**Supporting information**

**Bridging experiment and theory: morphology, optical, electronic, and magnetic properties of MnWO4**

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**Table S1 –** 2D lattice parameters of surface primitive cell, surface area in , number of Mn atoms in the slab **,** number of layers in the optimized slab and total number of unpaired electrons.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Surface** | **2D Lattice parameter** | **Area** | **Mn** |  |  |
| **(100)** |  | 0.283 | 10 | 30 | 0 |
| **(010)** |  | 0.235 | 7 | 28 | 5 |
| **(001)** |  | 0.278 | 10 | 50 | 0 |
| **(101)** | ° | 0.394 | 11 | 55 | 55 |
| **(011)** | ° | 0.364 | 12 | 60 | 0 |
| **(110)** |  | 0.371 | 12 | 60 | 0 |
| **(111)** |  | 0.462 | 12 | 60 | 60 |
| **(012)** |  | 0.604 | 12 | 60 | 0 |

**Fig. S1A** shows the XRD patterns of MnWO4 samples. All XRD patterns of these powders correspond to a wolframite-type monoclinic structure with special group 𝑃2/𝑐 and 𝐶2ℎ4 symmetry, which is in agreement with the respective *Inorganic Crystal Structure Database* (ICSD) No. 67907.1 These samples have sharp and well-defined diffraction peaks, indicating a good degree of structural order at long range. No other additional phase was observed, confirming the purity of the phase obtained. **Fig. S1B** shows an expanded view of the 2θ window between 29 and 31°, where the most prominent and peaks occur. We can first observe that the increase in MI leads to a progressive displacement of the Bragg peaks to smaller angles, resulting in greater interplanar distances due to a symmetry breaking of the structure.2 In addition, the sample synthesized at 32 min shows a decrease in the definition of and peaks, further indicating that MI time contributes to the increase in the symmetry breaking of the material. We must also mention that MnWO4 has two different distorted octahedral clusters, [MnO6] and [WO6], and that these clusters along with the primitive cell are displayed in **Fig. S1C**. According to Deniard et al,3 the 3D structure can be described as an infinite zigzag of (MnO4)∞ and (WO4)∞ chains, running parallel to the same direction as either edge-sharing [MO6] or [WO6d] distorted octahedra.4

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**Figure S1** - A) X-ray diffraction for MnWO4 samples. B) Expanded view of the 2θ dependence between 29 and 31°, where Bragg and planes take place. (C) Primitive unit cell and clusters of MnWO4.

Rietveld refinements were performed and the results are shown in **Tab. S2**. The powder diffraction data were analyzed according to the Rietveld refinement by using the GSAS software. The reliability coefficients Rp and χ2 show that the refinements have a high degree of reliability. There is a slight tendency to reduce lattice parameters *b* and *c* and the angle β, which cause a slight reduction in the volume of the crystalline cell with the increase in the MI time. **Table S3** displays the values of distance and bond angles obtained through the Rietveld refinements for the [MnO6] and [WO6] clusters. As the MI time increases, the bond distances remain unchanged, while the bond angles of the [WO6] and [MnO6] clusters increase. These changes are responsible for symmetry breaking processes, which is reflected in the displacements observed in the XRD of the peaks and .

**Table S2** - Results of Rietveld refinement for MnWO4 with monoclinic structure and space group (P2/c).

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Time** |  |  | **)** | **)** | **)** |  | **)** |
| 2 | 10.12 | 1.992 | 4.829 | 5.787 | 5.024 | 140.412 | 91.086 |
| 4 | 10.59 | 1.731 | 4.829 | 5.784 | 5.022 | 140.262 | 91.100 |
| 8 | 11.48 | 1.575 | 4.831 | 5.785 | 5.022 | 140.348 | 91.098 |
| 16 | 9.55 | 1.714 | 4.829 | 5.782 | 5.019 | 140.152 | 91.111 |
| 32 | 9.75 | 1.269 | 4.830 | 5.777 | 5.015 | 139.912 | 91.113 |
| ICSD | -- | -- | 4.830 | 5.760 | 4.994 | 138.920 | 91.140 |
| Theoretical | -- | -- | 4.766 | 5.834 | 4.924 | 136.936 | 89.571 |

**Table S3 –** Values of distance and bond angles obtained through Rietveld refinements for [MnO6] and [WO6] clusters. Theoretical results are also shown.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample** | **W-O1** | **W-O2** | **W-O3** | **O1-W-O2** | **O1-W-O3** | **O2-W-O3** | **Mn-O1** | **Mn-O2** | **Mn-O3** | **O1-Mn-O2** | **O1-Mn-O3** | **O2-Mn-O3** |
| 2 | 1.918 | 1.789 | 2.146 | 96.076 | 85.961 | 89.116 | 2.110 | 2.171 | 2.293 | 94.310 | 87.547 | 84.493 |
| 4 | 1.918 | 1.789 | 2.145 | 96.058 | 85.951 | 89.115 | 2.109 | 2.170 | 2.292 | 94.316 | 87.529 | 84.500 |
| 8 | 1.918 | 1.789 | 2.145 | 96.042 | 85.936 | 89.109 | 2.109 | 2.170 | 2.292 | 94.336 | 87.526 | 84.514 |
| 16 | 1.918 | 1.789 | 2.144 | 96.022 | 85.923 | 89.107 | 2.109 | 2.169 | 2.292 | 94.347 | 87.512 | 84.522 |
| 32 | 1.916 | 1.787 | 2.143 | 95.974 | 85.893 | 89.074 | 2.108 | 2.167 | 2.291 | 94.387 | 87.473 | 84.559 |
| ICSD | 1.911 | 1.784 | 2.137 | 95.791 | 85.762 | 89.012 | 2.104 | 2.161 | 2.286 | 94.551 | 87.371 | 54.692 |
| Theoretical | 1.838 | 1.731 | 2.374 | 93.271 | 89.827 | 87.396 | 2.044 | 2.148 | 2.352 | 95.452 | 85.405 | 81.904 |

