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# Polymeric precursor method to the synthesis of $XWO_4$ (X = Ca and Sr) thin films—Structural, microstructural and spectroscopic investigations

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#### ABSTRACT

Stoichiometric XWO<sub>4</sub> (X = Ca, and Sr) thin films were synthesized using the polymeric precursor method. In this soft chemical method, soluble precursors such as strontium carbonate, calcium carbonate and tungstic acid, as starting materials, were mixed in an aqueous solution. Through the polyesterification reaction, evidences of the formation of the W-citrate complex and the strontium were obtained by <sup>13</sup>C NMR and FT-Raman spectroscopy. The thin films were deposited on silicon and platinum-coated silicon substrates through the spinning technique. The surface morphology and crystal structure of the thin films were investigated using atomic force microscopy (AFM), X-ray diffraction (XRD), specular reflectance infrared Fourier transform spectroscopy, and micro-Raman spectroscopy. Nucleation stages and surface morphology evolution of the thin films on silicon substrates were studied by atomic force microscopy. X-ray diffraction characterization of these films showed that the XWO<sub>4</sub> (X = Ca, and Sr) thin film phases crystallize at 500 °C from an inorganic amorphous phase, given that no intermediate crystalline phase was identified.

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# 1. Introduction

The tungstate tetrahedral species have been of major interest due to their approved use in electro-optic applications as well as a scintillating medium [1–3]. In addition, the tungstates can be easily doped with rare-earth ions and are available in the form of large single crystals; consequently, they are objects of interest as laser materials [4,5]. The more common tungstate tetrahedral species with scheelite-type structure are SrWO<sub>4</sub>, CaWO<sub>4</sub>, PbWO<sub>4</sub> and BaWO<sub>4</sub>, with C<sub>4h</sub> point group symmetry [6,7]. In the scheelitetype structure, W ions are within tetrahedral O-ion cages and are isolated from each other, while Ca, Ba, Sr and Pb ions are surrounded by eight oxygen ions [8].

In addition, tungstates represented by  $CaWO_4$  and  $SrWO_4$  have been widely used as typical phosphors and scintillators in medical applications as well as laser host materials in quantum electronics [9,10]. Cho and Yoshimura [11] reported the structural evolution of  $SrWO_4$  films prepared on a tungsten substrate by a solution reaction assisted by the electrochemical dissolution of tungsten. The crystallization of the SrWO<sub>4</sub> films was characterized by threedimensional nucleation. Christofilos et al. [12] studied the induced pressure phase transition for SrWO<sub>4</sub>. The authors observed that the structure of the high pressure phase is closely related to the scheelite structure, being the latter formed by closely packed distorted tetrahedral WO<sub>4</sub> units, rather than involving octahedrally coordinated W ions. Lou and Cocivera [13] prepared CaWO<sub>4</sub> and SrWO<sub>4</sub> thin films on glass substrates by spray pyrolysis. Polycrystalline CaWO<sub>4</sub> and SrWO<sub>4</sub> films formed a scheelite structure after being annealed at above 300 °C.

Various preparation techniques have been proposed to produce these materials in the form of single crystals and powders, including the solid-state reaction, hydrothermal, sputtering, and sol-gel processes [14–16]. However, less extensive researches have been conducted on the preparation of thin films [17–19].

Therefore, new routes for obtaining solutions for thin film deposition and crystal growth remain an interesting subject. The use of the chemical process for thin film production allows the accurate control of the chemical composition. Nowadays, new solution deposition methods, based on wet chemistry, have been used for the preparation of oxide thin films. In this regard, chemical processing using solutions, including soft solution processing, has been attracting increasing interest. In the field of materials chemistry, the

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use of aqueous solutions in the soft solution processing is widely accepted for being environmentally friendly [20–22]. The liquid nature of the constituents and the relatively low processing temperatures enable the use of polymeric precursor method added to the few techniques of soft solution processing [23–26]. Padan et al. [27], using the polymeric citrate precursor route, reported powders of nano-sized  $Ba_{1-x}Sr_xTiO_3$  oxides, showing a single phase crystallizing in the cubic structure at 500 °C.

