

Effect of different strontium precursors on the growth process and optical properties of SrWO₄ microcrystals

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Abstract In this paper, an experimental study was performed on the effect induced by different strontium precursors in the growth processes and optical properties of strontium tungstate (SrWO₄) microcrystals synthesized by the co-precipitation method. The structural behavior was analyzed by means of X-ray diffractions, Rietveld refinements, Fourier transform (FT)-Raman, and FT-infrared spectroscopies. X-ray absorption near-edge structure spectra performed at the W-L₁ and L₃ edges revealed the first coordination shell around the tungsten atoms is composed of four oxygens, i.e., existence of tetrahedral [WO₄] clusters inside the SrWO₄ structure. Field emission scanning electron microscopy (FE-SEM) images showed the presence of pitch and longleaf pine cone-like SrWO4 microcrystals for most of the strontium precursors employed in the synthesis. Based on these FE-SEM images, a hypothetical crystal growth mechanism was proposed to explain the origin of these microcrystals. The optical properties were investigated by ultraviolet-visible spectroscopy and photoluminescence (PL) measurements at room temperature. The different

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optical band gap values found for this material, depending on the type of strontium precursor, were correlated with the existence of intermediary energy levels within the forbidden region. Finally, PL profiles were associated to the degree of distortions in tetrahedral $[WO_4]$ clusters.

Introduction

Strontium tungstate (SrWO₄) is an important material belonging to the scheelite class with excellent optical properties, especially for technological applications in solid-state lasers and stimulated Raman scattering [1, 2]. Basically, this tungstate has attracted the attention of the scientific community and technological areas because of its interesting physicochemical properties, mainly including blue-green phosphors [3], photocatalytic activity for degradation of organic dyes [4, 5], cathodoluminescence [6], thermal expansion [7, 8], luminescence [9, 10], and so on.

Over the last few years, pure and doped $SrWO_4$ phase has been normally formed by solid-state reaction [11, 12], Czochralski crystal growth [13, 14], and flux evaporation [15]. These preparation methods usually require complex experimental procedures, sophisticated equipments, and rigorous synthesis conditions. Also, there is the probability of formation of deleterious phases, polydisperse particle size distribution, and uncontrolled morphology. Thus, new synthesis methods as electrochemical [16], molten salt [17], sonochemical [18], mechanically assisted solution reaction [19], chemical solution [20], pulsed laser [21], microemulsion [22], solvothermal-mediated microemulsion [23], hydrothermal [24], microwave irradiation [25], and microwave-hydrothermal [26] have been developed with the intention of minimizing these drawbacks. In materials science, there is a particular interest in the development of simple synthetic routes with efficient control on the particle shapes and sizes at micro/nanoscale [27]. For example, Thongtem et al. [28] reported the synthesis of $SrWO_4$ nanoparticles using a microwave-assisted solvothermal route. In this study, these researchers analyzed the influence of pH condition, microwave power, and synthesis times in the formation of these nanoparticles.

In recent years, several researchers have employed $SrWO_4$ crystals as host matrix for the incorporation of trivalent rare earths (Eu³⁺, Er³⁺, Yb³⁺, and Tb³⁺) [29] in order to apply in light emission diodes, anode material for lithium-ion batteries [30], and catalyst to removal of toxic metal lead (II) from water [31]. On the other hand, scientific studies on the formation of SrWO₄ microcrystals by the co-precipitation method with different strontium precursor salts have not found in the literature.

Therefore, in this paper was analyzed the effect of different strontium precursors on the growth processes and optical properties of SrWO₄ microcrystals synthesized by the co-precipitation method at room temperature. These microcrystals were characterized by X-ray diffraction (XRD), Rietveld refinement, X-ray absorption near-edge structure (XANES), Fourier transform Raman (FT-Raman), Fourier transform infrared (FT-IR), ultraviolet-visible (UV-Vis) absorption spectroscopy, photoluminescence (PL) measurements, and field emission scanning electron microscopy (FE-SEM). A plausible growth mechanism for the formation of SrWO₄ microcrystals was proposed. Finally, PL properties were analyzed in terms of distortions in [WO₄] clusters, according with effect induced by the strontium precursor in the synthesis of SrWO₄ microcrystals.

Experimental details

Synthesis of SrWO₄ microcrystals

SrWO₄ microcrystals were synthesized according to the following experimental procedure: 5×10^{-3} mols of tungstic acid [H₂WO₄] (99 % purity, Aldrich), 5×10^{-3} mols of different strontium salts: strontium acetate [Sr(CH₃CO₂)₂] (99.5 % purity, Aldrich), strontium nitrate [Sr(NO₃)]₂ (99.5 % purity, Aldrich), and strontium chloride hexahydrate [SrCl₂·6H₂O] (99.5 % purity, Aldrich) were dissolved in 100 mL of deionized water. In the precipitation reaction, Sr²⁺ cations are electron pair acceptors (Lewis acid), while the WO₄²⁻ anions are electron pair donors (Lewis base). The reaction between these two species in solution at room temperature with different strontium salts resulted in the formation of SrWO₄ microcrystals, as shown in following equations: (1, 2)

strontium acetate, (3, 4) strontium nitrate, and (5, 6) strontium chloride hexahydrate.

