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Toward an Understanding of the Growth of Ag Filaments on α - Ag_2WO_4 and their Photoluminescent Properties: A Combined Experimental and Theoretical Study

Elson Longo,[†] Diogo P. Volanti,^{‡,*} Valéria M. Longo,[†] Lourdes Gracia,[§] Içamira C. Nogueira,[⊥] Marcio A. P. Almeida,[†] Antonio N. Pinheiro,[⊥] Mateus M. Ferrer,[⊥] Laécio S. Cavalcante,^{||} and Juan Andrés[§]

[†]Instituto de Química, UNESP—Universidade Estadual Paulista, R. Francisco Degni, 55, Araraquara, 14800-900, Brazil

[‡]Departamento de Química e Ciências Ambientais, UNESP—Universidade Estadual Paulista, R. Cristóvão Colombo, 2265, São José do Rio Preto, 15054-000, Brazil

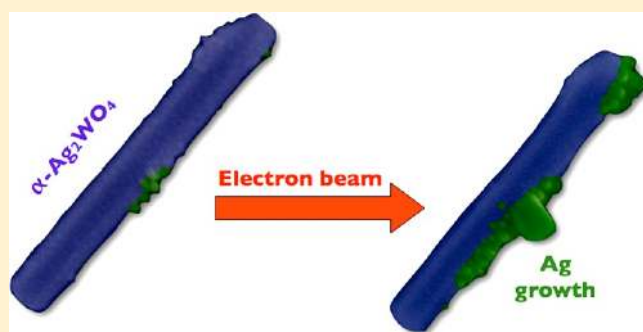
[§]Departament de Química Física i Analítica, UJI—Universitat Jaume I, Av. de Vicent Sos Baynat, s/n, Castelló de la Plana, 12071, Spain

[⊥]Departamento de Química, UFSCar—Universidade Federal de São Carlos, Rod. Washington Luis, km 235, São Carlos, 13565-905, Brazil

^{||}Departamento de Química, UESPI—Universidade Estadual do Piauí, R. João Cabral, 2231, Teresina, 64002-150, Brazil

S Supporting Information

ABSTRACT: A combined experimental and theoretical study was conducted on the structure and electronic properties of α - Ag_2WO_4 to clarify the nucleation and growth processes of Ag filaments on α - Ag_2WO_4 crystals induced by electron beam irradiation under electron microscopy. X-ray diffraction with Rietveld analysis, micro-Raman and Fourier-transform infrared spectroscopy were used to analyze the structural order/disorder of α - Ag_2WO_4 crystals. These complementary techniques indicated that the microwave-assisted hydrothermal method employed in the synthesis of α - Ag_2WO_4 crystals leads to the freezing of distorted $[\text{WO}_6]$ and $[\text{AgO}_y]$ ($y = 2, 4, 6$ and 7) clusters as the constituent polyhedra of α - Ag_2WO_4 . On the basis of the theoretical and experimental results, we provide a complete assignment of the structure of α - Ag_2WO_4 and describe the relationship among the disorder, nucleation growth, rate of Ag formation, and photoluminescence behavior before and after the irradiation of the accelerated electron beam. Density functional theory (DFT) studies indicated significant changes in the order–disorder of the initial α - Ag_2WO_4 electronic structure, with a decrease in the band gap value from 3.55 to 2.72 eV. The first stages of the electron irradiation on α - Ag_2WO_4 crystal were investigated by DFT calculations, and we have derived a mechanism to describe the formation and growth of Ag filaments during the electronic excitation of the $[\text{AgO}_2]$ cluster.



1. INTRODUCTION

Nanoparticle growth mechanisms have received much attention in recent years; controlling the size and morphologies of nanostructures is important for technological application. In this context, *in situ* electron microscopy constitutes an elegant technique that uncovers dynamic processes in the growth of nanocrystals. Recent technological advancements, in conjunction with high-resolution imaging, provide a new opportunity to view nanoscale processes. These advancements have been made possible as a result of the expansion and diffusion of transmission electron microscopy (TEM) heating holders for *in situ* electron microscopy.^{1–5} Several studies have reported using the TEM heating holder to monitor the crystal growth of different nanomaterials, such as bismuth,⁶ germanium,⁷ indium–arsenide,⁸ and vanadium oxide,⁹ and *in situ* liquid

TEM has been employed to understand the growth process of copper and lead sulfide nanostructures.^{10–12} The greatest impact of this new method of investigating the stages of crystal growth is the possibility to observe the step-by-step evolution of the crystal at the nanoscale.^{13,14}

The preparation and characterization of noble metal nanoparticles is an interdisciplinary subject and has attracted much attention due to the fundamental and applied scientific value of nanometer-sized metals.^{15–20} Among these metals, Ag nanoparticles possess unique properties with a wide range of applications, from surface-enhanced Raman spectroscopy^{21,22}

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59 to their use as an antibacterial agent.^{23–29} Over the past decade,
 60 Ag nanocrystals of myriad shapes have been synthesized using
 61 various methods.^{18,30–36} In this context, an emerging trend in
 62 nanotechnology is the creation of new nanomaterials and the
 63 exploration of their novel physical and chemical proper-
 64 ties.^{37–39} Often, newly identified nanomaterials bring to light
 65 previously undiscovered phenomena. One example, which
 66 changed the direction of noble metal research, is the first real-
 67 time, *in situ* nucleation and growth of Ag filaments on α -
 68 Ag_2WO_4 crystals, driven by an accelerated electron beam from
 69 an electronic microscope under high vacuum.⁴⁰
 70 In the present paper, a combined experimental and
 71 theoretical study was conducted on the structural arrangement
 72 that leads to the interesting growth process of Ag filaments on
 73 the α - Ag_2WO_4 crystal surface induced by field-emission
 74 scanning electron microscopy (FESEM) and complementary
 75 transmission electron microscopy (TEM) with selected-area
 76 diffraction (SAD) characterization; the photoluminescence
 77 (PL) enhancement of the Ag filaments was also investigated.
 78 X-ray diffraction (XRD) with Rietveld refinement, micro-
 79 Raman (MR) spectroscopy and Fourier transform infrared
 80 spectroscopy (FTIR) were used to analyze the structural order
 81 and disorder conditions of the α - Ag_2WO_4 structure prior to the
 82 Ag growth. The shape evolution and growth process of the α -
 83 Ag_2WO_4 crystals synthesized using a microwave-assisted
 84 hydrothermal (MAH) method at different temperatures was
 85 analyzed. The first stages of the Ag formation on α - Ag_2WO_4
 86 crystal provoked by electron irradiation were simulated by first-
 87 principles calculations based on density functional theory
 88 (DFT). The order–disorder structural conditions of the growth
 89 evolution and photoluminescence (PL) enhancement were
 90 inferred based on the theoretical results.

