

# A diagnosis approach for semiconductor properties evaluation from ab initio calculations: Ag-based materials investigation

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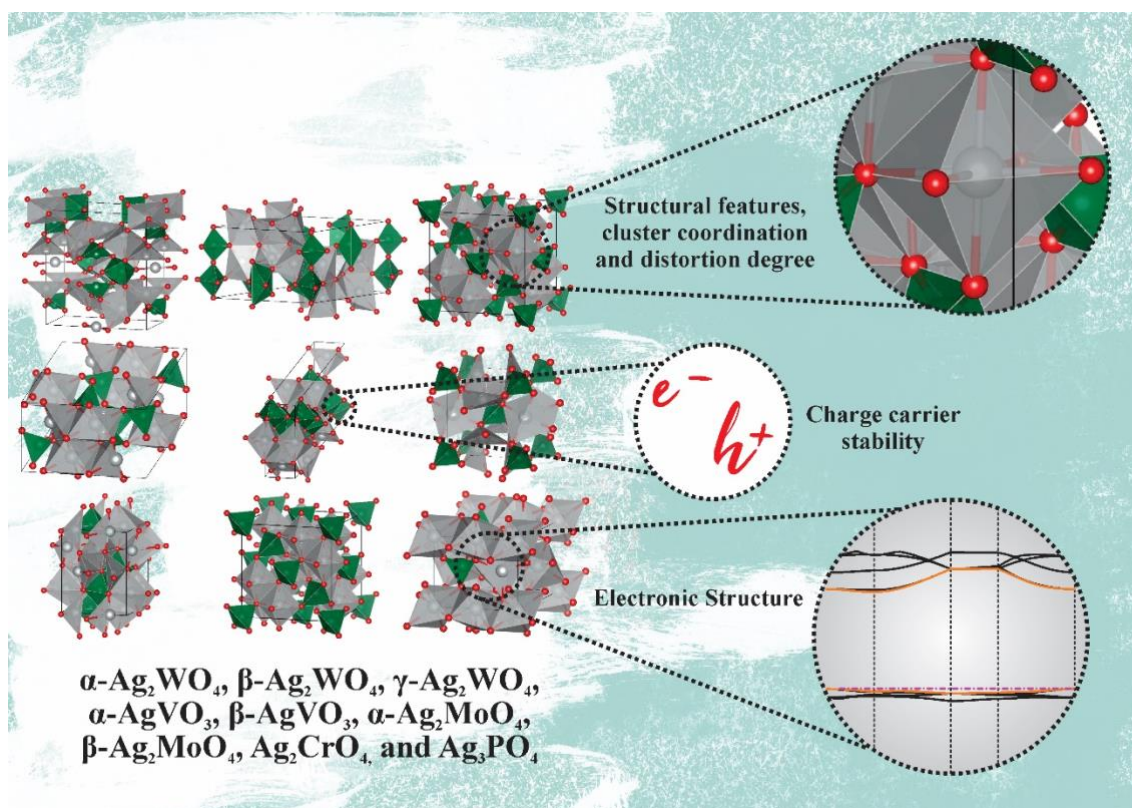
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**Abstract:** Ag-based semiconductors have been extensively employed as photocatalysts for several decades due to their excellent electronic properties, photochemical properties, and relatively low synthesis cost. In this work, the  $\alpha$ -Ag<sub>2</sub>WO<sub>4</sub>,  $\beta$ -Ag<sub>2</sub>WO<sub>4</sub>,  $\gamma$ -Ag<sub>2</sub>WO<sub>4</sub>,  $\alpha$ -AgVO<sub>3</sub>,  $\beta$ -AgVO<sub>3</sub>,  $\alpha$ -Ag<sub>2</sub>MoO<sub>4</sub>,  $\beta$ -Ag<sub>2</sub>MoO<sub>4</sub>, Ag<sub>2</sub>CrO<sub>4</sub>, and Ag<sub>3</sub>PO<sub>4</sub> materials were systematically investigated by DFT/B3LYP calculations. The structural features were described by cations coordination, cluster distortion degree, and structure formers and modifiers. In turn, the evaluation of electronic properties indicates band gap values in the range of 2.54 eV to 4.32 eV. The calculated density of charge carriers shows that the holes are the predominant charge carrier for all evaluated semiconductors, except for  $\alpha$ -Ag<sub>2</sub>MoO<sub>4</sub>. The effective masses of charge carriers were also computed, and good stability for generated electrons and holes are expected for  $\alpha$ - and  $\beta$ -Ag<sub>2</sub>WO<sub>4</sub>,  $\alpha$ -AgVO<sub>3</sub>,  $\beta$ -AgVO<sub>3</sub>,  $\beta$ -Ag<sub>2</sub>MoO<sub>4</sub>, Ag<sub>2</sub>CrO<sub>4</sub>, and Ag<sub>3</sub>PO<sub>4</sub> materials. Finally, the valence and conduction band edge potentials point to the Ag-based semiconductors as promising candidates for photocatalytic and biocide activities.