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$$\begin{split} & H_2WO_{2(s)} + Sr(CH_3CO_2)_{2(s)} \xrightarrow{H_2O} Sr_{(aq)}^{2+} + WO_{4(aq)}^{2-} + 2H_{(aq)}^+ \\ & + 2CH_3CO_{2(aq)}^- \end{split}$$

$$Sr_{(aq)}^{2+} + WO_{4(aq)}^{2-} + 2H_{(aq)}^{+} + 2CH_{3}CO_{2(aq)}^{-} \rightarrow SrWO_{4(s)} + 2H_{(aq)}^{+} + 2CH_{3}CO_{2(aq)}^{-}$$
(2)

$$\begin{aligned} &H_2 WO_{2(s)} + Sr(NO_3)_{2(s)} \xrightarrow{H_2 O} Sr_{(aq)}^{2+} + WO_{4(aq)}^{2-} + 2H_{(aq)}^+ \\ &+ 2NO_{3(aq)}^- \end{aligned}$$
(3)

$$Sr_{(aq)}^{2+} + WO_{4(aq)}^{2-} + 2H_{(aq)}^{+} + 2NO_{3(aq)}^{-} \rightarrow SrWO_{4(s)} + 2H_{(aq)}^{+} + 2NO_{3(aq)}^{-}$$
(4)

$$\begin{split} &H_2WO_{2(s)} + SrCl_2 \cdot 6H_2O_{(s)} \xrightarrow{H_2O} Sr_{(aq)}^{2+} + WO_{4(aq)}^{2-} + 2H_{(aq)}^+ \\ &+ 2Cl_{(aq)}^- + 6H_2O \end{split}$$

$$\begin{aligned} & Sr_{(aq)}^{2+} + WO_{4(aq)}^{2-} + 2H_{(aq)}^{+} + 2Cl_{(aq)}^{-} + 6H_2O \\ & \rightarrow SrWO_{4(s)} + 2H_{(aq)}^{+} + 2Cl_{(aq)}^{-} + 6H_2O. \end{aligned}$$

In order to increase the ionization rate of H_2WO_4 , the pH solution was adjusted up to 10 by the addition of 6 mL of ammonium hydroxide [NH₄OH] (30 % in NH₃, Mallinckrodt). Thereafter, these aqueous solutions were stirred for 30 min at room temperature. After the co-precipitation reaction is completed, these systems were washed and centrifuged several times with deionized water to neutralize the pH (\approx 7). Finally, the collected precipitates were dried in a lab oven at 60 °C for some hours.

Characterizations of SrWO₄ microcrystals

The synthesized microcrystals were structurally characterized by X-ray diffraction (XRD) using a DMax/2500PC diffractometer (Rigaku, Japan). XRD patterns were obtained with Cu-K α radiation in the 2 θ range from 10° to 90°, using a scanning speed of 2°/min. For Rietveld routines were adopted a 2θ range from 10° to 110° with a scanning speed of 0.02°/s. The electronic and local atomic structures around tungsten (W) atoms were checked by X-ray absorption near-edge structure (XANES). W L1.3edge XANES spectra were measured at the National Synchrotron Light Laboratory (LNLS) in Brazil, using the D04BXAFS1 beam line. XANES data were collected in transmission mode at room temperature with the samples deposited on polymeric membranes. These spectra were recorded for each sample using an energy step of 1.0 eV, before and after the edge, and 0.7 eV near the edge for $W-L_1$ and L_3 edge, respectively. The tungsten oxide (WO₃)

(>99 %) purchase from Aldrich was employed as reference compound in these measurements. FT-Raman spectra were recorded by means of a RFS100 spectrophotometer (Bruker, Germany) equipped with a Nd:YAG laser $(\lambda = 1064 \text{ nm})$, operating at 100 mW. FT-IR spectra were performed in the range from 50 to 1200 cm^{-1} , using an Equinox 55 spectrometer (Bruker, Germany) in transmittance mode. The morphologies were analyzed using a Supra 35-VP FE-SEM (Carl Zeiss, Germany) operated at 15 kV. UV-Vis absorption were taken using a Cary 5G spectrophotometer (Varian, USA) in diffuse reflection mode. PL spectra were obtained with a Monospec 27 monochromator (Thermal Jarrel Ash, USA) coupled to a R446 photomultiplier (Hamamatsu Photonics, Japan). A krypton ion laser (Coherent Innova 200K, USA) $(\lambda = 350 \text{ nm})$ was used as excitation source. The incident laser beam power on the samples was kept at 14 mW. UV-Vis and PL measurements were taken three times for each sample to ensure the reliability of the results. In our study, all experimental measurements were performed at room temperature.

Results and discussion

X-ray diffraction and Rietveld refinement analyses

Figure 1 shows the XRD patterns of SrWO₄ microcrystals co-precipitated with different strontium precursors.

The diffraction peaks can be used to evaluate the structural order at long range or periodicity of the material. In our case, the intense and sharp peaks of $SrWO_4$ crystals co-precipitated at room temperature indicate a good



Fig. 1 XRD patterns of $SrWO_4$ microcrystals synthesized with *a* SrNO₃, *b* SrCl₂·6H₂O, and *c* Sr(CH₃CO₂)₂. The vertical lines indicate the respective positions and intensities found in ICSD card no. 155793

crystallinity or periodicity at long range [32]. In Fig. 1a–c, XRD patterns provided the SrWO₄ microcrystals synthesized with Sr(NO₃)₂, SrCl₂·6H₂O, and Sr(CH₃CO₂)₂ precursors have single phase, which were perfectly assigned to the scheelite-type tetragonal structure with space group $I4_1/a$ (ICSD card no. 155793) [33].

Figure 2a–c illustrates the Rietveld refinement plots of $SrWO_4$ microcrystals co-precipitated with different strontium precursors.