The basic idea behind the polymeric precursor method is to reduce individualities of different metal ions, which can be achieved by encircling stable metal complexes with growing polymer networks. Immobilization of metal-complexes in such rigid organic polymeric networks can reduce the segregation of particular metals, thus ensuring the compositional homogeneity at a molecular scale. This is of vital importance for the synthesis of multicomponent oxides with complicated compositions as the chemical homogeneity, regarding the distribution of cations throughout the entire gel system, often determines the compositional homogeneity of the final complex mixed oxides.

This work presents the synthesis of XWO<sub>4</sub> (X = Ca and Sr) thin films based on the polymeric precursor method. The surface morphology and crystal structure of the thin films were investigated using atomic force microscopy (AFM), X-ray diffraction (XRD), specular reflectance infrared Fourier transform spectroscopy, and micro-Raman spectroscopy.

#### 2. Experimental procedure

The flow chart of the XWO<sub>4</sub> (X=Ca, and Sr) synthesis used in this study is outlined in Fig. 1. Tungsten citrate was formed by the dissolution of tungstic acid  $(H_2WO_4)$  in an aqueous solution of citric acid under constant agitation to homogenize the tungsten citrate solution. After this solution homogenization, SrCO3 or a CaCO3 salt was also slowly added. The complex was well stirred for several hours at 80 °C to produce a clear, homogenous solution. After that, the solution containing Ca or Sr was homogenized and ethylene glycol was added to promote the citrate polymerization by the polyesterification reaction. With constant heating at 90 °C, the solution became more viscous, without any visible phase separation though. The molar ratio between the cations calcium or strontium and tungsten was 1:1, and the citric acid/ethylene glycol was fixed as 60:40 (mass ratio). The viscosity of the deposition solution was adjusted to 15 MPa/s by controlling the water content. The polymeric precursor solution was spin-coated on different substrates using a commercial spinner (spin-coater KW-4B, Chemat Technology), operating at 7000 rev./min for 40 s. The polymeric precursor solution was deposited onto the silicon substrates, via a syringe filter to avoid particulate contamination. After the spinning onto the substrates, the films were kept in ambient air at 150 °C on a hot plate for 20 min to remove residual solvents. After the pre-annealing, the films were annealed between 200 °C and 500 °C for 4 h in air atmosphere.

The film thickness was controlled by adjusting the number of coatings, and each layer was pyrolyzed at 200 °C and then crystallized before the next layer was coated. These coating/drying operations were repeated until the desired thickness was achieved.

The XWO<sub>4</sub> (X = Ca, and Sr) thin films were structurally characterized by the X-ray diffraction patterns obtained using a Cu  $K_{\alpha}$  radiation source in order to determine their structure evolution. The lattice parameters of the thin films were measured using the least-square method. Infrared analyses were performed through an Equinox/55 (Bruker) Fourier Transformed Infrared (FT-IR) spectrometer to observe the variation in chemical bond densities. The FT-IR reflectance spectra of XWO<sub>4</sub> (X=Ca, and Sr) thin films on Pt/Ti/SiO<sub>2</sub>/Si substrates were recorded at room temperature in the frequency range of 400-1200 cm<sup>-1</sup> equipped with a 30° specular reflectance accessory. Spectroscopic techniques, such as FT-Raman, play an important role in identifying such a heterometallic complex in solution. Therefore, the FT-Raman spectra of the polymeric precursor solution was recorded by means of a Bruker RFS100 instrument, with an Nd-YAG laser (1064 nm), using 200 mW laser power, 150 scans and 4 cm<sup>-1</sup> resolution. The micro-Raman measurements were performed at room temperature in the XWO<sub>4</sub> (X = Ca, and Sr) thin films, using the 514.5 nm line of an argon ion laser as an excitation source. The power was kept at 15 mW and a 100 $\times$  lens was used. The spectra were recorded using a T-64000 Jobin-Yvon triple-monochromator coupled to a CCD detector.