2. EXPERIMENTAL SECTION

91 **2.1. Synthesis of α - Ag_2WO_4 .** The typical α - Ag_2WO_4 crystal
 92 synthesis procedure was followed: 1×10^{-3} mol sodium tungstate
 93 dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 99.5% purity, Sigma-Aldrich) and 2×10^{-3}
 94 mol silver nitrate (AgNO_3 , 99.8% purity, Sigma-Aldrich) were
 95 separately dissolved in test tubes containing 50 mL deionized water.
 96 Before the addition of the salts, 0.5 g sodium dodecyl sulfate (SDS)
 97 ($\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$, 99% purity, Sigma-Aldrich) was dissolved in both of
 98 the tubes. The 100-mL combined suspension was transferred into a
 99 fluorinated ethylene propylene (PTFE) autoclave without stirring. The
 100 autoclave was then sealed and placed in a microwave-aided device for
 101 hydrothermal synthesis.⁴¹ α - Ag_2WO_4 samples were prepared at
 102 different temperatures (100, 120, 140, and 160 °C) for 1 h. The α -
 103 Ag_2WO_4 crystals were obtained as light beige, fine powder. The
 104 precipitates were collected and washed several times with acetone and
 105 dried at room temperature for 6 h.

106 **2.2. Characterizations.** The samples were characterized by XRD
 107 using a D/Max-2500PC diffractometer (Rigaku, Japan) with Cu $K\alpha$
 108 radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range from 10° to 70° in the normal
 109 routine with a scanning velocity of $2^\circ/\text{min}$ and from 10° to 110° with
 110 a scanning velocity of $1^\circ/\text{min}$ in the Rietveld routine, both with a step
 111 of 0.02° . MR measurements were recorded using a LabRAM HR 800
 112 mm model (Horiba, Jobin-Yvon, France). High-resolution Raman
 113 spectra were recorded with a He–Ne laser at 632.81 nm (model CCD
 114 DU420AOE325) operating at $25\text{--}1000 \text{ cm}^{-1}$ and keeping its
 115 maximum output power at 6 mW. A $50\text{-}\mu\text{m}$ lens was used to prevent
 116 sample overheating. FTIR spectra were recorded from 250 to 1000
 117 cm^{-1} using KBr pellets and a Bomem-Michelson spectrophotometer in
 118 transmittance mode (model MB-102). UV–vis spectra were recorded
 119 using a Varian spectrophotometer (model Cary 5G) in diffuse
 120 reflectance mode. The shapes and sizes of the α - Ag_2WO_4 microcrystals
 121 were observed with a field-emission scanning electron microscope
 122 (model Inspect F50, FEI Company, Hillsboro, OR) operating at 10

kV. TEM analyses were performed with a CM200-Philips microscope 123
 operating at 200 kV. The structural characterization of the samples was 124
 estimated using SAD. Specimens for TEM images were obtained by 125
 drying droplets of as-prepared samples from an acetone dispersion that 126
 had been sonicated for 10 min and deposited on 300-mesh Cu grids. 127
 PL measurements were performed with a Monospec 27 mono- 128
 chromator (Thermal Jarrel Ash) coupled to an R446 photomultiplier 129
 (Hamamatsu Photonics, Japan). A krypton-ion laser (Coherent Innova 130
 90K; $\lambda = 350.7 \text{ nm}$) was used as the excitation source; its maximum 131
 output power was maintained at 500 mW. The laser beam was passed 132
 through an optical chopper, and its maximum power on the sample 133
 was maintained at 40 mW. PL measurements were performed at room 134
 temperature. 135

2.3. Theoretical Calculation. Calculations for α - Ag_2WO_4 crystal 136
 were performed with a CRYSTAL09 program package.^{42,43} Tungsten 137
 was described by a large-core ECP, derived by Hay and Wadt, and 138
 modified by Cora et al.⁴⁴ Silver and oxygen centers were described 139
 using HAYWSC-311d31G and O (6-31d1G) basis sets, respectively, 140
 which were taken from the Crystal Web site.⁴⁵ Becke's three-parameter 141
 hybrid nonlocal exchange functional,⁴⁶ was used in combination with a 142
 Lee–Yang–Parr gradient-corrected correlation functional (B3LYP).⁴⁷ 143
 The diagonalization of the Fock matrix was performed at adequate k - 144
 points grids in the reciprocal space. The thresholds controlling the 145
 accuracy of the calculation of the Coulomb and exchange integrals 146
 were set to 10^{-8} (ITOL1 to ITOL4) and 10^{-14} (ITOL5), and the 147
 percent of Fock/Kohn–Sham matrices mixing was set to 40 (IPMIX = 148
 40).⁴² The band structure and the density of states (DOS) projected 149
 on atoms and orbitals of bulk α - Ag_2WO_4 were constructed along the 150
 appropriate high-symmetry directions of the corresponding irreducible 151
 Brillouin zone. To take into account the negative charged system, we 152
 inserted two additional electrons in the Ag atom of the $[\text{AgO}_2]$ 153
 clusters, and in order to simulate properly this electron excess an all- 154
 electron basis set (9766-3114d1G),⁴⁵ was used to describe this Ag 155
 center. 156

3. RESULTS AND DISCUSSION

The XRD patterns (Figure 1) indicate that all prepared α - 157
 Ag_2WO_4 crystals have an orthorhombic structure without any 158
 deleterious phases and belong to the space group $Pn2n$, with a 159
 C_{2v} symmetry.⁴⁸ These crystals have sharp and well-defined 160

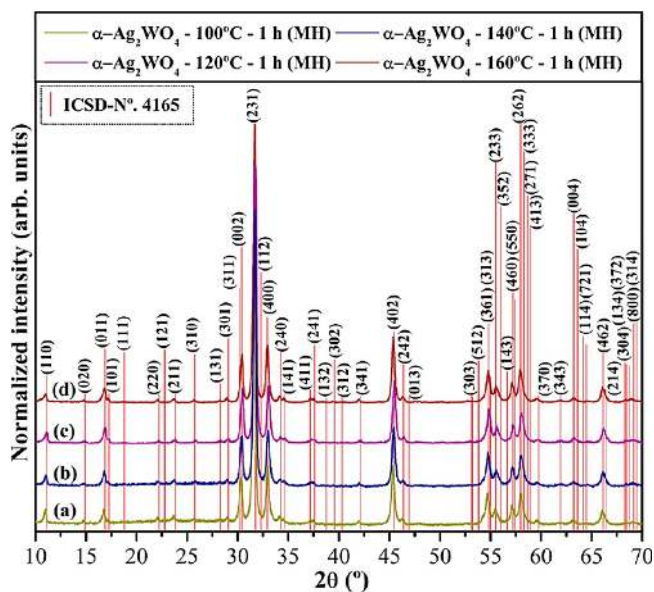


Figure 1. XRD patterns of α - Ag_2WO_4 microcrystals prepared at (a) 100, (b) 120, (c) 140, and (d) 160 °C for 1 h by the MAH method. The vertical lines indicate the position and relative intensity of the data from ICSD No. 4165 for the α - Ag_2WO_4 phase.

