuWO₄ nanocrystals; (k) crystal growth of flake-like CuWO₄ nanocrystals.

Fig. 8. Schematic representation of the growth mechanism of CuWO₄·2H₂O crystals obtained by the SC method: (a) reaction between complex ions; (b) appearance of the first CuWO₄·2H₂O nuclei; (c) rotation and alignment of nanocrystals sharing common crystallographic planes; (d) self-assemble process; (e) aggregation of petals-like crystals; (f) formation of flower-like CuWO₄·2H₂O microcrystals; (g) crystal growth via heat treatment; (h) irregular stone-like CuWO₄·xH₂O microcrystals; (i) stone-like CuWO₄·xH₂O microcrystals and flake-like CuWO₄ nanocrystals; (j) formation of aggregated CuWO₄ nanocrystals; (k) crystal growth of flake-like CuWO₄ nanocrystals.

In summary, CuWO₄·2H₂O and CuWO₄ crystals were obtained by the sonochemistry method, followed by heat treatment performed at different temperatures (from 100°C to 500°C) for 1 h. XRD patterns, Rietveld refinement, micro-Raman and FT-IR spectroscopies proved that CuWO₄ crystals crystallize in a triclinic structure with space group (P1). XRD patterns revealed that the temperature of 300°C is responsible for a phase transition from CuWO₄·2H₂O (monoclinic) to single CuWO₄ (triclinic). M-Raman spectra presented eighteen Raman-active vibrational modes for CuWO₄ nanocrystals, which are caused by external modes of distorted octahedral [CuO₆] clusters and internal modes ascribed to distorted octahedral [WO₆] clusters. These M-Raman spectra also showed the existence of short-range structural ordering in these crystals. FT-IR spectra detected eleven IR-active vibrational modes for CuWO₄ crystals, which are related to anti-symmetric, symmetric stretch, interaction forces in a chain and symmetric bending, which are present due to (O–Cu–O and O–W–O) bonds. FE-SEM images showed a dependence between the morphological aspects with the heat treatment temperature. In these micrographs, it
was verified that CuWO₄·2H₂O crystals have irregular flower- and stone-like shaped at 100 °C and 200 °C, respectively. On the other hand, CuWO₄ crystals exhibited only the stone-like shaped. All these morphological shapes are composed of uncountable aggregated nanocrystals, which grew by means of self-assembly process, as observed by TEM and HR-TEM images. The decrease in $E_{\text{gap}}$ values with the increase of the temperature was caused by the reduction of intermediary energy levels between the VB and CB. CuWO₄ crystals heat treated at 300 °C for 1 h exhibited the highest PL emission at room temperature. This behavior was favored due to the effective participation of intermediary energy levels arising from both CuWO₄·2H₂O and CuWO₄ crystals.

Fig. 9. UV–vis spectra of CuWO₄ crystals synthesized by the SC-C method and heat treated at (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C and (e) 500 °C for 1 h, and (f) $E_{\text{gap}}$ as a function of heat treatment temperature.
Fig. 10. PL emission spectra at room temperature of CuWO₄ crystals heat treated at (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C and (e) 500 °C for 1 h, respectively. Insets show the digital photos of the powders, which exhibit different colors, depending on the heat treatment temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ulsonech.2017.03.007.

References