The Rietveld refinement is a method in which the profile intensities obtained from step-scanning measurements of solid samples allow to estimate an approximate structural model for the real structure [34]. In our study, the Rietveld refinements were performed using the general structure analysis system (GSAS) software package with the EXPGUI graphical interface [35]. The refined parameters were scale factor, background, shift lattice constants, profile half-width parameters (u, v, w), isotropic thermal parameters, strain anisotropy factor, atomic functional positions, bond lengths, and bond angles. The background was corrected using the Chebyshev polynomials of the first kind [36]. The diffraction peak profiles were better fitted by Thompson-Cox-Hastings pseudo-Voigt (pVTCH) the function [37] and asymmetry function described by Finger et al. [38]. The strain anisotropy was corrected by the phenomenological model described by Stephens [39]. The theoretical diffraction pattern was taken from ICSD card no. 155793 [33], which is based on the SrWO₄ phase with scheelite-type tetragonal structure and space group $I4_1/a$. The Rietveld refinements of SrWO₄ microcrystals are shown in Fig. 2a-c, which are in good agreement with XRD results illustrated in Fig. 1. The obtained results from Rietveld refinements are listed in Table 1.

In this table, the fitting parameters (R_{wp} , R_p , R_{Bragg} , χ^2 , and S) indicate a good agreement between refined and observed XRD patterns for SrWO₄ phase. The lattice parameter values, unit cell volume, atomic positions, and bond angles confirmed the SrWO₄ phase has a tetragonal structure. All refinements reported in our study are in good agreement with those previously published [40, 41].

Structural representation of SrWO₄ crystals

Figure 3 illustrates the SrWO₄ structure modeled through the Diamond Crystal and Molecular Structure Visualization software [42], using the lattice parameters and atomic positions obtained from Rietveld refinements as input data.

SrWO₄ crystallizes in a tetragonal structure with space group $I4_1/a$ [43]. Chen et al. [44] described the tetragonal SrWO₄ structure constituted of four molecules per unit cell (Z = 4). Jia et al. [45] explained the A-sites related to strontium (Sr) atoms present point symmetry (S_4). Thus, SrWO₄ structure exhibits the Sr atoms bonded to eight



Fig. 2 Rietveld refinement plots of SrWO₄ microcrystals synthesized with the precursors salts: a SrNO₃, b SrCl₂·6H₂O, and c Sr(CH₃CO₂)₂

oxygens ([SrO₈] clusters), forming snub-disphenoid polyhedra (8 vertices, 12 faces, and 18 edges) and point-group symmetry (D_{2d}). On the other hand, tungsten (W) atoms are coordinated to four oxygens ([WO₄] clusters) with tetrahedral geometry (4 vertices, 4 faces, and 6 edges) and point-group symmetry (T_d). The tetrahedral [WO₄] clusters are slightly distorted inside the structure, as consequence of O–W–O bond angles ($\alpha = 106.1^{\circ}$ and $\beta = 116.43^{\circ}$) as shown in Fig. 3.

XANES spectroscopy analyses

Figure 4a shows W L_1 -edge XANES spectra, (b) area of the W L_1 -edge peak, and (c) W L_3 -edge XANES spectra of SrWO₄ microcrystals co-precipitated with different strontium precursors, respectively.

According to the literature [46–48], W L₁-edge XANES spectrum is a powerful tool to provide any information on the coordination environment (tetrahedral, square-based pyramid, octahedral, etc.), oxidation state, and local geometry of tungsten atoms. A closer examination in Fig. 4a revealed the XANES spectra of SrWO₄ microcrystals present intense and narrow W-L1 pre-edge absorption peaks (X) at around 12108 eV. This particular behavior is related to the existence of distorted tetrahedral [WO₄] clusters (Inset in Fig. 4a) [49]. On the other hand, the spectrum of WO₃ (standard sample) exhibited a slight shoulder in this same energy region. Kuzmin and Purans [50] reported the W-L₁ pre-edge absorption peak (X) is originated by the electronic transitions from 2s(W) to 5d(W) + 2p(O) orbitals. In other published studies [51], these authors explained that these electronic transitions are

Table 1 Lattice parameters, unit cell volume, site occupancy, andstatistical parameters obtained from Rietveld refinements of $SrWO_4$ microcrystals synthesized with different strontium precursors

	Wyckoff	Site	x	у	z
▼Atoms					
Strontium	4b	-4	0 0.25		0.625
Tungsten	4a	-4	0	0.25	0.125
Oxygen	16 <i>f</i>	1	0.2395	0.1062	0.0453
♣ Atoms					
Strontium	4b	-4	0	0.25	0.625
Tungsten	4a	-4	0	0.25	0.125
Oxygen	16 <i>f</i>	1	0.2465	0.1106	0.0455
▲Atoms					
Strontium	4b	-4	0	0.25	0.625
Tungsten	4a	-4	0	0.25	0.125
Oxygen	16 <i>f</i>	1	0.2497	0.0925	0.0421

 $R_{wp} = 6.16 \%, R_p = 4.54 \%, R_{Bragg} = 3.28 \%, \chi^2 = 3.9, S = 1.975,$ α = β = γ = 90° (a = b = 5.4277(6) Å e c = 11.9727(5) Å). $<math>R_{wp} = 7.20 \%, R_p = 5.37 \%, R_{Bragg} = 2.78 \%, \chi^2 = 5.0, S = 2.236,$ α = β = γ = 90° (a = b = 5.4281(2) Å e c = 11.9762(2) Å). $R_{wp} = 6.95 \%, R_p = 5.29 \%, R_{Bragg} = 1.99 \%, \chi^2 = 4.0, S = 2.0,$ α = β = γ = 90° (a = b = 5.4276(3) Å e c = 11.9761(4) Å). ▼SrWO₄ with Sr(CH₃CO₂)₂ precursor, ♣ SrWO₄ with SrCl₂·6H₂O precursor, and ♠ SrWO₄ with Sr(NO₃)₂ precursor