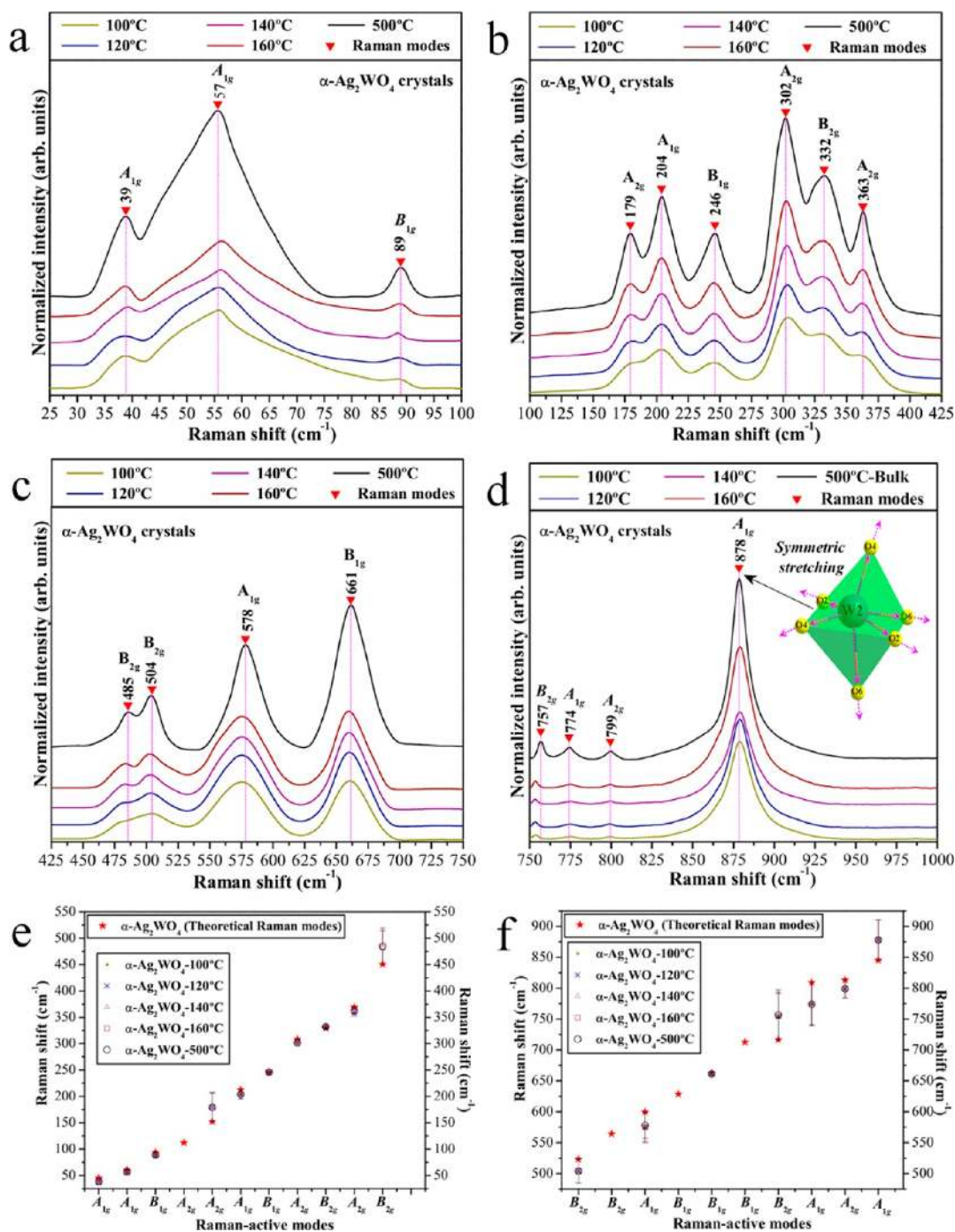


Figure 2. Micro-Raman spectra of α - Ag_2WO_4 prepared at different temperatures (100, 120, 140, and 160 °C) for 1 h by the MAH method, and by the coprecipitation method heat treated at 500 °C for 1 h (a) from 25 to 100 cm^{-1} , (b) from 100 to 425 cm^{-1} , (c) from 425 to 750 cm^{-1} , and (d) from 750 to 1,000 cm^{-1} . The vertical lines indicate the relative positions of the Raman-active modes. (e, f) Comparison of the theoretical and experimental Raman-active modes from 25 to 550 cm^{-1} and from 500 to 900 cm^{-1} , respectively.

161 diffraction peaks, which indicate a structural order and
 162 crystallinity at long-range. However, it is difficult to confirm
 163 the existence of Ag nanoparticles in these crystals based on
 164 XRD measurements.⁴⁹ Moreover, all diffraction peaks are in
 165 close agreement with the inorganic crystal structure database
 166 (ICSD) (N^o. 416525) and the literature.⁵⁰ The Rietveld
 167 analysis also corroborates these results (Figures S1 and S2 and
 168 Tables S1–S5, Supporting Information).

169 The MR spectra of the α - Ag_2WO_4 crystals synthesized using
 170 the MAH method, and the relative positions of the theoretical

and experimental Raman-active modes are depicted in Figure 2,
 171 including labels for the A_{1g} , A_{2g} , B_{1g} , and B_{2g} modes. The active
 172 Raman modes can exhibit a variable intensity because the
 173 rotation of the x -, y - and z -axes of the α - Ag_2WO_4 crystals occurs
 174 at different scattering of the tensors and components.⁵¹ As can
 175 be observed in Figure 2a–d, the MR spectra revealed the
 176 presence of 17 Raman-active vibrational modes. Four additional
 177 Raman modes (two B_{1g} , one A_{2g} and one B_{2g}) were not
 178 detectable experimentally because of their low intensities.
 179 Raman spectroscopy can be employed as a probe to investigate
 180

181 the degree of structural order–disorder at short-range in the
 182 materials.^{52,53} Therefore, 17 well-defined Raman-active vibra-
 183 tional modes can be observed for typical α - Ag_2WO_4 crystals,
 184 indicating a high degree of short-range structural order in the
 185 lattice. However, this behavior was not observed in the α -
 186 Ag_2WO_4 crystals synthesized by the MAH method, particularly
 187 in the sample treated at 100 °C. It is notable that the MR
 188 spectra of the synthesized crystals exhibited broad vibrational
 189 modes, indicating structural disorder at short-range. In addition,
 190 the disorder increased with the temperature treatment. This
 191 characteristic can be related to the very rapid kinetics of the
 192 MAH synthetic conditions. The MR spectrum of the sample
 193 treated at 100 °C did not present well-defined Raman peaks
 194 due to major short-range structural disorder.