AFM was used to obtain a 3D image reconstruction of the sample's surface. These images enabled an accurate analysis of the sample's surface and the quantification of highly relevant parameters, such as roughness and grain size. A Digital Instrument Multi-Mode Nanoscope IIIa was used.



**Fig. 1.** Flow chart illustrating the procedure for the preparation of XWO<sub>4</sub> (X = Ca, and Sr) thin film production.

Nuclear magnetic resonance (NMR) experiments were carried out on a BRUKER, DRX400, operating at hydrogen frequency of 400 MHz. A capillary tube with D2O/TSPd4 for calibration of the <sup>13</sup>C spectra field homogeneity was used. The temperature was kept constant at 303 K in the whole experiment.

### 3. Results

#### 3.1. Characterization of the polymeric precursor solution

Liquid-state <sup>13</sup>C NMR was used to study the formation of the tungsten citrate complex with strontium. Fig. 2a shows the <sup>13</sup>C NMR spectrum of the citric acid in aqueous solution, the <sup>13</sup>C NMR spectrum of tungsten citrate complex can be seen in Fig. 2b, and Fig. 2c presents the <sup>13</sup>C NMR spectrum tungsten citrate complex plus strontium.

In the spectrum of the pure citric acid solution (Fig. 2a), the peaks at 176.3 and 179.8 ppm were linked to the terminal carbon (C1, C6) of the carboxyl group and to the carbon of the central carboxyl carbon (C4), respectively. The peaks between 40–60 ppm were associated with the methylene carbons (C2, C5), and the peaks between 70 and 90 ppm were related to the central carbons (C3).



Fig. 2. (a) NMR <sup>13</sup>C spectrum to pure citric acid – CA, (b) NMR <sup>13</sup>C spectrum to tungsten citrate – CTW e, (c) NMR <sup>13</sup>C spectrum to strontium tungsten citrate – CTWSr.

By comparing the NMR <sup>13</sup>C spectra of citric acid (CA) to the tungsten citrate complex (CW), a tetracoordinated tungsten formation was observed (Fig. 2a and b, respectively). This result is confirmed by *ab-initio* calculations (Harttree-Fock minimum base), Fig. 3. It was possible to observe in the <sup>13</sup>C spectrum for the CW



**Fig. 3.** More likely theoretical model of the tungsten citrate complex (CW), by *abinitio* Harttree-Fock method with minimum basis.

the presence of two peaks at 47.2 and 47.4 ppm relating to the methylenes, which were affected by the charge density decrease due to tungsten complexation and the free CA (no complexed CA molecules) characteristic peak at 48.2 ppm (Fig. 2b). On the other hand, the peak at 87.9 ppm showed that the CA central carbon was affected by the tungsten, and the free CA peak was at 77.6 ppm (Fig. 2a). Similar results were observed by Zampieri et al. where the correlation between the experimental and theoretical data enabled the proposal of a model for titanium and lead citrate complex [28]. A protection ranging from 170–180 ppm (free CA) was noticed by observing the chemical displacements to the lateral carboxylic carbons (Fig. 2b). Such fact was caused by the anisotropic effect triggered by tungsten atom electronic cloud on carboxyls carbons and lateral methylenes. This effect also happened in the range of 45-50 ppm methylenic carbons. The peaks at 188.6 and 188.8 ppm correlate for the regions of the coupling of the side and central carboxyls of the complexed CA molecules (Fig. 2b), which led to the conclusion that the predominant effect in this region was an electrons extractor with very little or no anisotropic interaction.

