Synthesis and characterization of solid solution of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals obtained by the sonochemical method and their sonophotocatalytic properties

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Abstract

In this paper, the solid solution of strontium molybdate-tungstate $[\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4]$ crystals with ($x = 0; 0.25; 0.50; 0.75$; and 1) were synthesized by the sonochemical method. Their structure, morphology, optical, and sonophotocatalytic (SPC) properties were evaluated as a function of the replacement of Mo^{6+} by W^{6+} cations into the lattice. Structural characterizations performed by X-ray diffraction, Rietveld refinement, micro-Raman, and Fourier transform infrared spectroscopies proved that all samples are monophasic and crystalline, with a scheelite-type tetragonal structure. Field-emission scanning electron microscopy images revealed the octahedral and dumbbell-like morphologies for SrMoO_4 and SrWO_4 crystals. Moreover, it was noted to pass through spindle-like morphology for the microcrystals containing both Mo^{6+} and W^{6+} cations ($x = 0.25; 0.50$; and 0.75). The absorption spectra obtained through ultraviolet-visible diffuse reflectance spectroscopy showed a directly proportional increase in the optical band gap (E_{gap}) values from 4.27 to 5.01 eV. These data indicate an increase in the intermediary electronic levels between valance and conduction band with the raise of the concentration of W^{6+} cations in the lattice. Finally, we have found that the $\text{Sr}(\text{Mo}_{0.25}\text{W}_{0.75})\text{O}_4$ crystals displayed the best SPC activity, around 98% of the Rhodamine B dye was degraded in 240 min.

1. Introduction

In the last decades, molybdenum and tungsten oxides have been widely studied due to their excellent chemical, physical and structural properties [1]. Among them, alkaline earth metals, with general formula ABO_4 , have shown promise, offering several application opportunities aimed at different areas, such as electrochemical sensors, humidity sensors, scintillators, optical fibers, electrocatalysts, photocatalysts, capacitors, solar cells, microwave dielectric devices, light-emitting diodes, solid-state lasers, Raman lasers, electrodes for lithium-ion batteries, drug releasers, and many others [2–8].

Depending on the size of the divalent cation (A^{2+}), they crystallize into the scheelite-type tetragonal structure or wolframite-type monoclinic structure. In the scheelite structure ($r_A^{2+} > 1.0 \text{ \AA}$, $A = \text{Ca, Sr, Ba, and Pb}$), the A^{2+} cations are coordinated with eight oxygen atoms, assuming a $[\text{AO}_8]$ deltahedral configuration, while the B^{6+} cations (tungsten (W^{6+}) or molybdenum (Mo^{6+})) are surrounded by four equivalent O atoms, displaying a $[\text{WO}_4]$ or $[\text{MoO}_4]$ tetrahedral coordination. In the wolframite structure ($r_A^{2+} < 1.0 \text{ \AA}$, $A = \text{Mg}$), both the A^{2+} and the W^{6+} or Mo^{6+} cations are coordinated by six O atoms [1, 9]. The scheelite structure is characterized by the space group I_4/a (No. 88) with 4 units of molecular formula per unit cell ($Z = 4$), in which the deltahedral and tetrahedral groups are then slightly distorted [5, 10]. Several types of defects are associated with the degree of structural order-disorder, such as oxygen vacancies and intermediate energy levels, giving these materials the ability to emit blue and green light under ultraviolet (UV)-excitation [9, 11, 12]. Therefore, they are widely used as host materials for lanthanide ions. When doped, they transfer the absorbed energy to the doping ions, expanding the luminescent spectrum and application possibilities [13, 14].

It is known that the physical, chemical, and structural properties of these materials strongly depend on the obtention method [15, 16]. Until now, several synthesis methods have been developed, such as solid-state synthesis, co-precipitation, sol-gel, hydrothermal, solvothermal, electrochemical, sonochemical, polymeric precursor method, by ion injection, microwave [12, 17, 18]. Among the methods mentioned, the sonochemical emerged as a powerful technique capable of promoting a variety of chemical reactions with savings of time and energy [19]. Considered as technique ecologically correct due to its simplicity and fast processing, it allows the large-scale production of a variety of materials with a high degree of crystallinity and purity, with size and morphology control, without the need for high temperature or pressure, using low-cost equipment [20–22]. The fast processing is due to the effects arising from the phenomenon of acoustic cavitation [23].

According to the literature [24, 25], when aqueous suspensions are subjected to ultrasonic waves, vapor bubbles are generated in the liquid medium that constantly grows and implodes, producing microscopically located hot spots with temperatures that can exceed 5000 K, pressures above 1000 atm, and heating/cooling rates close to 10^{10} K.s^{-1} . The extreme conditions of temperature and pressure created followed by a very fast cooling rate can be favorable for a wide range of chemical reactions [16, 26]. The shock waves created during the implosive collapse of the cavitation bubbles generate a strong turbulent flow in the liquid, improving mass transport, causing a considerable increase in the speed of reactions. Furthermore, suspended solid particles can be accelerated by increasing inter-particle collision rates directly influencing their size, morphology, distribution, and surface composition [27, 28]. During the cavitation process, the large amount of energy released forms hydroxyl radicals ($\text{HO}^\bullet$) and reactive hydrogen ($\text{H}^\bullet$) by sonolysis of water molecules [29], which is why the sonochemical method has also been applied as one of the advanced oxidative methods for removal of organic pollutants from residual waters [30].