Fig. 3 Schematic representation of tetragonal SrWO₄ structure

all dipole forbidden in undistorted octahedral [WO₆] clusters (inversion center) and allowed in both distorted octahedral [WO₆] and tetrahedral [WO₄] clusters. Moreover, the intensity of the W-L₁ pre-edge absorption peak (**X**) is very sensitive and dependent on the degree of distortion in octahedral [WO₆] clusters relate to 5d(W) + 2p(O) orbitals [52]. We calculate the area of the W-L₁ pre-edge peak to evaluate the effect of strontium



Fig. 4 XANES spectra of SrWO₄ microcrystals at the **a** W-L₁ preedge, **b** area of the W-L₁ pre-edge peaks, and **c** XANES spectra at the (**a**) W-L₃ edge. WO₃ with monoclinic structure (Sigma-Aldrich 99.9 % purity) was used as standard sample

precursors in the degree of distortion of $[WO_4]$ clusters (order–disorder at short range) found in SrWO₄ microcrystals (Fig. 4b). For this purpose was employed the peakFit program (4.12 version), using the Voigt function [53]. According to the literature [54], the high area of the W-L₁ pre-edge peak of SrWO₄ microcrystals synthesized with SrNO₃ is associated to the strong interaction between tungsten and oxygen atoms. WO₃ used as standard sample exhibited a low value for the area of W-L₁ pre-edge peak; however, this behavior was ascribed to change of coordination in octahedral [WO₆] clusters, as a consequence of a split into e_g and t_{2g} orbitals by the ligand field theory. However, SrWO₄ microcrystals have only tetrahedral [WO₄] clusters, which present a split into t_2 and e orbitals.

XANES spectra at the W L3-edge of SrWO4 microcrystals are illustrated in Fig. 4c. Over again, WO₃ was employed as reference sample in these spectra. The preedge peak was located at around 10208 eV for SrWO₄ microcrystals and approximately 10210 eV for WO₃. SrWO₄ microcrystals synthesized with different strontium precursors have their W atoms bonded to four oxygens in a tetrahedral environment ([WO₄] clusters), while the WO₃ has W atoms bonded to six oxygens in a distorted octahedral configuration ($[WO_6]$ clusters). As a response to these differences in the coordination number, a slight shift in the respective positions of edge peak (Y) was detected between these samples in XANES spectra (\approx 10208 eV for SrWO₄ microcrystals ($\mathbf{\nabla}$) and ≈ 10210 eV for WO₃ powder (\blacksquare)). The origin of this pre-edge peak at the W L₃edge is ascribed to the permitted dipole transition from $2p_{3/2}(W)$ level to quasi-bound mixed state 5d(W) +2p(O) [55]. XANES spectra in our study of SrWO₄ microcrystals are in good agreement with those previously published on tungstates with scheelite-type tetragonal structure [56].

FT-Raman and FT-IR spectroscopies analyses

According to group theory calculations, $SrWO_4$ microcrystals are able to present 26 different vibration modes (Eq. (7)) [57]:

$$\Gamma_{[\text{Raman}]+(\text{infrared})} = \begin{bmatrix} 3A_g + 5B_g + 5E_g \end{bmatrix} + (5A_u + 3B_u + 5E_u), \tag{7}$$

where A_g , B_g , and E_g are Raman-active vibration modes; A and B modes are nondegenerate, while E modes are doubly degenerate. The subscripts [g] and (u) indicate the parity under inversion in centrosymmetric of SrWO₄ microcrystals. A_u and E_u modes correspond to zero frequency of acoustic modes, while the others are optic modes. In addition, A_g , B_g , and E_g modes arise from the same motion of SrWO₄ microcrystals. Therefore, it is expected 13 zone-center Raman-active modes for SrWO₄ microcrystals, as presented in Eq. (8) [58]:

$$\Gamma_{[\text{Raman}]} = 3A_g + 3B_g + 5E_g. \tag{8}$$

Degreniers et al. [59] reported the vibrational modes observed in Raman spectra of SrWO₄ can be classified into two groups: external and internal modes. The vibrational external modes are related to lattice phonon, which corresponds to the motion of [SrO₈] clusters and the rigid units. The vibrational internal modes are correspondent to the vibration inside tetrahedron [WO₄] clusters, considering the center of mass in stationary state. The isolated $[WO_4]$ clusters have a cubic symmetry point (T_d) and its vibrations are composed of four internal modes $(v_1(A_1), v_2(E_1))$, $v_3(F_2)$), and $v_4(F_2)$), one free rotation mode $(v_{fr}(F_1))$ and one translation mode (F_2) . On the other hand, the tungsten atoms belonging to tetrahedral [WO₄] clusters occupy the 4a Wyckoff positions with point symmetry (S_4), while the O atoms occupy the 16f Wyckoff positions with point symmetry (C_1) .

Figure 5 shows the FT-Raman spectra in the range from 50 to 1200 cm⁻¹ of SrWO₄ microcrystals co-precipitated with different strontium precursors.