Through the addition of strontium to CW, an even wider variety in the peaks of <sup>13</sup>C of tungsten citrate and strontium (CWSr)



**Fig. 4.** More likely theoretical model of the strontium and tungsten citrate complex (CWSr), by *ab-initio* Harttree-Fock method with minimum basis.

spectrum was observed (Fig. 2c), in which it was observed that the strontium was joining the CW complex, and the strontium complexation caused a change in the plan conformation of oxygens with the tungsten atom. By analyzing the region between 70 and 90 ppm concerning the central carbon, the presence of two peaks, rather than a single CW characteristic one, was noticed (Fig. 2c), which led to the belief that, through the addition of a strontium atom, a new CA molecule linked to the complex was originated (Fig. 4). The appearance of new peaks in the other regions of the <sup>13</sup>C spectrum for the CWSr, both for the methylenes and carboxyls regions, could also be observed. These modifications allowed the assertion that the strontium atom has a linking trait much more radial than directional, joining CW molecule at different points and subtly altering the carbons charge involved in the complexation, hence the new peaks appearance. The strontium admission triggered a change in the plan of the oxygens associated to the tungsten atom in the CWSr complex. This fact supports the affirmation that the strontium atom works further as a net guide than as an electrons extractor.

The tungsten/citric acid metallic complex formation and polymerization processes, involved in the preparation of the polymeric



**Fig. 5.** FT-Raman spectra of the investigated systems with (a) ethylene glycol, (b) citric acid, (c) tungsten/citric acid, (d) tungsten/strontium/citric acid/ethylene glycol and (e) tungsten/calcium/citric acid/ethylene glycol.

precursor solution, were followed by FT-Raman spectroscopy. Fig. 5 shows the FT-Raman spectra of ethylene glycol (a), citric acid (b), citric acid/ethylene glycol solutions containing W ions (c), and both Ca or Sr and W ions (d) and (e). A relevant observation here is that the tungsten/citric acid metallic complex formation and polymerization must involve the carboxyl groups of the citric acid [29]. Thus, all our analyses in the FT-Raman experiments focused on the spectral range related to this organic group –COOH (2000–1500 cm<sup>-1</sup> wavenumber range).

The spectrum of citric acid presented two intense bands at 1736 and 1692 cm<sup>-1</sup> and one weak and broad band at 1634 cm<sup>-1</sup>, all of them assigned to the carboxyl groups. The two strong bands at 1736 and 1692 cm<sup>-1</sup> could be assigned to the stretching mode of the central carboxyl  $\nu$ (C=O) and to the stretching mode of the terminal carboxyl  $\nu$ (C=O), respectively (see Fig. 5). Besides, the weak and broad band at 1634 cm<sup>-1</sup> was assigned to the stretching vibration mode of the carboxyl group related to a strong intramolecular hydrogen bond [30]. Therefore, the two strong bands were used as a guide for knowing whether or not a specific type of carboxyl group -COOH in citric acid was coordinated to metals for the formation of a metallic citrate and, later, of the polymeric precursor solution. Thus, modifications in the central and terminal bands (see Fig. 5) could indicate the formation of tungsten/citric acid metallic complex. A schematic representation of the procedure for the preparation of polymer network is shown in Fig. 6. It is clear that the synthesis started with the chelation of the W cations (Fig. 2) by the citric acid. The second step was the reaction of  $Ca^{2+}$  or Sr<sup>2+</sup> with citric acid yielding the initiator core unit in an aqueous solution (see Fig. 6). The initiator core unit presented two reactive carboxyl groups that reacted with two equivalents of the bifunctional monomer (ethylene glycol) to generate the first startbranch (see Fig. 6). This startbranch had two O-H groups, the same number of carboxyls found in the initiator core unit. A further reaction with initiator core units regenerated the reactive carboxyl functional groups at the periphery and the first-generation of dendrimer occurred (see Fig. 6). A repetition of this two-step process generated larger and larger dendrimers that had an increasing number of chain end groups. The polymerization of these molecular building blocks permitted the rapid formation of polymers (see Fig. 6, polymer network). Furthermore, the organic groups, which comprise the material, were an integral part of the network architecture.