Sonochemical degradation can be increased by the fusion of ultrasound with appropriate heterogeneous catalysts and a light source in a process known as sonophotocatalysis [31]. Just as ultraviolet or visible light can provide energy to stimulate the photocatalyst to generate electron-hole pairs ($e^- \leftrightarrow h^+$) and produce more reactive species, ultrasound can also through sonoluminescence. Additionally, the photocatalysts can act as an additional nucleus to form more cavitation bubbles [32, 33]. On the other hand, the successive implosions of cavitation bubbles contribute to the continuous cleaning of the catalyst surface (regenerating its active sites) and prevent the agglomeration of particles, thus increasing the accessible surface area for the successive reactions mentioned above that lead to degradation of the contaminant [34, 35].

Notably, strontium molybdates and tungstates (SrMoO_4 and SrWO_4 , respectively) are considered to be promising photocatalysts for the degradation of many organic pollutants [36, 37] because they are low-cost materials with a diversity of syntheses, improved thermal and chemical stability, and attractive electrical, magnetic, and optical properties [3, 10, 12]. Among these organic pollutants are the dyes commonly present in industrial residual waters sometimes discharged into the aquatic environment without proper treatment, seriously harming its ecosystem, directly affecting human, fauna, and flora

health due to the carcinogenic, genotoxic, and mutagenic nature of most of these dyes. Therefore, studies aimed at the complete degradation of these pollutants are of paramount importance [38, 39].

Previously, the authors focused their attention on the investigation of the structural, morphological, optical, and sonophotocatalytic (SPC) properties of calcium and strontium tungstate ($\text{Ca}_{1-x}\text{Sr}_x\text{WO}_4$ with ($x = 0; 0.25; 0.50; 0.75$; and 1) synthesized by the sonochemical method, evaluating the influence of the gradual replacement of Ca^{2+} by Sr^{2+} cations on such properties [40]. As a way of continuing this study, this work attention was directed to the solid solution of strontium molybdate-tungstate [$\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$] crystals with ($x = 0; 0.25; 0.50; 0.75$; and 1), also synthesized by the sonochemical method. However, this time, the influence of substitution in the B-site into the tetragonal lattice, that is, of the Mo^{6+} by the W^{6+} cations, in the structure, morphology, optical and SPC properties against of Rhodamine B (RhB) dye will be evaluated.

2. Experimental Details

2.1. Sonochemical synthesis of solid solution of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals

Solid solutions of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals with ($x = 0; 0.25; 0.50; 0.75$; and 1) were synthesized by the sonochemical method in which 1×10^{-3} mol of strontium nitrate [$\text{Sr}(\text{NO}_3)_2$, ACS; 99.0% purity, Synth], previously dissolved in 50 mL of deionized water, was slowly dripped with a graduated burette (approximately one drop/second) in 50 mL of a solution containing 1×10^{-3} mol of sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$; 99% purity, Sigma–Aldrich) and/or 1×10^{-3} mol of sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$; 99.5% purity, Sigma–Aldrich) according to the desired stoichiometric ratio. This resulting solution was maintained at an average temperature of 40°C for 3 h by using an ultrasonic bath (TABLETOP 402 DIGITAL, Delta Ultrasound).

The following equation below (1–4) describes the chemical reactions involved in the formation of solid solution of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals:

All suspensions and solid precipitated obtained after the sonochemical method were washed with deionized water (twenty times) and centrifuged (5000 RPM for 10 min). The precipitates were collected and dried in a muffle furnace (W-One, EDG equipment) at 65°C for 12 h with a heating rate of $5^\circ\text{C}/\text{min}$.

2.2. Characterizations

The structural analysis of the solid solution of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals with ($x = 0; 0.25; 0.50; 0.75$; and 1) was performed by means of X-ray diffraction (XRD) and Rietveld refinement. The measurements of X-ray patterns were carried out using a LabX XRD-6000 diffractometer (Shimadzu®, Japan), operating at 40 kV and 20 mA, Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) in a 2θ range from 10° to 110° with a scan rate of $1^\circ/\text{min}$. Rietveld refinement [41] of the measured XRD pattern was carried out using the general structure analysis (GSAS) program [42]. The diffraction peak profiles were adjusted using the Thompson–Cox–Hastings pseudo-Voigt (pV-TCH) function and by an asymmetry function, as described by Finger *et al.* [43]. The background was corrected using a Chebyshev polynomial of the first order. The strain anisotropy broadening was corrected using the phenomenological model described by Stephens [44]. The structural data obtained were used to simulate the sample structures through the 3D Visualization for Electronic and Structural Analysis (VESTA) software, version 3.5.7 for 64-bit version of Windows7® [45, 46]. The analyzes of Raman spectroscopy were carried out in a Senterra II micro-spectrometer (Bruker®, Germany) using a laser of 785 nm as excitation source, output power of 100 mW, spectral resolution of 3 cm^{-1} and the range from 50 to 1000 cm^{-1} . Fourier-transform infrared (FT-IR) spectra were acquired on a Vertex 70 spectrometer (Bruker®, Germany) ranging from 400 to 1000 cm^{-1} , using cesium iodide (CsI) as standard. The particle shapes and sizes were observed in a field-emission scanning electron microscope (FE-SEM), JSM-7100F (JEOL®, Japan), over an electron acceleration voltage of 15 kV. The optical properties were investigated by ultraviolet-visible (UV–Vis) spectroscopy on a UV-2600 spectrophotometer (Shimadzu®, Japan) in diffuse reflectance mode.