195 Another interesting and important feature is the more
 196 pronounced structural local order presented by the lattice in the
 197 form of $[\text{WO}_6]$ clusters (see Figure 2d), as opposed to the
 198 lattice modifier assigned to $[\text{AgO}_y]$ ($y = 7, 6, 4$ and 2) clusters
 199 (Figure 2a–c). Specifically, the α - Ag_2WO_4 crystals prepared by
 200 the MAH method presented more well-defined Raman-active
 201 vibrational modes related to the symmetric stretching of (\leftarrow
 202 $\text{O}\leftarrow\text{W}\rightarrow\text{O}\rightarrow$) bonds of the octahedral $[\text{WO}_6]$ clusters than for
 203 the external vibrational modes of the distorted $[\text{AgO}_y]$ ($y = 7, 6,$
 204 4 and 2) clusters. The theoretical Raman-active modes were
 205 calculated through the atomic positions and lattice parameters
 206 for the optimized α - Ag_2WO_4 crystals and are illustrated in
 207 Figure 2e and f and presented in Table S6. There is good
 208 agreement among the Raman-active modes of the α - Ag_2WO_4
 209 crystals obtained in our samples, the first-principles calculation
 210 and the previously reported results from Turkovic et al.⁵¹ The
 211 two B_{1g} , one A_{2g} and one B_{2g} modes that were not
 212 experimentally observed (Figure 2e,f) were predicted by the
 213 first-principles calculation, suggesting that their intensity may
 214 be too low in the Raman spectrum. The slight variations in the
 215 positions of the typical vibrational modes of our sample when
 216 compared with those reported in the literature can be attributed
 217 to the preparation method, average crystal size, distortions of
 218 the $(\text{O}-\text{Ag}-\text{O})/(\text{O}-\text{W}-\text{O})$ bonds at short-range and/or
 219 intermolecular forces between the $[\text{AgO}_y]-[\text{WO}_6]-[\text{AgO}_y]$
 220 clusters at intermediate range. Moreover, our theoretical
 221 calculations do not consider the nonharmonic contribution to
 222 the crystal-lattice vibration phonons.

223 Figure 3 shows the FTIR spectra for the α - Ag_2WO_4 samples
 224 and the specific theoretical/experimental infrared modes.
 225 Figure 3a indicates that four active IR vibrational modes are
 226 possible. According to the literature,⁵⁴ the IR spectrum
 227 provides information on the degree of structural order–
 228 disorder in the metal–oxygen bonds. Figure 3a–d reveals two
 229 intense absorption bands at 830 and 862 cm^{-1} for all of the α -
 230 Ag_2WO_4 microcrystals. These modes are ascribed to the
 231 asymmetric stretching vibrations of the ($\leftarrow\text{O}\leftarrow\text{W}\leftarrow\text{O}\leftarrow$)/(\rightarrow
 232 $\text{O}\rightarrow\text{W}\rightarrow\text{O}\rightarrow$) bonds within the distorted octahedral $[\text{WO}_6]$
 233 clusters (see the inset in Figure 3). The active IR vibrational
 234 internal mode at 320 cm^{-1} is related to the symmetric bending
 235 vibrations within the distorted $[\text{WO}_6]$ clusters,⁵⁵ and the active
 236 IR vibrational external mode at 296 cm^{-1} is assigned to the
 237 torsional motion of the distorted octahedral $[\text{WO}_6]$ clusters.⁵⁶
 238 Peak positions refer to the IR-active vibrational modes, which
 239 are shown in Table S7 and are compared with other methods as
 240 reported in the literature.^{55,57} Figure 3b shows the close
 241 agreement between the experimental IR-active modes and the
 242 theoretically calculated modes, indicated by the \star symbol. In
 243 terms of spectral positions, small deviations in the IR-active

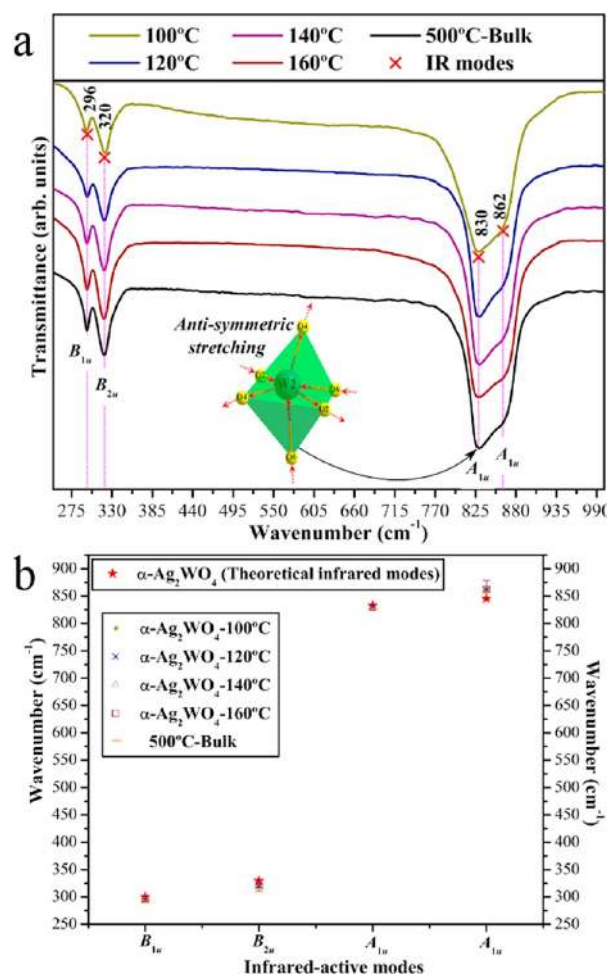


Figure 3. (a) FTIR spectra of α - Ag_2WO_4 prepared at different temperatures (100, 120, 140, and 160 °C) for 1 h by the MAH method. The vertical lines indicate the relative positions of the infrared-active modes. (b) Comparison between the theoretical and experimental infrared-active modes from 250 to 900 cm^{-1} .

244 modes of the α - Ag_2WO_4 crystals can be attributed to different
 245 degrees of interaction and modification of the $\text{O}-\text{Ag}-\text{O}$ and
 246 $\text{O}-\text{W}-\text{O}$ bond lengths and/or angles within the $[\text{AgO}_y]$ and
 247 $[\text{WO}_6]$ clusters. The optical band gap energy (E_{gap}) of the α -
 248 Ag_2WO_4 crystals was experimentally investigated using the
 249 method proposed by Kubelka and Munk.⁵⁸ This methodology
 250 is based on the transformation of diffuse reflectance measure-
 251 ments to estimate E_{gap} values with high accuracy within the
 252 limits of assumptions when modeled in three dimensions.⁵⁹
 253 According to Tang et al.⁶⁰ and Kim et al.,⁶¹ silver tungstate
 254 crystals exhibit an optical absorption spectrum governed by the
 255 direct electronic transitions between the valence and
 256 conduction bands; this behavior is supported by the theoretical
 257 calculations. In this electronic process, after the electronic
 258 excitation, the electrons located in the maximum-energy states
 259 in the valence band fall back to the minimum-energy states in
 260 the conduction band under the same point in the Brillouin
 261 zone.