In order to investigate the structural order/disorder of the samples at short range, micro-Raman measurements were performed at room temperature (**Fig. S2**). According to our group theory, MnWO4 with a wolframite structure has 18 Raman active modes or optical phonons represented in the center of the Brillouin zone after decomposition of the Г point (Г = 8Ag + 10Bg).5

**Figure S2** - A) Micro-Raman spectra of MnWO4 samples. B) Correlation between the experimental Micro-Raman spectra and the frequency values obtained theoretically.

**Fig. S2A** shows the micro-Raman spectra of MnWO4 samples. As it can be seen, of the 18 active Raman modes, only 10 are clearly observed. This might be due to the overlap and low intensities in some Raman modes. Despite not being possible to observe all Raman modes, they are clear and well-defined, featuring a high order at short range for all MnWO4 samples. The vibrational modes active in MnWO4 are certainly related to [WO6] clusters with specific vibrations, evidencing that the center of mass is in a stationary state.6 The internal lattice modes (L) related to the [WO6] clusters refer to two transitions: (i) (Ag + Bg), located at 141 cm-1, and (ii) another at 184 cm-1. Symmetrical deformations (δs - 2Ag) and symmetrical stretching (γs - Ag) of the W-O-W bonds of [WO6] clusters are assigned to the modes located at 218, 268, and 551 cm-1, respectively. From the data in **Fig. S2A**, bands related to symmetric deformation (δs-Ag) and symmetrical strains (γs - Bg + Ag) of the W-O bonds of the [WO6] cluster can also be noted, i.e., bands located at 410, 782, and 895 cm-1, with the latter corresponding to the most intense mode. The asymmetric deformation (δas - Ag) and the asymmetric stretching (γas - Ag) of the W-O connections can also be observed, being associated with the bands located at 340 and 706 cm-1. There is also a shift to higher energy values (shorter wavelength) in the bands of the samples. The comparison between the relative experimental and theoretical positions of these vibrational modes is illustrated in **Fig. S2B** and confirms the good agreement between experimental and theoretical predictions for MnWO4. These data are listed in **Table S4**, and as found in the DRX analysis correlate well the displacement and the symmetry break in the semiconducting structure of the material.

**Table S4** **–** Experimental and theoretical Raman modes. Frequencies are given in (

|  |  |  |  |
| --- | --- | --- | --- |
| **Mode** | **IRREP** | **Experimental** | **Theoretical** |
| 1 | (Ag) | 141 | 134 |
| 2 | (Bg) | 184 | 227 |
| 3 | (Ag ) | 218 | 239 |
| 4 | (Bg) | 268 | 269 |
| 5 | (Bg) | 340 | 346 |
| 6 | (Ag) | 410 | 439 |
| 7 | (Ag) | 551 | 535 |
| 8 | (Ag) | 706 | 661 |
| 9 | (Ag) | 782 | 793 |
| 10 | (Ag) | 895 | 824 |

The XPS measurements were performed to gain information about the chemical composition of the samples and to analyze their valence surface states. **Fig. S3A** shows the survey spectra of the MnWO4 samples. It can be seen that all samples are comprised of Mn, W and O atoms since C comes from the equipment's sample holder. The Mn 2*p* core level spectrum in **Fig. S3B** displays two well defined peaks at 640.2 and 652.3 eV, corresponding to Mn 2*p*3/2 and 2*p*1/2 orbitals, respectively, whic are characteristic of Mn with oxidation state 2+.7, 8 **Fig.** **S3C** shows three peaks of W with oxidation state 6+. The peaks located at 34.1 and 36.2 eV refer to the 4*f* orbital in 4*f*7/2 and 4*f*5/2 components, respectively, while the peak located at 39.3 eV refers to the 5*p* orbital of W.7, 9 In **Fig. S3D**, the characteristic peak of O 1*s* was deconvolved into two specific components: one at 529 eV referring to the O atoms of the crystal lattice of MnWO4 (OL), and another at 531 eV, corresponding to OH groups adsorbed on the MnWO4 surface.11-12

**Figure S3 -** XPS spectra of MnWO4 samples. A) survey spectra, B) Mn 2*p*, C) W 4*f* and 5*p*, and D) O 1*s* core level spectra.

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**Figure S4** **–** Structure of the **A**. (010), **B**. (110), **C**. (001), **D**. (011), **E**. (111), **F**. (012), **G**. (101) and **H**. (100) surfaces based on slab models. Green, grey and red balls represent Mn, W and O atoms, respectively. The more superficial Ag and W clusters are also shown in each surface.

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**Figure S5 –** Band structure and DOS of the different surfaces of MnWO4. **A**. (010), **B**. (110), **C**. (001), **D**. (011), **E**. (111), **F**. (012), **G**. (101) and **H**. (100).

**Figure S6 –** Values of bond lengths (in ) in the ] and ] clusters at the (010), (110), (001), (011), (111), (012), (101), and (100) surfaces of MnWO4

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