2.3. Sonophotocatalytic activities measurements

The SPC properties of the samples synthesized were investigated for the degradation of RhB dye ($\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$, CAS: 81889, 95% purity, Sigma-Aldrich) in aqueous solution ($1 \times 10^{-5} \text{ mol.L}^{-1}$) under UV-C light for 240 min. In these tests, 50 mg of the sample and 100 mL of RhB dye solution were placed in a 250 mL beaker which was then placed inside the ultrasonic bath (M1800 model, BRANSON®, 40 kHz, 70 W) and illuminated by four UV-C lamps (OSRAM®, 15 W each, $\lambda_{\text{max}} = 254 \text{ nm} \approx 4.88 \text{ eV}$) positioned at a distance of, approximately, 45 cm from the solution. However, before UV-C illumination, the suspensions were only kept under sonication for 5 min in the dark in order to achieve the adsorption-desorption equilibrium. At intervals of 5, 10 and 20 min, aliquots of 2.2 mL were collected and centrifuged (6000 rpm for 20 min) to separate the catalysts from the liquid phase. The variations in the

maximum absorption band ($\lambda_{\text{max}} = 554 \text{ nm}$) of RhB solutions were monitored by means of UV–Vis absorption spectroscopy on a UV-2600 spectrophotometer (Shimadzu®, Japan). Eq. (5) was used to calculate the catalytic efficiency:

$$\text{Catalytic Efficiency of Sr(Mo}_{1-x}\text{W}_x\text{)O}_4 \text{ crystals (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

5
where C_0 correspond to the concentrations of dye solution at the beginning and C_t , at time t .

The photocatalytic (PC) and sonocatalytic (SC) activities of the samples were also investigated, as well as the photolysis (P), sonolysis (S) and sonophotolysis (SP) of RhB dye, in order to understand the synergistic and individual effects of each system.

2.4 Radical-trapping experiments

The participation of reactive species: hydroxyl radical ($\text{HO}^\bullet$), superoxide radical ($\text{O}_2^{\bullet-}$) and the photogenerated $e^- \leftrightarrow h^+$ pairs in the SC and SPC of the RhB were investigated by the radical-trapping experiments. Isopropyl alcohol (ISO, $\text{C}_3\text{H}_8\text{O}$, 99.5% purity, Dinâmica), *p*-benzoquinone (BQ, $\text{C}_6\text{H}_4\text{O}_2$, 98% purity, Dinâmica), silver nitrate (AgNO_3 , 99% purity, Sigma-Aldrich), and ammonium oxalate (AO, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, 99% purity, Dinâmica) were used as scavengers to trap $\text{OH}^\bullet$, $\text{O}_2^{\bullet-}$, e^- , and h^+ , respectively. $1 \times 10^{-4} \text{ mol.L}^{-1}$ of scavengers (except the $\text{C}_3\text{H}_8\text{O}$ which was used in the proportion of $1 \times 10^{-1} \text{ mol.L}^{-1}$) were added to the system after the 5 min in the dark and the tests proceeded as described above.

3. Results And Discussion

3.1. XRD patterns of the solid solution of $\text{Sr(Mo}_{1-x}\text{W}_x\text{)O}_4$ crystals

Figures 1(a–e) show the XRD patterns of the solid solution of $\text{Sr(Mo}_{1-x}\text{W}_x\text{)O}_4$ crystals ($x = 0; 0.25; 0.50; 0.75$; and 1) samples in the 2θ range from 10 to 70° .

<Insert Figs. 1(a–e) here>

For the pure SrMoO_4 crystals, all the diffraction peaks were in good agreement with those registered and reported in the Inorganic Crystal Structure Database (ICSD) card No. 250491 [47]. Already for our SrWO_4 crystals, the diffraction peaks were matched with those registered according to the ICSD card No. 291536 [48]. These pure crystals presented the scheelite-type tetragonal structure, space group $I4_1/a$, symmetry point group C_{4h}^6 , four molecular formula units per unit cell ($Z = 4$), and No. 88 at International Tables of Crystallography. The solid solutions of $\text{Sr(Mo}_{0.25}\text{W}_{0.75}\text{)O}_4$, $\text{Sr(Mo}_{0.50}\text{W}_{0.50}\text{)O}_4$, and $\text{Sr(Mo}_{0.75}\text{W}_{0.25}\text{)O}_4$ crystals present their crystallographic information files (CIF) generated after Rietveld refinement using both ICSD cards of the samples pure proportionally to the desired stoichiometric information for each one. It is possible to observe that with the increase in the amount of Mo^{6+} cations, the diffraction peaks located around 18° and 54° almost disappeared, confirming the replacement. However, the other peaks exhibit practically identical locations and profiles due to the similarity between the ionic radii of Mo^{6+} and W^{6+} cations ($0.41 \text{ \AA}$ and $0.42 \text{ \AA}$, respectively, when the coordinate number for both is 4) [49]. The absence of additional peaks suggests the chemical homogeneity of solid solutions. The sharp diffraction peaks indicate a good crystallinity of the obtained products [50].

3.2 Rietveld refinements of solid solution $\text{Sr(Mo}_{1-x}\text{W}_x\text{)O}_4$ crystals

Figures 2(a–e) display the Rietveld refinement plots of the solid solution of $\text{Sr(Mo}_{1-x}\text{W}_x\text{)O}_4$ crystals with ($x = 0; 0.25; 0.50; 0.75$; and 1) obtained by the sonochemical method.

<Insert Figs. 2(a–e) here>

The structural study and investigation for all solid solution of $\text{Sr(Mo}_{1-x}\text{W}_x\text{)O}_4$ crystals synthesized by the sonochemical method was performed by means of XRD with Rietveld refinement. The measured diffraction patterns were adjusted to the ICSD No. 250491 [41] and ICSD No. 291536 [42]. As displayed in Figs. 2(a–e), the Rietveld refinement plots of these crystals showing good agreement between the experimentally observed XRD patterns and theoretically fitted results and presented in Table 1, which indicate the success of this method.