As can be observed in Fig. 5, FT-Raman spectra revealed the presence of twelve Raman-active vibration modes. One B_g mode was not detectable because of its low intensity. The literature [56] describes the Raman spectroscopy can be employed as a structural probe to investigate the degree of structural order–disorder at short range in ABO₄ materials. Based on this concept, Raman spectra consisting of sharp, intense, and well-defined vibration bands are commonly verified in solids with local structural order. This phenomenon was verified in all SrWO₄ microcrystals obtained at room temperature by the



Fig. 5 FT-Raman spectra of $SrWO_4$ microcrystals synthesized with different strontium precursors. *Insets* show the typical bending and stretching vibrations exhibited by O–Sr–O and O–W–O bonds of $[SrO_8]$ and $[WO_4]$ clusters, respectively

co-precipitation method with [Sr(CH₃CO₂)₂], [Sr(NO₃)]₂, and [SrCl₂·6H₂O]. Our Raman results for SrWO₄ microcrystals are in good agreement with those previously published [58, 59]. Insets in Fig. 5a illustrate each assignment to Raman-active external and internal modes of SrWO₄ microcrystals. The first Raman-active B_g mode (83 cm^{-1}) is related to symmetric bending vibrations of (O-Sr-O) bonds in [SrO₈] clusters, the second Ramanactive E_g mode (100 cm⁻¹) is assigned to free motion at (x, y, z-axis) of [SrO₈] clusters, and the third Raman-active E_{ρ} mode (129 cm^{-1}) is ascribed to symmetric stretching vibrations of $(\leftarrow O \leftarrow Sr \rightarrow O \rightarrow)$ bonds in [SrO₈] clusters. The fourth and fifth Raman-active A_g and E_g modes (188 and 236 cm^{-1}) are classically identified as free rotation of tetrahedral $[WO_4]$ clusters. The sixth Raman-active B_g mode was not possible to detect it. The seventh and eighth Raman-active A_{ϱ}/B_{ϱ} modes are overlapped (335 cm^{-1}) , which are designed to asymmetric bending vibrations of $(\leftarrow O \leftarrow W/Sr\downarrow O\downarrow)$ bonds in $[WO_4]$ clusters. The ninth and tenth Raman-active B_g and E_g modes (370 and 380 cm^{-1} , respectively) are assigned to symmetric bending vibrations of [WO₄] clusters, and the eleventh and twelfth Raman-active E_g and B_g modes (796 and 835 cm⁻¹, respectively) are related to asymmetric stretching vibrations of $(\leftarrow O-W \rightarrow / \leftarrow O-W \rightarrow)$ bonds in [WO₄] clusters. Finally, the thirteenth Raman-active A_g mode (919 cm⁻¹) is referent to symmetric stretching vibrations of ($\leftarrow 0 \leftarrow$ $W \rightarrow O \rightarrow$) bonds in [WO₄] clusters. In addition, a comparison was made with the literature [58, 59] (Table 2).

In this table, the slight variations in the typical positions of Raman-active vibration modes are caused by distortions or changes in the length (O-W-O)/(O-Sr-O) bonds, modifications in the interaction forces involving the $[WO_4]-[SrO_8]-[WO_4]$ clusters, and the presence of structural order-disorder in the lattice, in consequence of the preparation methods and their experimental conditions.

Figure 6a, b shows FT-IR spectra in the range from 395 to 1000 cm^{-1} and from 1000 to 4000 cm^{-1} of SrWO₄ microcrystals, respectively.

In infrared spectra are expected 13 infrared vibrational modes $(5A_u + 3B_u + 5E_u)$ for tungstates. However, $1A_u$ and $1E_u$ are acoustic vibrations, i.e., infrared-inactive modes, while the others $3B_u$ are forbidden infrared modes. Therefore, only 8 infrared-active vibration modes remain, as presented in Eq. (9) [60]:

$$\Gamma_{(\text{infrared})} = 4A_u + 4E_u. \tag{9}$$

In our FT-IR spectra illustrated in Fig. 6a, only two of eight IR-active modes were verified. $3A_u$ and $3E_u$ modes may not have been detected due to limitations imposed by the FT-IR equipment. As was previously described, the tungstates with scheelite-type tetragonal structure have eight stretching and/or bending vibrational modes in their

FT-IR spectra. In our spectra were verified no more than two modes $(1(A_u) \text{ and } 1(E_u))$, which were identified at specific positions in the spectra (Fig. 6a). The first strong absorption band located at around 417 cm⁻¹ is ascribed to A_u mode. The strong and broad absorption band related to E_u mode located at 823/844 cm⁻¹ was ascribed to (\leftarrow $O \leftarrow W \leftarrow O \leftarrow)/(\rightarrow O \rightarrow W \rightarrow O \rightarrow)$ anti-symmetric stretching vibrations inside the [WO₄] clusters. In Fig. 6b was verified other absorption bands in FT-IR spectra due to the presence of carbon dioxide (CO₂) and water (H₂O) arising from the room atmosphere and humidity. The small band noted at 2500 cm⁻¹ is due to v(C=O) stretching mode. The broad absorption band at 3400 cm⁻¹ corresponds to O–H stretching vibrations of adsorbed water on the surface of SrWO₄ microcrystals.

FE-SEM image analyses

Figure 7 illustrates the FE-SEM images at low and high magnifications of $SrWO_4$ microcrystals co-precipitated at room temperature with (a–c) [SrNO₃], (d–f) $Sr(CH_3CO_2)_2$, and (g–i) [SrCl₂·6H₂O], respectively.