262 Figure 4a reveals that the band structures for the optimized
 263 bulk α - Ag_2WO_4 crystal are characterized by well-defined direct
 264 electronic transitions, which is typical of crystalline semi-
 265 conductor materials. Fundamentally, the top of the VB and the
 266 bottom of the CB are in the same Γ to Γ point in the Brillouin
 267 zone. The value of the theoretically calculated band gap, 3.55

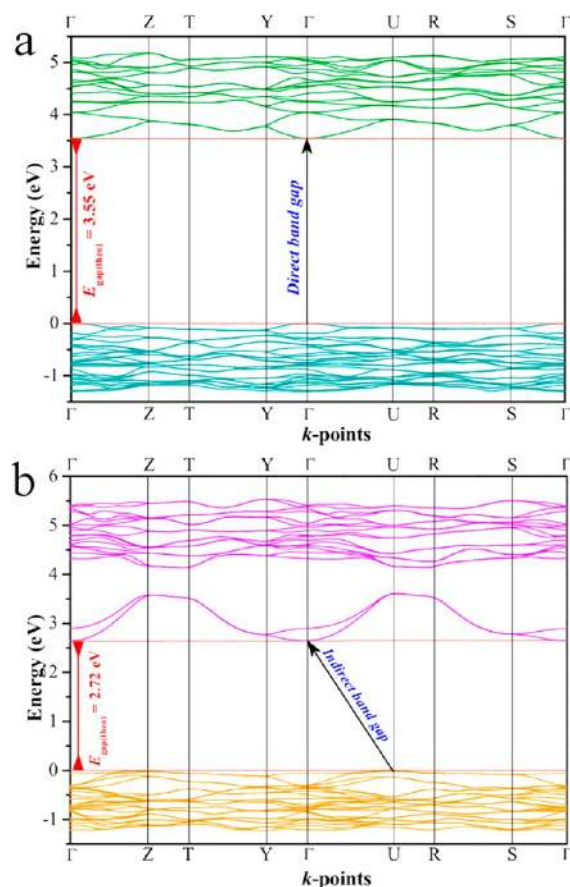


Figure 4. Band structures for optimized bulk α -Ag₂WO₄ crystal (a) in the neutral state and (b) charged with two electrons on the [AgO₂] clusters.

268 eV, was slightly higher than the experimental value of ~ 3.2 eV,
 269 estimated by UV–vis spectroscopy, for all samples synthesized
 270 by the MAH method. This overestimation of the predicted
 271 band gap can be due to the fact that it is calculated from the
 272 difference between the bottom of the conduction band (CB)
 273 and the top of the valence band (VB) within the Kohn–Sham
 274 formalism. However, it must be considered that the theoretical
 275 calculations estimate the optimized structure with a minimum
 276 energy, and the experimental structure derived from the MAH
 277 treatment conserves freezing distortions at short and
 278 intermediate range, which are not the most stable structures.
 279 Moreover, the band structure of this complicated network
 280 arrangement of [WO₆] and [AgO_y] clusters is basically
 281 determined by the W 5d orbitals in the conduction band
 282 (CB) and a valence band (VB) derived mostly from hybridized
 283 O 2p and Ag 4d orbitals. This reduction in the experimentally
 284 optical band gap value is most likely linked to distortions of the
 285 [WO₆]/[AgO_y] that are favorable to the formation of
 286 intermediate energy levels (photogenerated electron–hole
 287 pairs) between the VB and CB.

288 To simulate the electron absorption process based on the α -
 289 Ag₂WO₄ structure, theoretical calculations were performed
 290 while taking into account the incorporation of two electrons in
 291 the structure. An analysis of the α -Ag₂WO₄ structure shows that
 292 the [AgO₂] cluster presents the largest value of positive
 293 Mlliken charge for the Ag moiety, with only two adjacent
 294 oxygen anions. Therefore, this cluster was the most appropriate
 295 candidate to receive the external electron beam irradiation; in a

sense, we inserted two additional electrons in the Ag atom of 296
 the [AgO₂] cluster as a starting point and atomic positions were 297
 optimized. The resulting geometry is presented in Table S5b. 298
 Figure 4b depicts the band structure for optimized neutral bulk 299
 α -Ag₂WO₄ crystal charged with two electrons on the [AgO₂] 300
 clusters. An analysis of the band structure and the DOS (Figure 301
 S3a) for the charged system points out that intermediate levels 302
 are formed in the vicinity of the CB, which are composed of 5s 303
 orbitals of [AgO₂]. Therefore, new energy levels are created in 304
 the forbidden region of the band gap, leading to a disordered 305
 structure (Figure S3b). The Fermi level is now located at 306
 approximately 3.0 eV, considering the VB maximum at the 307
 zero-energy level, and the presence of these electron traps 308
 reduces the band gap energy to 2.72 eV, becoming indirect 309

from the U point to the Γ point (Figure 4b, Figure S3). 310
 Figure 5 shows the DOS projected on the 4d, 5d, and 2p 311
 orbitals of Ag, W and O atoms, respectively, for neutral α - 312
 Ag₂WO₄. The DOS structure of this complex network 313
 arrangement can be analyzed in terms of orbitals contribution 314
 of the atoms that form [WO₆] and [AgO_y] ($y = 7, 6, 4$ and 2) 315
 polyhedra. Figure 5a and b show that the projected DOS on the 316
 orbitals of the Ag1 and Ag2 atoms, coordinated by seven 317
 oxygens ([AgO₇]), are basically derived from the 4d_{xz} orbital of 318
 the valence band. The same relationship occurs with the Ag3 319
 atom, coordinated by six oxygens ([AgO₆]), as depicted in 320
 Figure 5c. When the coordination changes to four ([AgO₄]), as 321
 in the Ag4 and Ag5 atoms, the major contribution is derived 322
 from the 4d_{xz} and 4d_{z²} orbitals (see Figure 5d,e). Finally, in the 323
 bicoordinated Ag6 atom ([AgO₂]) the VB is mostly composed 324
 by 4d_{xz} orbital (see Figure 5f). The projected DOS on the W 325
 atom is basically determined by the 5d orbitals in the 326
 conduction band (CB) with more important role of 5d_{z²} 327
 orbitals (Figure 5g). The valence band (VB) is primarily 328
 derived from hybridized O 2p (Figure 5h) and Ag 4d orbitals. 329

A study of the growth of Ag on the α -Ag₂WO₄ surface as a 330
 function of exposure time to a scanning electron microscope 331
 under an accelerating voltage of 10 kV was carried out. The 332
 onset of Ag nanoparticle nuclei on the surface of the α -Ag₂WO₄ 333
 crystals was observed by the FESEM images (Figure 6) as soon 334
 as the samples began to be analyzed. This behavior was 335
 observed for all the samples synthesized at different temper- 336
 atures, namely, 100, 120, 140, and 160 $^{\circ}$ C (Figure 6, parts a, c, e 337
 and g, respectively). After 5 min of irradiation, the growth of 338
 the initial particles of Ag and the onset of new nuclei growth 339
 were observed in all the samples (100, 120, 140, and 160 $^{\circ}$ C) 340
 (Figure 6, parts b, d, f, and h, respectively). It is important to 341
 emphasize that the sample prepared at 160 $^{\circ}$ C (Figure 6h) has 342
 a higher number of Ag nuclei as well as a higher absorption of 343
 existing particles. This behavior was also demonstrated in our 344
 previous work.⁴⁰ In this way, the most organized sample (160 345
 $^{\circ}$ C) favors the nucleation of metallic Ag nanorods. However, 346
 the growth process occurs preferentially in samples where the 347
 nucleation is smaller. Table S9 (of the Supporting Information) 348
 presents the calculated values of the surface energy for (001), 349
 (100), (010), (011), (101) and (110) facets of α -Ag₂WO₄. The 350
 surface (100) is the most stable facet, with the higher 351
 percentage of the relaxing process. If charged α -Ag₂WO₄ 352
 structure is focused on the plane (100) compared to the 353
 equilibrium geometry, it can be seen an approaching of Ag4 and 354
 Ag5 centers (from 4.0 to 3.26 Å) when the system is charged in 355
 the vicinity of Ag6 atoms. In addition, Ag6–O distance 356
 increases from 2.34 to 2.54 Å showing that this situation favors 357
 an accumulation of Ag atoms along the most stable (100) 358