<Insert Table 1 here>

The good quality of the structural refinements is also indicated by low deviations of the statistical parameters (R_{wp} , R_p , R_{Bragg} , and χ^2). These parameters, listed in Table 1, indicate that measured diffraction patterns are well adjusted and corroborated to the ICSD No. 250491 [47], and ICSD No. 291536 [48]. Also, Table 1 contains the lattice parameters, unit cell volumes, and site occupancy factor by W and Mo atoms for each solution solid in the crystal lattice calculated by the Rietveld refinement. The Rietveld refinement showed that solution solids $\text{Sr(Mo}_{1-x}\text{W}_x\text{)O}_4$ crystals with ($x = 0; 0.25; 0.50; 0.75$; and 1) present a scheelite-type tetragonal structure with the Hermann–Mauguin symmetry space group $I4_1/a$ and four molecular formula units per unit cell ($Z = 4$), without the presence of secondary phases. Thus, it was proved that there was the substitution of Mo^{6+} for W^{6+} cations in the SrMoO_4 crystal lattice,

forming solid solutions of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals. It was also observed that the substitution of Mo^{6+} by W^{6+} ions on the crystal lattice, causes changes in the lattice parameters and consequently in the unit cell volume.

In the Table 2 is presented the data which contains the atomic coordinates of atoms of the solid solution of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals calculated by the Rietveld refinement. It was observed variations in the atomic positions related to O atoms, while Sr, Mo and W atoms have fixed atomic positions. This suggests the existence of structural distortions on the tetrahedral $[\text{MoO}_4]/[\text{WO}_4]$ clusters and deltahedral $[\text{SrO}_8]$ clusters.

<Insert Table 2 here>

3.3. Unit cell representation of the solid solution of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals

Figures 3(a–e) show the schematic representations of the unit cells for solid solutions of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals with ($x = 0; 0.25; 0.50; 0.75$; and 1), in which exhibit the scheelite-type tetragonal structure, as previously identified by XRD patterns and confirmed by the Rietveld refinement. All structures and clusters were modeled by means of VESTA program (version 3.5.7) using the lattice parameters and atomic positions listed in Table 1 and Table 2.

<Insert Figs. 3(a–e) here>

As can be observed in Figs. 3(a–e), in all unit cells the Mo and W atoms are lattice formers at tetragonal crystal lattice, and are bonded to four O atoms, forming distorted tetrahedral $[\text{MoO}_4]$ and/or $[\text{WO}_4]$ clusters (4 vertices, 4 faces, and 6 edges) with T_d symmetry groups e different internal (O–Mo–O) and/or (O–W–O) bond angles [51]. However, the solid solutions of $\text{Sr}(\text{Mo}_{0.75}\text{Sr}_{0.25})\text{O}_4$, $\text{Sr}(\text{Mo}_{0.50}\text{W}_{0.50})\text{O}_4$ and $\text{Sr}(\text{Mo}_{0.25}\text{W}_{0.75})\text{O}_4$ crystals exhibit tetrahedral $[\text{MoO}_4]/[\text{WO}_4]$ clusters more distorted that in pure crystals. Moreover, in all unit cells the Sr atoms are lattice modifiers and are coordinated to eight O atoms, resulting in distorted deltahedral $[\text{SrO}_8]$ clusters (8 vertices, 12 faces, and 18 edges) and D_{2d} symmetry group [52]. As previously discussed, these distortions at the long-range are caused by variations in the (O–Mo–O) and (O–W–O) and (O–Sr–O) bonding angles due to disturbances in the atomic positions at O atoms after the substitution of Mo^{6+} by W^{6+} ions (of greater ionic radius and electronic density), providing different levels of structural order-disorder in crystal lattices [52, 53].

3.4. Micro-Raman and FT-IR spectra of solid solution of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals

The Raman spectroscopy technique is of fundamental importance for providing information about the structural order-disorder variations at short range in the crystal lattice of the materials, complementing the data obtained by XRD and Rietveld refinement [54].

According to group theory, molybdate and tungstate crystals with the scheelite-type tetragonal structure present 26 different vibration modes, as described in the equation below:

$$\Gamma = 3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u \quad (2)$$

The 13 modes A_g , B_g and E_g are only active in the Raman spectra, while the modes A_u and E_u are displayed only in the Infrared spectra. The three B_u modes are prohibited, and one A_u and one E_u modes are acoustic (of zero frequency). A and B modes are nondegenerate while E modes are doubly degenerate. The “g” and “u” subscripts indicate the parity under inversion in centrosymmetric crystals [55, 56].

It was noted by means of Raman spectra, the presence of a weak coupling between the ionic groups, which is related to distorted tetrahedral $[\text{MoO}_4]$ and/or $[\text{WO}_4]$ clusters and the metallic cations, which is related to deltahedral distorted $[\text{SrO}_8]$ clusters in the scheelite-type structures.

The vibrational modes active in the characteristic Raman spectra of these crystals can be classified as one of seven internal modes, which correspond to the oscillations inside the tetrahedral $[\text{MoO}_4]$ and/or $[\text{WO}_4]$ clusters with an immovable mass center, or as one of the six external modes, which correspond to the motion of the metallic cations in relation to rigid molecular units [57, 58].

Figure 4 shows the Raman spectra of the solid solution of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ ($x = 0; 0.25; 0.50; 0.75$; and 1) samples with the corresponding band assignments.