Figure 7a reveals the SrWO₄ microcrystals obtained with SrNO₃ precursor are basically formed of several nanocrystals governed by self-assembled process, resulting in pitch pine cone-like microcrystals [61]. FE-SEM images at high magnification (Fig. 7b) proved the SrWO₄ microcrystals are not dense and faceted structures. This behavior was related to significant amount of SrWO₄ nanocrystals that have not completely migrated from crystal surface to internal region of pitch pine cone-like microcrystals. These microcrystals have an average size of approximately 1.8 µm. In Fig. 7c was noted a mutual aggregation between pitch pine cone-like microcrystals in a chemical environment under basic pH conditions, leading to the growth of its lateral edges (longleaf pine cone-like microcrystals). The literature [62] have reported the growth of shuttle-like BaWO₄ structures in water and ethanol by means oriented attachment, which is related to assembled from several small primary nanoparticles. These same morphological shapes were identified for SrWO₄ microcrystals synthesized with Sr(CH₃CO₂)₂ precursor (Fig. 7d-f); however, these microcrystals have an average size of approximately 2.2 μ m. In Fig. 7g, we can verify the [SrCl₂·6H₂O] precursor promoted an incomplete growth and agglomeration of some pitch and longleaf pine cone-like SrWO₄ microcrystals. This behavior can be associated to the influence of chloride ions (Cl⁻) in aqueous solution, during the interaction process between Sr^{2+} and WO_4^{2-} ions and formation of first nanocrystals. This particular characteristic of Clions can inhibit the crystal growth process via selfassembly, resulting in defects and irregularities in the pitch and longleaf pine cone-like SrWO₄ microcrystals (Fig. 7h,

Lattice mode symmetry (C_{4h}^6)	٨	•	*	[58]	[59]	Assignments	
Bg	83	83	83	_	75	vext	
E_g	100	100	100	-	102		
E_g	129	129	129	-	133		
B_g	-	-	-	-	-		
A_g	188	188	188	187	190	$v_{r.f.}(F_1)$	
E_g	236	236	236	-	238		
A_g	335	335	335	334	336	$v_2(E)$	
B_g	335	335	335	-	336		
B_g	370	370	370	373	374	$v_4(F_2)$	
E_g	380	380	380	-	-		
E_g	796	796	796	791	800	$v_3(F_2)$	
B_g	835	835	835	831	837		
A_g	919	919	919	912	921	$v_1(A_1)$	

i). Particularly, these microcrystals have an average size of approximately $1.6 \ \mu m$.

Growth mechanism of SrWO₄ crystals

Figure 8a–e illustrates a hypothetical growth mechanism of SrWO₄ microcrystals formed by the co-precipitation route at room temperature with different strontium precursors.

Figure 8a shows the initial synthesis stage of SrWO₄ microcrystals by the co-precipitation reaction, which involves the solubilization in water of H₂WO₄ and different strontium precursors, SrNO₃, Sr(CH₃CO₂)₂, and SrCl₂ ·6H₂O. The resulting solutions were placed in ultrasonic bath for 30 min to accelerate the co-precipitation rate. In the sequence, 6 mL of NH₄OH was added in each system to intensify the ionization rate of H₂WO₄ in the aqueous solution. In this case, Sr^{2+} cations are electron pair acceptors (Lewis acid), which are arising from strontium precursors with distinct solubility product constant $[K_{sp}]$ in water at room temperature, such as $[SrNO_3] \rightarrow$ $K_{sp} = 70.9 \text{ g/100 mL}; \text{ [SrCl}_2 \cdot 6H_2 \text{O}] \rightarrow K_{sp} = 53.8 \text{ g/100}$ mL, and Sr(CH₃CO₂)₂ \rightarrow K_{sp} = 36.9 g/100 mL. The WO_4^{2-} anions are electron pair donors (Lewis base), which are arising from H_2WO_4 in water. The reaction at pH 10 involving these two species ($Sr^{2+} \leftarrow WO_4^{2-}$ ions) results in a covalent bond. The covalent bond occurs due to Lewis acid to occupy the lowest molecular orbital (LUMO), which interacts with the highest molecular orbital (HOMO) of the Lewis base. In Fig. 8b is illustrated the interaction process between Sr^{2+} and WO_4^{2-} ions. Before these interactions occur, the solvation energy of water molecules promotes a rapid dissociation of the salts involved in the reaction, so that the Sr^{2+} and WO_4^{2-} ions are rapidly solvated by the water molecules. The partial negative charge of water molecules is electrostatically attracted by Sr²⁺ ions, while the other positive charge is attracted by WO_4^{2-}

ions [63]. However, there is a strong electrostatic attraction between Sr^{2+} and WO_4^{2-} ions, resulting in the formation of first SrWO₄ precipitates or nucleation seeds. After this interaction, instantaneously occurs the formation of first nucleation seeds (Fig. 8c). These nuclei interact with other, forming the SrWO₄ nanocrystals (pine nut-like nanocrystals), which are able to grow via self-assembly mechanism (Fig. 8d). Basically, in this type of growth mechanism, there is a spontaneous and mutual aggregation between nanocrystals by means of uncountable collision events (particle-particle interactions) followed by the coalescence of SrWO₄ nanocrystals. The growth and agglomeration of these nanocrystals promotes the origin of complex superstructures or large SrWO₄ microcrystals. It is important to highlight that the average yield (%) results for the formation of nanoparticles of each strontium precursor are correlated with their solubility product constants at 28 °C/ 100 mL in water. On the other hand, when SrNO₃, Sr(CH₃CO₂)₂, and SrCl₂·6H₂O precursors were used in the co-precipitation synthesis, there is the formation of pitch and longleaf pine cone-like SrWO₄ microcrystals (Fig. 8d). In principle, we report, based on our FE-SEM images, that longleaf pine cone-like SrWO₄ microcrystals are originated by the aggregation of several pitch pine cone-like microcrystals (Fig. 8e). The formation and growth of these microcrystals are in agreement with the morphological aspects of other tungstates published in the literature [63].