After the reaction between citric acid and tungstic acid, modifications in the characteristics of the bands at 1735 and 1692 cm<sup>-1</sup> were observed. That was assigned to the carboxyl stretching mode in the –COOH carboxylic acid groups of citric acid, which were significantly modified by the appearance of a distinct shoulder in the lower frequency region, at about  $1649 \text{ cm}^{-1}$ . In addition, it was noticed that the three bands associated with the carboxyl  $\nu$ (C=O) stretching mode in the citric acid were transformed in a broad and single band centered at  $1724 \text{ cm}^{-1}$  and in a shoulder at  $1649 \text{ cm}^{-1}$ . These results confirmed that calcium or strontium ions interacted, during the chelation, with carboxylic acid groups of citric acid to form a heterometallic complex (see Fig. 6, initiator core unit).

# 3.2. Preparation and characterization of the thin films

Figs. 7 and 8 show the X-ray patterns of the CaWO<sub>4</sub> and SrWO<sub>4</sub> thin films deposited onto silicon substrates after calcination at several temperatures. A diffused XRD pattern was observed at 300 °C, indicating the formation of an inorganic amorphous phase after the pyrolysis process for CaWO<sub>4</sub> thin films. At the temperature of 350 °C, the crystallization of the CaWO<sub>4</sub> phase initiated. No intermediate phase was observed, which implies a direct crystallization from the amorphous phase to the scheelite-type structure. All the peaks were ascribed to a tetragonal structure having a = 5.241 Å



**Fig. 6.** Formation of polymers called dendrimers. Dendrimers are highly branched symmetrical three-dimensional macromolecules with a polyfunctional central core unit:  $[W(citrate)_2 \cdot Me (citrate)_1 \cdot Me (citrate)_2 \cdot Me (cit$ 

and c = 11.403 Å lattice parameters, which were obtained by a least-square method. These values were close to the bulk material (a = 5.242 Å and c = 11.373 Å).

XRD patterns for SrWO<sub>4</sub> thin films also showed the formation of an inorganic amorphous phase at 300 and 350 °C. The crystallization of the SrWO<sub>4</sub> scheelite phase began at 400 °C and a well crystallized structure pattern was identified in the thin film heattreated at 500 °C. Again, no intermediate phase was observed. The diffractogram revealed well-defined peaks showing a good crystallinity. All the peaks were ascribed to a tetragonal structure. A further analysis of the XRD data indicated lattice parameters of a = 5.407 Å and c = 11.921 Å. These values were also close to the ones of the bulk material (a = 5.416 Å and c = 11.951 Å). The cross-section of the film layers revealed a uniform microstructure throughout the film, with a thickness of about 200–300 nm.

Fig. 9 shows the FT-IR reflectance spectra of XWO<sub>4</sub> (X = Ca, and Sr) thin films pre-annealing at 150 °C and after annealed at 500 °C on platinum-coated silicon substrate. From the FT-IR spectra (Fig. 9a) it could be observed that wide bands were detected in the 700–1000 cm<sup>-1</sup> range, which had been previously identified with a W–O absorption in a non-developed network. Several bands associated with carboxylate group stretching modes were also detected. Vibrations at 1730 and 1192 cm<sup>-1</sup>, related to the C=O stretching mode for the (R–COO–R) ester, were also observed [31,32]. The complexation of W and Sr or Ca metallic ions could be analyzed by the vibrations at 1657, 1610 and 1398 cm<sup>-1</sup>[33]. The vibration at



**Fig. 7.** X-Ray diffraction patterns of CaWO<sub>4</sub> thin films heat-treated at different temperatures: (a)  $300 \degree$ C, (b)  $350 \degree$ C, (c)  $400 \degree$ C and (d)  $500 \degree$ C.



Fig. 8. X-Ray diffraction patterns of SrWO<sub>4</sub> thin films heat-treated at different temperatures: (a) 300 °C, (b) 350 °C, (c) 400 °C and (d) 500 °C.



**Fig. 9.** The FT-IR reflectance spectra of XWO<sub>4</sub> (X = Ca, and Sr) thin films annealed at; (a) 150 °C, (b) SrWO<sub>4</sub> at 500 °C and (c) CaWO<sub>4</sub> at 500 °C.