<Insert Fig. 4 here>

Twelve active Raman modes were detected for the $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ ($x = 0, 0.25, 0.50, 0.75$ and 1) samples obtained by the sonochemical method in this work. The intense bands located at 921 cm^{-1} (A_g) in the Raman spectrum of SrWO_4 and at 887 cm^{-1} (A_g) in the Raman spectrum of SrMoO_4 were attributed to the symmetric stretching vibrations of the O–W–O and/or O–Mo–O bonds within the tetrahedral $[\text{WO}_4]$ and/or $[\text{MoO}_4]$ clusters, as displayed in Fig. 4 and Inset Fig. 4. It is interesting to note that both are present in the Raman spectra of the $\text{Sr}(\text{Mo}_{0.25}\text{W}_{0.75})\text{O}_4$, $\text{Sr}(\text{Mo}_{0.50}\text{W}_{0.50})\text{O}_4$ and $\text{Sr}(\text{Mo}_{0.75}\text{W}_{0.25})\text{O}_4$ samples, whose intensities are directly proportional to the Mo/W ratio. The Raman modes at 837 (B_g) and 798 cm^{-1} (E_g) were attributed to the anti-symmetric stretch vibrations of the O–W–O and/or O–Mo–O bonds. The bands located at 382 (E_g) and 372 cm^{-1} (B_g) were associated with anti-symmetric bending vibrations of the O–W–O and/or O–Mo–O bonds, while the band at 337 cm^{-1} ($A_g + B_g$) was associated with symmetric bending vibrations. The modes at 237 cm^{-1} (E_g) and 190 cm^{-1} (B_g) were assigned to the free rotation motions of the distorted tetrahedral $[\text{WO}_4]$ and/or $[\text{MoO}_4]$ clusters. The external modes generated with the interactions between the Sr^{2+} cations and the distorted tetrahedral $[\text{WO}_4]$ and/or

[MoO₄] clusters are shown between 150 and 65 cm⁻¹, as shown in Fig. 4. The bands around 133 cm⁻¹ (E_g) and 75 cm⁻¹ (B_g) were assigned to symmetric stretching, and symmetric bending vibrations of O–Sr–O bonds, respectively. The band around 100 cm⁻¹ (E_g) was attributed to free motion (x , y , z -axis) of tetrahedral [SrO₄] clusters [1, 3, 40, 47, 59–61]. Therefore, for all solid solution of Sr(Mo_{1-x}W_x)O₄ (x = 0, 0.25, 0.50, 0.75 and 1), the Raman spectra showed characteristic vibrational active modes related to scheelite-type tetragonal structure in good agreement with the literature [53] and our XRD patterns and Rietveld refinement.

The FT-IR spectra for the Sr(Mo_{1-x}W_x)O₄ crystals with (x = 0; 0.25; 0.50; 0.75; and 1), at the wavenumber range of 400–1000 cm⁻¹, are shown in Fig. 5(a) and inset Fig. 5(b).

<Insert Fig. 5(a) and inset Fig. 5 here>

Three infrared-active vibrational modes identified were considered internal modes because they originate from movements related to vibrational within the tetrahedral [MoO₄] and/or [WO₄] clusters. The wide and intense band located between 950 and 750 cm⁻¹ (1Eu and 1Au) and a narrow located between 400 e 415 cm⁻¹ [1(Au + Eu)] were attributed, respectively, to the anti-symmetric stretching and symmetric bending vibration of the O–Mo–O and/or O–W–O bonds [12, 40, 62, 63]. The proportional replacement of Mo⁶⁺ by W⁶⁺ cations promoted a shift in the band close to 400 cm⁻¹ for higher wavenumbers. This is due to the difference in electronegativity between the atoms of Mo (2.16) and W (2.36) [64]. Since the W atom is more electronegative, the O–W–O bond tends to be stronger than the O–Mo–O bond, so they vibrate at higher frequencies (in regions with higher wavenumbers) [65, 66].

3.5. FE-SEM images analysis of the solid solution of Sr(Mo_{1-x}W_x)O₄ crystals

The FE-SEM images of the solid solution of Sr(Mo_{1-x}W_x)O₄ crystals with (x = 0; 0.25; 0.50; 0.75; and 1) are shown in Fig. 6(a-j).

<Insert Figs. 6(a–j) here>

As shown in Figs. 6(a,b), the SrMoO₄ samples (x = 0) formed mostly octahedral-type morphologies (3 μm long and 2 μm wide, approximately) with an apparently smooth surface. Similar results were achieved by Jiang et al. [67] also using the sonochemical method and by Rendón-Angeles et al. [66] through the hydrothermal method. As the x content increased, the octahedron assumed a spindle-like morphology (3 μm long and 1 μm diameter, approximately) with a rougher surface, Fig. 6(c–h), until some evolved into dumbbell-like morphologies (3.5 μm long and 1 μm diameter, approximately), predominant in SrWO₄ (x = 1) samples, Fig. 6(i,j). Mukherjee, et al. [68], by the sonochemical method, and Karthik et al. [12], by the coprecipitation method, obtained similar morphologies for SrWO₄ crystals. A few star-like and flower-like morphologies also emerged (with a mean size of approximately 3 μm) possibly due to agglomeration of spindle-like morphologies [69]. However, according to Dos Santos et al. [55], star-like morphologies can also arise from a single spindle after dividing its ends, generating new tips and so on, until the morphologies evolve into flower-like crystals.

3.6. UV-Vis spectra of the solid solution of Sr(Mo_{1-x}W_x)O₄ crystals

The Figs. 7(a–e) show the UV–Vis absorption spectra of the Sr(Mo_{1-x}W_x)O₄ (x = 0; 0.25; 0.50; 0.75; and 1) crystals constructed applying the methodology proposed by Kubelka and Munk [70], as described by De Sousa et al. [40]. In sequence, the E_{gap} values were estimated by extrapolation the linear portion of the spectra to zero absorption coefficient. All spectra showed characteristic profiles of semiconductor crystalline materials with direct transitions between the valence band (VB) and conduction band (CB) [71].