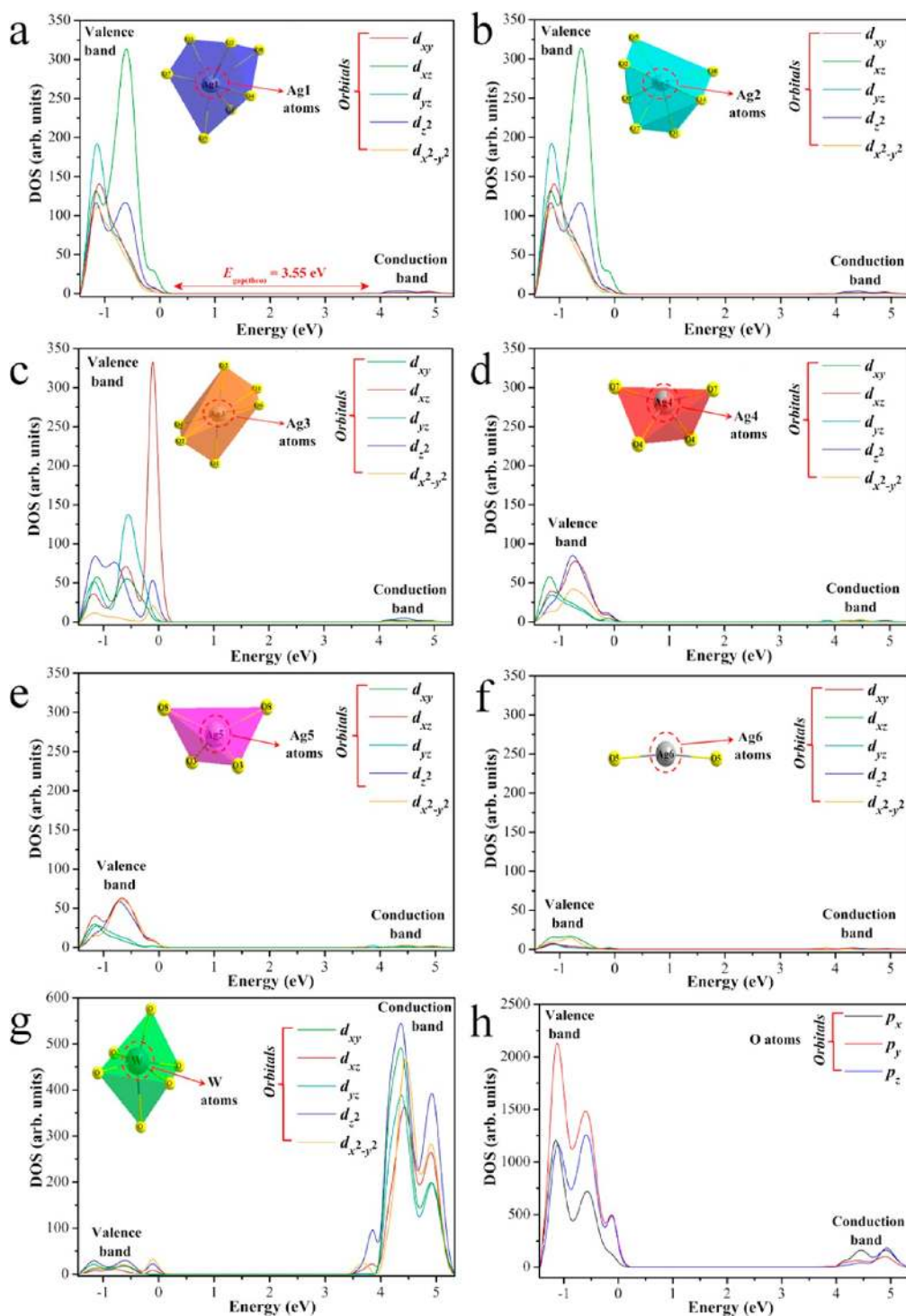


Figure 5. DOS projected on the 4d, 5d, and 2p orbitals of (a–f) Ag, (g) W, and (h) O atoms, respectively.

359 surface. Therefore, the *ab initio* calculations indicate that the
 360 absorption of electrons leads to the disordered structure that
 361 facilitates Ag nucleation. It is possible that a more ordered
 362 structure has a more homogeneous surface and thus facilitates a
 363 more homogeneous nucleation; a more detailed study of this
 364 system is necessary to test this possibility. The TEM images of
 365 all samples and the structural electron diffraction (SAD) details
 366 of the growth process of Ag on the α -Ag₂WO₄ crystals are
 367 shown in Figures S4 and S5 and Table S8 in the Supporting
 368 Information.

Figure 7 shows the PL spectra recorded at room temperature 369 for the α -Ag₂WO₄ samples, excited by a 350.7 nm line of a 370 krypton ion laser, before and after irradiation by an accelerated 371 electron beam. The PL spectral profiles show typical behavior 372 for multiphonon or multilevel processes, i.e., a solid system 373 where relaxation occurs by several pathways, which involve the 374 participation of numerous energy states within the band gap. 375 It is generally assumed that the blue-green emission of 376 tungstate is due to the charge-transfer transitions within the 377 [WO₄]²⁻ complex in ordered systems,^{63–67} or complex cluster 378 vacancies in the former,^{68–70} and/or modified lattice.⁷⁰ It is 379