1398 cm<sup>-1</sup> was a typical trait of a COO<sup>-</sup> stretching mode for a bidentate complex [33]. The XWO<sub>4</sub> (X = Ca and Sr) thin films annealed at 500 °C presented deep modifications in their spectra. The metal oxygen (M–O) band between 700 and 1000 cm<sup>-1</sup>, which had its shape changed considerably with increasing temperature, enabled the monitoring of the XWO<sub>4</sub> (X = Ca and Sr) thin film crystallization. A broad absorption band was observed at the lower temperature, which indicated a non-developed network. The band was sharpened at 500 °C, and the definition of two sharp bands was observed in both thin films. They were assigned to W–O stretching modes in a developed network (Fig. 9b and c) [34]. This suggested that XWO<sub>4</sub> (X = Ca, and Sr) thin films crystallize at 500 °C, as shown by the XRD pattern described in Figs. 7 and 8.

Moreover, the assumption of a tetrahedral Td, point group symmetry for the WO<sub>4</sub> units in SrWO<sub>4</sub> and CaWO<sub>4</sub> thin films made  $\Gamma_{Td}$ , the representation for the tetrahedral symmetry as  $\Gamma_{\text{Td}} = A_1(\nu_1) + E(\nu_2) + F_2(\nu_3) + F_2(\nu_4)$ , in which all four vibrational modes were Raman active, but only the  $F_2(\nu_3, \nu_4)$  modes were IR active [35–37]. In agreement with Porto and Scott [38], the  $A_1(\nu_1)$ vibration mode was the symmetric stretch of the WO<sub>4</sub> unit, the  $F_2(v_3)$  vibration modes were the antisymmetric stretches, and  $E(v_2)$ and  $F_2(v_4)$  vibration modes were bending modes. Therefore, the observed bands at 787, 892  $cm^{-1}$  and 801, 890  $cm^{-1}$  were assigned to  $F_2(\nu_3)$  antisymmetric stretch vibrations for CaWO<sub>4</sub> and SrWO<sub>4</sub> thin films, respectively (see Fig. 9). Since no other FT-IR work on  $CaWO_4$  and  $SrWO_4$  thin film was yet published, no comparisons could be made. The room temperature micro-Raman spectra of  $XWO_4$  (X = Ca, and Sr) thin films are shown in Fig. 10. The number of bands observed was in agreement with the expectations based on the site symmetry analysis for T<sub>d</sub> point group symmetry previously discussed. In the XWO<sub>4</sub> (X = Ca, and Sr) thin film Raman spectra, it was clear, by comparison with the WO<sub>4</sub> reference (Fig. 10), that the intense bands observed at 912 and 909 cm<sup>-1</sup> for CaWO<sub>4</sub> and SrWO<sub>4</sub> thin films, respectively, were ascribed to the  $A_1(v_1)$  mode. The  $F_2(v_3)$  antisymmetric vibration modes appeared in the region from 840 to 750 cm<sup>-1</sup> in the Raman spectra. The XWO<sub>4</sub> (X = Ca and Sr) compounds split the triply degenerate  $F_2(\nu_3)$  vibration mode into two IR and two Raman bands, see Figs. 9 and 10, respectively [34]. Additionally, in agreement with Porto and Scott [38] some external vibration modes, which appeared in the region from 200 to 50 cm<sup>-1</sup>, were predicted for scheelite-type structures. The crys-



Fig. 10. Raman spectra of XWO<sub>4</sub> (X = Ca, and Sr) thin films and WO<sub>4</sub> reference.

tallization of the XWO<sub>4</sub> (X = Ca, and Sr) thin films was confirmed by Raman analysis. In summary, the assignments of all bands in the FT-IR and Raman spectra of XWO<sub>4</sub> (X = Ca and Sr) thin films are shown in Table 1.