<Insert Figs. 7(a–e) here>

The estimated E_{gap} values of the Sr(Mo_{1-x}W_x)O₄ (x = 0; 0.25; 0.50; 0.75; and 1) crystals were 4.27; 4.30; 4.39; 4.53; and 5.01 eV, respectively. The gradual replacement of the Mo⁶⁺ by the W⁶⁺ cations caused a directly proportional increase in the E_{gap} values. An expected behavior considering the E_{gap} values reported in the literature for SrMoO₄ and SrWO₄ crystals. Muralidharan and Sivaji [72] synthesized SrMoO₄ and SrWO₄ by precipitation method with E_{gap} values of 4.25 and 4.85 eV, respectively. Wang et al. [73] synthesized SrMoO₄ by hydrothermal method with E_{gap} of 4.32 eV. Khobragade et al. [74] synthesized SrWO₄ by solid state reaction method with E_{gap} value of 5.80 eV.

It's known that E_{gap} values are associated with the existence of intermediate energy levels within the gap of semiconductor materials that are directly affected by the degree of structural organization of the crystal lattice (oxygen vacancies, binding distortion and angle deformation) which in turn are affected by synthesis method, particle size, morphology, treatment temperature and pH of the precursor solution [72]. Therefore, the increase in the E_{gap} value proportional to the replacement of the Mo⁶⁺ by the W⁶⁺ cations suggest an increase in the degree of structural organization, although the difference between the ionic radii is small [75].

Dos Santos et al. [55] and Zhang et al. [50] synthesized SrMoO₄ microcrystal by the sonochemical method with E_{gap} of 4.05 eV and 3.72 eV, respectively, but, to date, no E_{gap} values associated with SrWO₄ crystals synthesized by the sonochemical method on the micro scale have been reported. Theoretical studies estimate E_{gap} values for SrMoO₄ crystals between 3.69 and 5.35 eV [5, 76–78] and for SrWO₄ between 4.41 and 5.37 eV [79–82]. Therefore, the data discussed so far suggest that the E_{gap} values estimated in this work are within the range of expected values.

3.7. Sonophotocatalytic activities of the solid solution of Sr(Mo_{1-x}W_x)O₄ crystals

The RhB dye was subjected to different degradation processes and the results obtained are shown in Figs. 8(a–d). The degradation rates (C_t/C_0 (%) vs. time) only under UV-C (photolysis – P) or ultrasonic (sonolysis – S) radiation, as well as under the combined radiations (sonophotolysis – SP), is shown in Fig. 8(a). Figures 8(b,c) show the degradation rates after photocatalysis (PC) and sonophotocatalysis (SPC) process, respectively, using the $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals as catalysts. The percentage of degradation of the processes assisted by sonication without and with catalysts were summarized in Fig. 8(d).

<Insert Figs. 8(a–d) here>

As can be seen from Fig. 8(a), UV-C radiation alone was not enough to degrade the RhB dye completely (under the conditions employed in this work), since the P process showed an efficiency of only 8%. Even after addition of the $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals as photocatalysts (PC, Fig. 8(b)) suggesting that the recombination rate between the $e^- \leftrightarrow h^+$ pairs photogenerated for these crystals is high [83].

On the other hand, the processes assisted by ultrasonic radiation proved to be promising, starting with S and SP with degradation rates of 31% and 42%, respectively. This is due to the appearance of highly reactive species (such as $\text{H}^\bullet$, $\text{HO}^\bullet$, e^- , $\text{HO}_2^\bullet$) formed from the cleavage of H_2O and dissolved O_2 molecules during acoustic cavitation events. However, it is known that the thermolytic degradation of the pollutant is also an option, given the high temperatures generated after the collapse of the cavitation bubbles [84].

The SP confirmed the benefits of the simultaneous use of UV-C and ultrasonic radiation and, after addition of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals as catalysts, a synergistic effect was observed during SPC process of the RhB dye illustrated in Figs. 8(c). This effect is due to the ability of the combined systems (ultrasound, light and catalyst) to compensate for the deficiencies presented by each degradation process [85].

One of the limitations of the photocatalysis is the high recombination rate between $e^- \leftrightarrow h^+$ pairs photogenerated on the catalyst surface, but reactive species formed during sonolysis can delay this recombination, contributing to the generation of more reactive species. Furthermore, the shock waves created after implosion of cavitation bubbles i) lead to fragmentation and deagglomeration of catalyst particles, increasing their surface area; ii) contribute to the continued cleaning of their active sites, preventing the accumulation of pollutants and their intermediates produced during degradation; and iii) accelerate the mass transfer between the organic pollutants and the catalyst surface. Meanwhile, the catalysts can act as additional cores to form more cavitation bubbles potentiating all the effects previously mentioned [31, 86].

The better SPC performance was observed for the $\text{Sr}(\text{Mo}_{0.25}\text{W}_{0.75})\text{O}_4$ crystals (98%) followed by SrMoO_4 (90%), $\text{SrMo}_{(0.75}\text{W}_{0.25})\text{O}_4$ (71%), SrWO_4 (67%), and $\text{Sr}(\text{Mo}_{0.50}\text{W}_{0.50})\text{O}_4$ crystals (59%). According to Fig. 8(d), starting from pure SrMoO_4 crystals, such a sequence seems to be inversely proportional to the increase of the x value and raise of E_{gap} value, with the exception of the $\text{Sr}(\text{Mo}_{0.25}\text{W}_{0.75})\text{O}_4$ crystal. In view of this and based in our structural data, clusters modeling, FE-SEM images and UV-Vis spectra we can attribute that the solid solution $\text{Sr}(\text{Mo}_{0.25}\text{W}_{0.75})\text{O}_4$ crystals exhibits favorable condition to the best performance catalytic, as specific defects on the crystal surfaces and optical band gap values near the energy (4.88 eV) of UV-C illumination. So, its structural organization seems to be ideally favorable (among the conditions investigated in this work) to achieve the highest SPC performance. Therefore, it was the catalyst chosen to carry out the concentration tests, whose results are shown in Fig. 9, in order to find the best proportion between the amount of catalyst (25, 50, 75 and 100 mg) and volume of solution (100 mL) in the SPC of RhB dye.