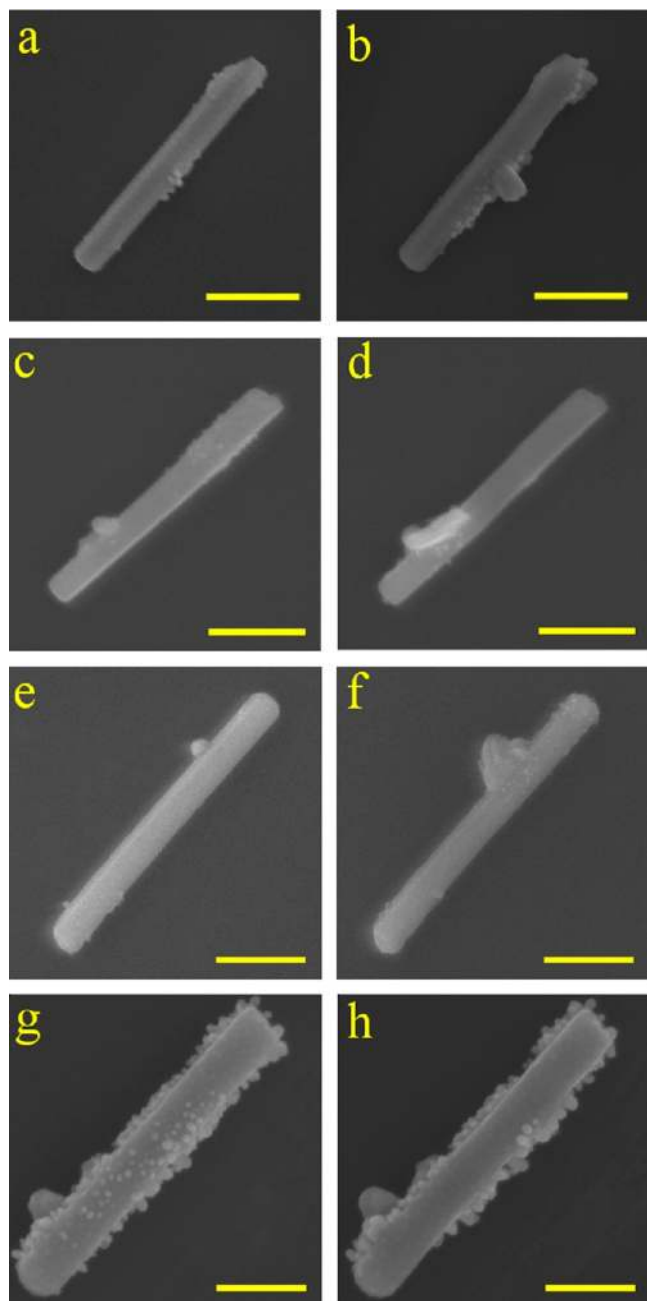


Figure 6. Initial FESEM images of the α - Ag_2WO_4 samples obtained by the MAH method at (a) 100, (c) 120, (e) 140 and (d) 160 °C. After 5 min, microscopy analyses of the same samples were recorded: (b) 100, (d) 120, (f) 140, and (h) 160 °C. (Scale bar = 400 nm in parts a–f and 200 nm in parts g and h.)

well-known that the physical and chemical properties of materials are strongly correlated with structural factors, primarily the structural order–disorder in the lattice. The materials can be described in terms of the packing of the constituent clusters, which can be considered as the structural motifs. A specific feature of tungstates with a scheelite structure is the existence of $[\text{WO}_6]$ and $[\text{AgO}_y]$ clusters in a crystal lattice.⁷¹ This orthorhombic structure can also be understood in terms of a network of $[\text{WO}_6]$ clusters, linked by strong bonds [...W–O–W...] between the neighboring clusters, whose internal vibration spectra provide information on the structure and order–disorder effects in the crystal lattices.^{72,73} Breaking

the symmetry of these clusters through distortions, breathings and tilts creates a large number of different structures with different material properties; this phenomenon can be related to local (short), intermediate and long-range structural order–disorder. Therefore, for α - Ag_2WO_4 , the material properties can be primarily associated with the constituent clusters, and the disparity or mismatch of both clusters can induce structural order–disorder effects, which significantly influence the luminescence properties of the tungstates.^{74–76}

Disorder in materials can be manifested in many ways; examples include vibrational, spin and orientation disorder (referenced to a periodic lattice) and topological disorder. Topological disorder is the type of disorder associated with glassy and amorphous solid structures in which the structure cannot be defined in terms of a periodic lattice. PL is a powerful probe of certain aspects of short-range (2–5 Å) and medium-range order (5–20 Å), such as clusters where the degree of local order is such that structurally inequivalent sites can be distinguished due to their different types of electronic transitions which are linked to a specific structural arrangement.⁶²

In Figure 7a, the maximum blue PL emission peak is centered at 449 nm for all the samples; however, another diffuse emission in the red region peaking from 621 to 640 nm was also observed. The nucleation–dissolution–recrystallization mechanism favored by the MAH process can be seen as an order–disorder–order process of nature and gives rise to a nonclassical crystallization process.⁷⁷ Using density functional calculations, Ghazi et al.⁷⁸ noted that growth is an order–disorder–order pattern of cyclic nature. Between two ordered clusters, growth proceeds via disordered clusters, and global order emerges suddenly with the addition of only one or two atoms. In this sense, the different intensities in the emission profiles can be attributed to slight differences in the defect densities linked to the distorted clusters and complex vacancies generated by the MAH heat treatment. The first emission peak can be related to distorted $[\text{WO}_6]$ octahedra that are, in the case of our samples, more ordered, in accordance with the MR and IR spectral data and previous reports.^{63–67} The emission in the red spectrum region is most likely linked to the $[\text{AgO}_y]$ clusters that form complex vacancies, inducing more disorder and deeper defects in the forbidden band gap. However, other factors may also be involved, such as the degree of aggregation and the orientation between particles, the variations in the particle size distribution, the morphology of the particles and surface defects. All these factors have an influence on the intensity of the PL emission.

The PL profile of irradiated α - Ag_2WO_4 depicted in Figure 7b is quite different from the nonirradiated PL profile (Figure 7a). No blue shift is observed in the emission maximum, indicating that the $[\text{WO}_6]$ clusters are unchanged by the irradiation (Figure 7c,f). However, the profile of the PL emission in the red region of the spectra is changed. As discussed above, these changes can be attributed to the $[\text{AgO}_y]$ clusters becoming more disordered by the Ag metallic growth on the surface. This process generates complex vacancies of V_{Ag}^{\bullet} and V_{O}^{\bullet} (where $V_{\text{O}}^{\bullet} = V_{\text{O}}^{\bullet}, V_{\text{O}}^{\bullet}, V_{\text{O}}^{\bullet\bullet}$), but it is clear that the $[\text{WO}_6]$ surface clusters should also be slightly disordered as a result of Ag migration and Ag nanorod formation. As predicted by first-principles calculations, in the disordered structure the electronic levels are significantly affected by the inclusion of electrons, as it is observed in the band gap structure, favoring the red emission. The samples prepared at 100 (Figure 7c), 120 (Figure 7d), and