Added to that, an observation made by AFM showed the difference in both thin films in terms of surface morphology of the films prepared at different temperatures, Figs. 11 and 12. This AFM analysis showed a considerable variation in the surface morphology between the samples submitted to annealing temperatures ranging from 300 to 500 °C. Table 2 shows the evolution of the sample roughness measured by AFM analysis. It was evident from the AFM analysis that the CaWO<sub>4</sub> and SrWO<sub>4</sub> heat-treated thin films at 300 and 350 °C showed a homogeneous surface morphology with very low roughness (see Table 2). When the sample was annealed at 400 °C, the increased roughness suggested that the material's structure became increasingly ordered. Furthermore, the AFM analysis showed that the CaWO<sub>4</sub> and SrWO<sub>4</sub> heat-treated thin films at 400 °C displayed a homogeneous nucleation leading to a grain size distribution of approximately 20-30 nm and 40-50 nm, respectively, at the initial growth stage (see Figs. 11 and 12). On the other hand, the surface morphology changed dramatically at 500 °C. At this stage of growth, the coalescence of nuclei occurred, resulting in a significant increase of roughness. This result was in agreement with the XRD analysis where, at 500 °C, a high crystallization could be observed.

Table 1
Band frequencies $(cm^{-1})$ and assignments of XWO <sub>4</sub> (X = Ca, and Sr) thin films

Td point group assignment	CaWO <sub>4</sub>		SrWO <sub>4</sub>		
	Raman	Infrared	Raman	Infrared	
$A_1(v_1)$	912		922		
$F_2(\nu_3)$	839	892	838	890	
$F_2(\nu_3)$	798	787	799	801	
$E_2(\nu_2)$	333		337		
$F_2(v_4)$	400		372		
E.V.M.					
Bg	85		76		
Eg	116		102		
B <sub>g</sub>	210		189		

E.V.M, external vibrations modes.



Fig. 11. Atomic force microscopy images of CaWO4 thin films heat-treated at different temperatures; (a) 300 °C, (b) 350 °C, (c) 400 °C, and (d) 500 °C.



Fig. 12. Atomic force microscopy images of SrWO<sub>4</sub> thin films heat-treated at different temperatures; (a) 300 °C, (b) 350 °C, (c) 400 °C, and (d) 500 °C.

#### Table 2

Evolution of the roughness and average grain size parameters of XWO4 (X = Ca, and Sr) thin films on silicon substrate.

	CaWO <sub>4</sub>	CaWO <sub>4</sub>				SrWO <sub>4</sub>			
Annealing temperature (°C)	300	350	400	500	300	350	400	500	
A.G.S (nm)	-	15	30	110	-	20	50	100	

A.G.S, average grain size; Rms, roughness.

# 4. Conclusions

We have successfully demonstrated, the growth of  $XWO_4$  (X = Ca and Sr) thin films with scheelite-type structure onto silicon substrates by a soft chemical route, the so-called polymeric precursor method. The experimental results by NMR and FT-Raman spectroscopy showed that the formation of the citric acid metallic complex took place with the COOH terminal group of citric acid. Polycrystalline, homogeneous, dense, and crack-free thin films were successfully prepared on silicon substrates using the spincoating technique. The XRD results showed that no intermediate phase was detected and a single  $XWO_4$  (X = Ca and Sr) phase was crystallized from an amorphous matrix. XRD results showed a tetragonal structure for the polycrystalline thin films with lattice parameters of a = 5.241 Å and c = 11.403 Å, a = 5.242 Å and c = 11.373 Å for CaWO<sub>4</sub> and SrWO<sub>4</sub> thin films, respectively. Analysis by AFM showed that XWO<sub>4</sub> (X=Ca and Sr) thin films presented a homogeneous nucleation since the early stage. FT-IR spectra revealed complete decomposition of the organic ligands at 500 °C and the presence of the two sharp and intense bands between 700 and  $1000 \text{ cm}^{-1}$ , corresponding only to the  $F_2(\nu_3)$  antisymmetric stretch vibration modes and showing high crystallinity for both thin films. These results were in agreement with XRD patterns. Added to that, the joint use of the FT-IR and Raman spectroscopy powerful techniques provides comprehensive information on the vibrational structure of the thin films.

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