<Insert Figs. 9 here>

The SPC degradation rate increased proportionally to the increase in the amount of catalyst up to the ratio of 50 mg/100 mL, and thereafter it decreased in the same proportion. This may be related to the fact that when the catalyst dosage increases, the number of available active sites also increases, as well as additional nuclei for the formation of cavitation bubbles, increasing the production of oxidizing radicals and, therefore, the rate of degradation. However, this synchronism seems to be efficient to a certain extent: as the catalyst dosage increases even more, the particle deagglomeration process seems to lose its efficiency, decreasing the catalyst surface area and, consequently, the number of active sites. Furthermore, catalyst concentration beyond an ideal value can cause light scattering due to increased solution turbidity, making it difficult for some catalyst particles to absorb light, thus reducing degradation efficiency [85, 87, 88].

After discovering the ideal ratio (under the conditions of this work) and to confirm the synergistic effect during SPC process, $\text{Sr}(\text{Mo}_{0.25}\text{W}_{0.75})\text{O}_4$ crystals were also used in the sonocatalysis (SC: only ultrasound and catalyst) of the RhB dye and the result shown in Fig. 10. The SC process presented a considerable degradation rate of 76% (2.45 times greater than S process). However, as expected, the degradation efficiency in the SPC process was superior to all other processes.

<Insert Figs. 10 here>

In general, photogenerated $e^- \leftrightarrow h^+$ pairs and superoxide ($\text{O}_2^{\bullet-}$) and hydroxyl ($\text{HO}^\bullet$) radicals are the predominant reactive species in the degradation process. However, to determine the main species during SC and SPC processes with $\text{Sr}(\text{Mo}_{0.25}\text{W}_{0.75})\text{O}_4$ crystals (in the proportion of 50 mg/100 mL), experiments were carried out with AO, AgNO_3 , BQ, and ISO scavengers of h^+ , e^- , $\text{O}_2^{\bullet-}$, and $\text{HO}^\bullet$ radicals, respectively. These results were shown in Fig. 11.

<Insert Figs. 11 here>

The inhibition of RhB dye degradation in both SC and SPC process was not as pronounced after addition of AO and AgNO₃ showing that the photogenerated $e^- \leftrightarrow h^+$ pairs are not the main reactive species in both processes, although they contribute to a certain degree, even in the absence of UV-C light, which can be explained by the phenomenon of sonoluminescence. When the light energy emitted during sonoluminescence equals or exceeds the E_{gap} of the catalyst, e^- can be excited from VB to CB and generate $e^- \leftrightarrow h^+$ pairs [32, 89, 90].

In SC process, the lowest rate of inhibition was observed after addition of BQ, indicating that the $O_2^{\cdot-}$ radical is the least participative reactive species, possibly because it is present in a smaller amount. The opposite was observed during SPC, which was shown to be the main species, followed by the $HO^{\cdot}$ radicals. Most of the $O_2^{\cdot-}$ radicals are formed by e^- in CB, generated in greater numbers in SPC due to the presence of UV-C light [91]. As expected, in SC the $HO^{\cdot}$ radical was shown to be the main degradation agent.

Figures 12(a–d) show the UV–Vis spectra of the RhB dye after the S, SP SC, and SPC processes using the solid solution of $Sr(Mo_{0.25}W_{0.75})O_4$ crystals as a catalyst.

<Insert Figs. 12(a–d) here>

Displacements in the RhB dye maximum absorption bands at 554 nm (characteristic of the chromophore group) were not observed in any of the processes, suggesting that there was no formation of secondary products [92]. Its considerable reduction, as well as the more discrete band located at 259 nm (attributed to aromatic rings), during SPC process is one of the indications of complete mineralization of RhB dye [93].

4. Conclusions

In summary, the solution solid of $Sr(Mo_{1-x}W_x)O_4$ crystals with ($x = 0; 0.25; 0.50; 0.75; \text{ and } 1$) were synthesized with success by means of sonochemical method at 40 °C for 3 h. All our crystals present a scheelite-type tetragonal structure with pure phases and crystalline as confirmed by the XRD patterns and proved by Rietveld refinement data. The Raman and FT-IR spectra exhibit symmetrical and asymmetrical stretching and bending bands characteristics, corroborating the XRD patterns and Rietveld refinement data. The $SrMoO_4$ crystals showed octahedral-like morphologies that assumed a spindle-like shape as the replacement of the Mo^{6+} by the W^{6+} cations happened until they assumed a dumbbell-like morphology for the pure $SrWO_4$ crystals. Some star and flower-like morphologies arose possibly due to agglomeration of spindle-like morphologies. The E_{gap} values of the materials varied directly proportionally to the substitution of the Mo^{6+} by the W^{6+} cations from 4.27 to 5.01 eV, suggesting an increase in the structural organization with the substitution. The best percentage for degradation of the RhB dye, approximately 98%, was achieved during the SPC process using the $Sr(Mo_{0.25}W_{0.75})O_4$ crystals as a catalyst in the proportion of 50 mg/100 mL. The $O_2^{\cdot-}$ radicals were shown to be the main degradation agent in the SPC process, while for the SC process, it was the $HO^{\cdot}$ radicals.

Declarations

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose

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Tables

Table 1: Lattice parameters, unit cell volume, site occupation and statistical parameters of quality of the solid solution $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals with ($x = 0$; 0.25; 0.50; 0.75; and 1) obtained by Rietveld refinement.