UV-Vis diffuse reflectance spectroscopy analyses

The optical band gap energy (E_{gap}) values were calculated by the Kubelka–Munk equation [64], which is based on the transformation of diffuse reflectance measurements to estimate E_{gap} values with good accuracy [65]. Particularly, it is used in limited cases of infinitely thick samples. The Kubelka–Munk equation for any wavelength is described by





Fig. 6 FT-IR spectra in the range from: **a** 395 to 1000 cm^{-1} and **b** 1000 to 4000 cm⁻¹ of SrWO₄ microcrystals synthesized with different strontium precursors. The *vertical lines dashed* indicate the positions of IR-active modes

$$\frac{K}{S} = \frac{\left(1 - R_{\infty}\right)^2}{2R_{\infty}} \equiv F(R_{\infty}),\tag{10}$$

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 sample in reflectance measurements; $R_{\infty} = R_{\text{sample}}/R_{\text{MgO}}$ (R_{∞} is the reflectance), *K* is the molar absorption coefficient, and *S* is the scattering coefficient. In a parabolic band structure, the optical band gap and absorption coefficient of semiconductor oxides [66] can be calculated by the following equation:

$$\alpha h v = C_1 (h v - E_{\text{gap}})^n, \tag{11}$$

where α is the linear absorption coefficient of the material, hv is the photon energy, C_1 is a proportionality constant, E_{gap} is the optical band gap, and n is a constant associated with different types of electronic transitions (n = 1/2 for direct allowed, n = 2 for indirect allowed, n = 1.5 for direct forbidden, and n = 3 for indirect forbidden). According to the theoretical calculations reported in the literature [67], scheelite (ABO₄) crystals exhibit an optical absorption spectrum governed by direct electronic transitions. In this phenomenon, after the electronic absorption, the electrons located in minimum energy states in the conduction band (CB) are able to go back to maximum energy states of the valence band (VB) in the same points in the Brillouin zone [68]. Based on this information, E_{gap} values of our SrWO₄ microcrystals were calculated using n = 1/2 in Eq. 11. Finally, using the diffuse reflectance function described in Eq. 10 with $K = 2\alpha$, we obtain the modified Kubelka–Munk equation as indicated in Eq. (12):

$$\left[F(\mathbf{R}_{\infty})h\nu\right)^{2} = C_{2}\left(h\nu - E_{gap}\right).$$
⁽¹²⁾

Therefore, finding the $F(R_{\infty})$ value from Eq. (12) and plotting a graph of $[F(R_{\infty})hv]^2$ versus hv, E_{gap} values of all SrWO₄ microcrystals can be calculated extrapolating the linear portion of UV–Vis curves.

Figure 9a–c shows UV–Vis spectra of SrWO₄ microcrystals co-precipitated at room temperature with different strontium precursors.

In this figure, there is slight changes in E_{gap} values according to the type of strontium precursor employed in the synthesis of SrWO₄ microcrystals. The exponential optical absorption edge and $E_{\rm gap}$ are controlled by the degree of structural order-disorder in the lattice [69]. Therefore, the lowest E_{gap} (4.84 eV) was detected for SrWO₄ microcrystals obtained with SrNO₃ precursor, suggesting the existence of uncountable intermediary energy levels within the forbidden band gap, as a consequence of a high defect density in the lattice, such as distortions in O-W-O or O-Sr-O bonds, oxygen vacancies, cracks, pores, dislocations, grain boundaries, etc. SrWO₄ microcrystals prepared with SrCl₂·6H₂O and $Sr(CH_3CO_2)_2$ precursors exhibited E_{gap} of 4.87 and 5.0 eV, respectively (Fig. 9b, c). These results suggest a lower concentration of structural defects in these microcrystals in relation to those obtained with SrNO₃ precursor. It is important to highlight that the types as well as the contribution single or joint of these energy levels within the band gap in these microcrystals can be achieved only by means of theoretical calculations.



Fig. 7 FE-SEM images at low and high resolution of SrWO₄ microcrystals synthesized with a-c SrNO₃, d-f Sr(CH₃CO₂)₂, and g-i SrCl₂·6H₂O

PL emission analyses

Figure 10 illustrates PL spectra recorded at room temperature of $SrWO_4$ microcrystals co-precipitated at room temperature with different strontium precursors.

These PL spectra present a broad band covering a large part of visible electromagnetic spectra (from 380 to 600 nm), indicating a contribution of several energy states within the band gap. These states are related to the numerous types of defects directly associated to the degree of structural order–disorder in the lattice. Topological disorder is a type of disorder associated with glassy and amorphous solid structures, in which the structure cannot be defined in terms of a periodic lattice. According to the literature [70–72], the blue-green PL emissions of SrWO₄ are caused by the surface and structural defects, particle

Fig. 8 Proposed growth mechanism of SrWO₄ microcrystals synthesized with different strontium precursors [SrNO₃, SrCl₂·6H₂O, and $Sr(CH_3CO_2)_2$] in **a** aqueous solution: **b** electrostatic attraction between Sr²⁺ and WO_4^{2-} ions in solution; c formation and interaction of first nucleation seeds, resulting in SrWO₄ nanocrystals; **d** growth stage of nanocrystals (pine nut-like nanocrystals) via self-assembly mechanism, forming pitch cone-like microcrystals; and e mutual aggregation of several pitch pine cone-like microcrystals. resulting in longleaf pine conelike microcrystals