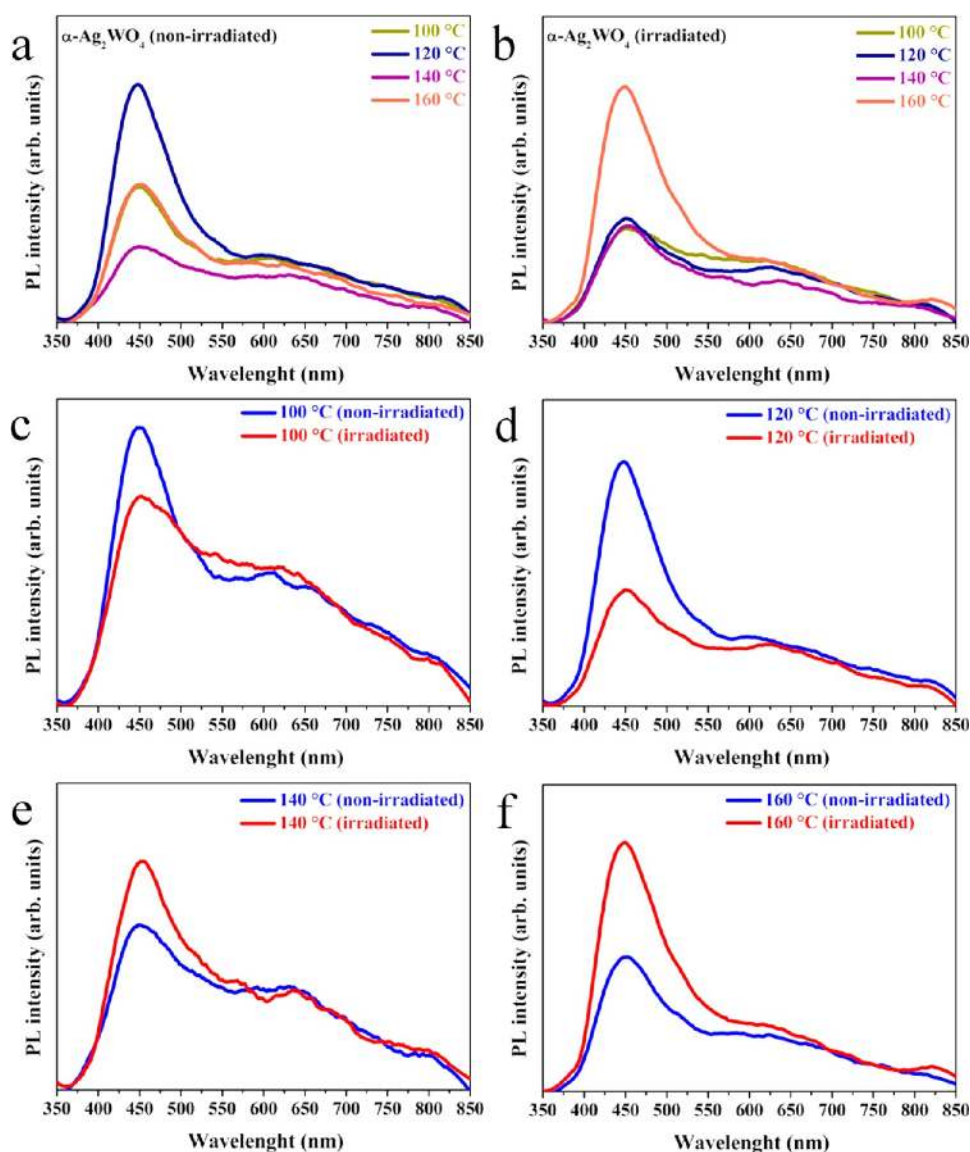


Figure 7. PL spectra recorded at room temperature of the α - Ag_2WO_4 crystals obtained by the MAH method at 100, 120, 140, and 160 °C, excited by a 350.7 nm line of a krypton ion laser (a) before and (b) after irradiation by an accelerated electron beam. For better visualization, we show the spectrum of each individual sample: (c) 100, (d) 120, (e) 140, and (f) 160 °C irradiated (red) and nonirradiated (blue).

455 140 °C (Figure 7c) show intermediate PL intensities. The
 456 maximum enhancement in PL emission after irradiation was
 457 observed in the sample heat-treated at 160 °C (Figure 7f). This
 458 sample presents the highest degree of structural order prior to
 459 irradiation, as discussed in the MR and FTIR analysis, and the
 460 highest nucleation rate after irradiation, as observed by FESEM
 461 (Figure 6h). The more abundant and homogeneous nucleation
 462 favored by the more ordered structure results in more V'_{Ag} and
 463 V'_0 complex vacancies and a larger effect on the PL
 464 enhancement.

4. CONCLUSIONS

465 In this study, α - Ag_2WO_4 particles were successfully synthesized
 466 by an MAH method; XRD patterns and Rietveld analysis
 467 confirmed the orthorhombic structure obtained. The physical/
 468 chemical properties and the corresponding performance of the
 469 α - Ag_2WO_4 crystals are closely related to the crystal structure,
 470 and in the present case, the local electric fields or polarized
 471 fields in the distorted metal–oxygen polyhedra, namely $[\text{WO}_6]$

and $[\text{AgO}_y]$ ($y = 7, 6, 4,$ and 2). MR and FTIR spectroscopy 472
 indicate that the MAH method employed in the synthesis of α - 473
 Ag_2WO_4 crystals leads to the freezing of distorted $[\text{WO}_6]$ and 474
 $[\text{AgO}_y]$ clusters. An external electron beam irradiation induces 475
 the formation and crystal growth of Ag filaments on the α - 476
 Ag_2WO_4 crystal and a PL enhancement. This finding is 477
 reshaping our understanding of these molecular processes, 478
 revealing previously hidden subtleties. A theoretical inves- 479
 tigation using density functional theory (DFT) was carried out 480
 to understand the introduction of electrons into the α - Ag_2WO_4 481
 lattice. The results indicate that the electron-induced growth 482
 process of Ag on α - Ag_2WO_4 crystal is closely connected with 483
 the structural and electronic properties of the $[\text{AgO}_2]$ cluster; 484
 this process results in a drastic increase of the structural and 485
 electronic disorder, as evidenced by the decrease in the band 486
 gap from 3.55 to 2.72 eV. Finally, no blue shift of the emission 487
 maximum was observed, indicating that the $[\text{WO}_6]$ clusters 488
 were unchanged by the irradiation; however, changes were 489
 observed in the red region of the PL profile. These changes 490

491 were attributed to unstable $[\text{AgO}_y]$ clusters that became
492 disordered by the growth of metallic Ag on the surface, leading
493 to complex vacancies. First-principles calculations predicted
494 that this process would lead to a disordered structure with deep
495 defects inserted in the band gap, favoring the red emission. The
496 results of this research provide fundamental insight into the PL
497 properties of $\alpha\text{-Ag}_2\text{WO}_4$ crystals, the electron-induced synthesis
498 of Ag/ $\alpha\text{-Ag}_2\text{WO}_4$ and its relationship with the morphology by
499 controlling surface/bulk defects. We believe that this process
500 may also be applicable for controlling other properties such as
501 microbial activity and photodegradation.

502 ■ ASSOCIATED CONTENT

503 ● Supporting Information

504 Figures and tables of Rietveld refinement analyses of the α -
505 Ag_2WO_4 crystal, DFT analysis, and TEM analysis with the
506 corresponding SAD characterization. This material is available
507 free of charge via the Internet at <http://pubs.acs.org>.

508 ■ AUTHOR INFORMATION

509 Corresponding Author

510 *E-mail: (D.P.V.) volanti@ibilce.unesp.br.

511 Notes

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