Refined formula $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$	Lattice Parameters			Site occupancy		R_{Bragg} (%)	χ^2	R_{wp} (%)	R_p (%)
	a, b (Å)	c (Å)	Cell volume (Å ³)	W	Mo				
$x = 0$	5.404357(27)	12.04033(12)	351.663(4)	0	1	6.29	1.74	9.93	7.56
$x = 0.25$	5.40818(6)	12.01880(28)	351.530(8)	0.28	0.72	6.71	1.78	10.13	7.69
$x = 0.50$	5.41346(6)	11.99928(30)	351.645(9)	0.51	0.49	5.76	1.63	9.32	7.14
$x = 0.75$	5.41936(5)	11.98283(23)	351.929(7)	0.73	0.27	5.22	1.54	9.26	7.02
$x = 1$	5.42243(5)	11.96108(21)	351.688(6)	1	0	3.04	1.66	8.86	6.53
ICSD 291536	5.4268(9)	11.9688(21)	352.48	1	0	-	-	-	-
ICSD 250491	5.402647	12.04112(8)	351.45	0	1	-	-	-	-

Table 2:Experimental values of the atomic coordinates (x , y , and z) of atoms of the solid solutions of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals with ($x = 0$; 0.25; 0.50; 0.75; and 1).

<i>Solution solid of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals</i>					
<i>Atoms</i>	$x = 0$	$x = 0.25$	$x = 0.50$	$x = 0.75$	$x = 1$
<i>Atomic Coordinates (x, y, z)</i>					
Sr	0;0.25;0.625	0;0.25;0.625	0;0.25;0.625	0;0.25;0.625	0;0.25;0.625
W	–	0;0.25;0.125	0;0.25;0.125	0;0.25;0.125	0;0.25;0.125
O	0.23196;0.11833;0.04717	0.63331;0.45883;0.21851	0.66478;0.46615;0.20859	0.63897;0.5103;0.29245	0.63597;0.48952;0.29343
Mo	0;0.25;0.125	0;0.25;0.125	0;0.25;0.125	0;0.25;0.125	–

Figures

Figure 1

XRD patterns of (a) SrMoO_4 , (b) $\text{Sr}(\text{Mo}_{0.75}\text{W}_{0.25})\text{O}_4$, (c) $\text{Sr}(\text{Mo}_{0.50}\text{W}_{0.50})\text{O}_4$, (d) $\text{Sr}(\text{Mo}_{0.25}\text{W}_{0.75})\text{O}_4$, and (e) SrWO_4 crystals. The vertical lines (|) denote the respective positions and intensities of XRD peaks described in the ICSD cards No. 250491, generated CIF files and No. 291536 for SrMoO_4 , $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ with ($x = 0.25; 0.50; 0.75$), and SrWO_4 phases, respectively.

Figure 2
Rietveld refinement plots of (a) $SrMoO_4$, (b) $Sr(Mo_{0.75}W_{0.25})O_4$, (c) $Sr(Mo_{0.50}W_{0.50})O_4$, (d) $Sr(Mo_{0.25}W_{0.75})O_4$, and (e) $SrWO_4$ crystals, respectively.

Figure 3

Schematic representations of the unit cell with scheelite-type tetragonal structures for (a) SrMoO₄, (b) Sr(Mo_{0.75}Sr_{0.25})O₄, (c) Sr(Mo_{0.50}W_{0.50})O₄, (d) Sr(Mo_{0.25}W_{0.75})O₄, and (e) SrWO₄ crystals, respectively.

Figure 4

Raman spectra of the solid solution of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals with ($x = 0; 0.25; 0.50; 0.75$; and 1).

Figure 5

(a) FT-IR spectra of the solid solution of $\text{Sr}(\text{Mo}_{1-x}\text{W}_x)\text{O}_4$ crystals ($x = 0; 0.25; 0.50; 0.7$; and 1) sample; (b) Inset in FT-IR spectra with magnified in the region from 400 to 420 cm^{-1} .

Figure 6

FE-SEM images for (a, b) SrMoO_4 , (c, d) $\text{Sr}(\text{Mo}_{0.75}\text{Sr}_{0.25})\text{O}_4$, (e, f) $\text{Sr}(\text{Mo}_{0.50}\text{W}_{0.50})\text{O}_4$, (g, h) $\text{Sr}(\text{Mo}_{0.25}\text{W}_{0.75})\text{O}_4$, and (i, j) SrWO_4 .

Figure 7

UV-Vis absorption spectra for (a) $SrMoO_4$, (b) $Sr(Mo_{0.75}Sr_{0.25})O_4$, (c) $Sr(Mo_{0.50}W_{0.50})O_4$, (d) $Sr(Mo_{0.25}W_{0.75})O_4$, and (e) $SrWO_4$ crystals.

Figure 8

(a) Photolysis, sonolysis and sonophotolysis of the RhB dye; **(b,c)** photocatalysis and sonophotocatalysis using Sr(Mo_{1-x}W_x)O₄ ($x = 0, 0.25, 0.50, 0.75$, and 1) crystals as catalysts; **(d)** degradation rate of the sonication-assisted processes.

Figure 9

Catalytic assays with concentration effect between the catalyst of the solid solutions of $\text{Sr}(\text{Mo}_{0.25}\text{W}_{0.75})\text{O}_4$ crystals (25, 50, 75 e 100 mg) and the RhB dye solution (100 mL).

Figure 10

Sonolysis, sonophotolysis, sonocatalysis and sonophotocatalysis of the RhB dye using the $\text{Sr}(\text{Mo}_{0.25}\text{W}_{0.75})\text{O}_4$ crystals as catalysts in the proportion of 50 mg/100 mL.

Figure 11
Effects of different scavengers on the SC and SPC process to degradation of RhB dye.

Figure 12
UV-Vis absorption spectra of RhB dye solution after (a) S, (b) SP, (c) SC, and (d) SPC processes by using $\text{Sr}(\text{Mo}_{0.25}\text{W}_{0.75})\text{O}_4$ as catalysts.