shapes, narrow particle size distribution, Jahn–Teller splitting effect in $[WO_4^{2-}]$ tetrahedron, preferred orientation, etc. Based on our Rietveld refinements and UV–Vis spectra, there is the possibility of electronic transitions involving single clusters ($[WO_4]$ or $[SrO_8]$) or from cluster to cluster ($[WO_4]$ – $[SrO_8]$ and/or $[SrO_8]$ – $[SrO_8]$) in the PL response of SrWO₄ microcrystals. Basically, PL properties of solids can be influenced by the concentration of different intrinsic (bulk/surface) and extrinsic defects (structural order–disorder), which are responsible for the modifications in the number of intermediary energy states within the band gap. These structural defects are able to promote a symmetry break, causing a polarization in the SrWO₄ structure by the electronic charge transfer from ordered (o) to disordered (d) clusters (formation of $e-h^{\bullet}$ pairs). Hence, we presume the existence of four types of complex clusters, in which the first and second are more distorted (d) and assigned as $[WO_4]_d$ and $[SrO_4]_d$ clusters, respectively. The third and fourth are considered less distorted or ordered (o) and designed as $[WO_4]_o$ and $[SrO_4]_o$ clusters. In this proposed mechanism, the possible charge transfers between $[WO_4]_d^x - [SrO_8]_o^x$, $[SrO_8]_d^x - [WO_4]_o^x$, $[WO_4]_d^x - [SrO_8]_o^x - [WO_4]_o^x$, and $[SrO_8]_d^x - [SrO_8]_o^x$ clusters are shown in the following equations below:



Fig. 9 UV-Vis spectra of SrWO₄ microcrystals synthesized with different strontium precursors

$$\stackrel{h\nu(\text{Excitation}=\lambda=350 \text{ nm})}{\longrightarrow} [\text{WO}_4]_d^x \xrightarrow{e'} [\text{SrO}_8]_o^x \to [\text{WO}_4]_d^{\cdot} - [\text{SrO}_8]_o'$$
(13)

$$[\operatorname{SrO}_8]_d^x \xrightarrow{e'} [\operatorname{WO}_4]_o^x \to [\operatorname{SrO}_8]_d^{-} - [\operatorname{WO}_4]_o^{\prime}$$
(14)

$$[WO_4]_d^x \xrightarrow{e'} [SrO_8]_o^x - [WO_4]_o^x \rightarrow [WO_4]_d^r - [SrO_8]_o'$$

$$-[WO_4]_o^x \rightarrow [WO_4]_d^r - [SrO_8]_o^x - [WO_4]_o'$$
(15)

$$[\operatorname{SrO}_8]_d^x \xrightarrow{e} [\operatorname{WO}_4]_o^x - [\operatorname{SrO}_8]_o^x \to [\operatorname{SrO}_8]_d^{-} - [\operatorname{WO}_4]_o^{\prime} - [\operatorname{SrO}_8]_o^x \to [\operatorname{SrO}_8]_o^{\prime} \xrightarrow{h\nu'(\operatorname{Emission} \neq \lambda \neq 350 \operatorname{nm})}.$$

$$(16)$$

In Eqs. (13-16), the cluster-to-cluster charge transfer (CCCT) in a crystal containing more than one type of

cluster is characterized by excitations involving electronic transitions from one cluster to another cluster. During the excitation process at room temperature, the electrons situated at lower intermediary energy levels (O 2*p* orbitals) absorb the photon energies (*hv*) (350 nm \approx 3.54 eV). As consequence of this phenomenon, the energetic electrons are promoted to higher intermediary energy levels (W 5*d* orbitals) located near the CB. When the electrons fall back to lower energy states, the energies arising from these electronic transitions are converted in photons (*hv'*). In this case, the several photons (*hv'*) originated by the participation of different energy states during the electronic transitions are responsible for the broad PL spectra. In addition, PL profiles of SrWO₄ microcrystals exhibit different emissions intensities, depending on the type of



Fig. 10 PL spectra of $SrWO_4$ microcrystals synthesized with different precursors salts

strontium precursor (Fig. 10). Moreover, insets in Fig. 10 illustrate different O–W–O bond angles (α and β), suggesting that the tetrahedral [WO₄] clusters are distorted in the lattice. These bond angles were estimated using the lattice parameters and atomic positions obtained from Rietveld refinements as input data in the crystal and molecular structure visualization software [42]. These distortions are key factors for the origin of intermediary energy states within the forbidden region, influencing in the PL response of SrWO₄ microcrystals.

Conclusion

In summary, SrWO₄ microcrystals were synthesize by the co-precipitation method at room temperature with different strontium precursors [SrNO₃, SrCl₂·6H₂O, and Sr(CH₃₋ CO₂)₂]. XRD patterns and Rietveld refinements revealed the SrWO₄ microcrystals have a scheelite-type tetragonal structure with a good degree of crystallinity (ordered at long range), in which the [WO₄] clusters are slightly distorted in the lattice. Independent of the type of strontium precursor, FT-Raman spectra showed the SrWO₄ microcrystals have well-defined vibrational bands, suggesting a structurally ordered matrix at short range. FT-IR spectra detected the IR-active modes of typical anti-symmetric stretching vibrations of tetrahedral [WO₄] clusters. According to the XANES spectra, all samples obtained in this work have their W atoms bonded to four oxygens ([WO₄] clusters). The calculated area of the W L₁-edge peaks indicated the SrWO₄ microcrystals synthesized with SrNO₃ have a strong interaction between O-W-O bonds in relation to other precursors. In morphological terms,

SrWO₄ is composed of pitch and longleaf pine cone-like microcrystals, when the SrNO₃, SrCl₂·6H₂O, and Sr(CH₃. CO₂)₂ precursors were used in the co-precipitation synthesis. Comparing the E_{gap} values, the results demonstrated the type of strontium precursor used in the formation of SrWO₄ microcrystals is able to originate distinct quantities and/or distributions of intermediary energy states within the band gap. The lowest E_{gap} was detected for SrWO₄ microcrystals obtained with SrNO₃ precursor, suggesting a structure with a high concentration of structural defects. The differences in PL profiles, especially in terms of intensity, were related to electronic transitions in distorted [WO₄] clusters and/or from cluster to cluster ([WO₄] \rightarrow [SrO₈] and/or [SrO₈] \rightarrow [SrO₈]).

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