**Keywords:** Electronic structure; Photocatalysis; Semiconductors; DFT; Biocide.

## Graphical Abstract



## 1. INTRODUCTION

The modern human society enjoys different privileges arising from fast technological advance which is strongly associated to novel functional materials.[1-4] The solid-state materials responsible for such technological developments are related to the presence of relevant electronic, optical, ferroelectric, magnetic, and other properties. In this context, semiconductor materials stand out as materials that offer such properties being successfully used for technological applications and produced on a large scale and low economic cost.[5, 6] In particular, the interest in semiconductors has increased drastically due to i) their potential to treat water effluents contaminated with organic pollutants through a photocatalytic process[7-9] and ii) biocide activity aiming to minimize the dissemination of the disease.[10, 11]

Over the last years, novel semiconductor materials with excellent properties have been proposed. Among such materials stands out the Ag-based semiconductors which present unique electronic, photocatalytic, and biologic properties. For this reason, our research group has devoted much effort to studying this class of materials characterizing different properties and unveiling their physical-chemical principles from theoretical approaches. The main Ag-based semiconductors are discussed below. The  $\text{Ag}_2\text{WO}_4$  is a semiconductor observed in three different polymorphs, being the  $\alpha$  structure (Pnn2) the most stable while the  $\beta$  (P63/m) and  $\gamma$  (Fd-3m) are meta-stable phases.[11] Silva *et al.*[12] reported ozone gas-sensors based on one-dimensional  $\alpha$ - $\text{Ag}_2\text{WO}_4$  nanostructures. Similarly, Laier *et al.*[13] have studied the surface dependency of the properties for the same polymorph. Other works focused on  $\text{Ag}_2\text{WO}_4$  have investigated their antitumor and antifungal activities[14, 15], photoluminescence[16-20], different synthesis techniques[21, 22], antibacterial potential[23-25] and photocatalytic properties[23, 26]. The  $\text{Ag}_3\text{PO}_4$  has also been extensively investigated, and their photocatalytic[27-30], electronic[31-35], antiviral and antibacterial[36] properties reported.

The  $\text{AgVO}_3$  also presents polymorphic behavior and has attracted attention due to its higher biocompatibility and minor Ag amount in the formula unit[37]. Other studies on  $\text{AgVO}_3$  properties depict their structural stability[38], photoluminescence[39, 40], and antibacterial features[41]. In turn, the  $\text{Ag}_2\text{MoO}_4$  polymorphs were described by means of electronic structure[42], photoluminescence[43], optical properties[44], and antibacterial

activity [45, 46]. Meanwhile, the  $\text{Ag}_2\text{CrO}_4$  is a recently investigated semiconductor aiming its application as a photocatalyst[47-49] and biological agent[50].

In this work, the  $\alpha\text{-Ag}_2\text{WO}_4$ ,  $\beta\text{-Ag}_2\text{WO}_4$ ,  $\gamma\text{-Ag}_2\text{WO}_4$ ,  $\alpha\text{-AgVO}_3$ ,  $\beta\text{-AgVO}_3$ ,  $\alpha\text{-Ag}_2\text{MoO}_4$ ,  $\beta\text{-Ag}_2\text{MoO}_4$ ,  $\text{Ag}_2\text{CrO}_4$ , and  $\text{Ag}_3\text{PO}_4$  materials were carefully investigated through *ab initio* simulations depicting their crystalline features and electronic structures. As well, some relevant insights into possible photocatalytic and biocide potential are presented.

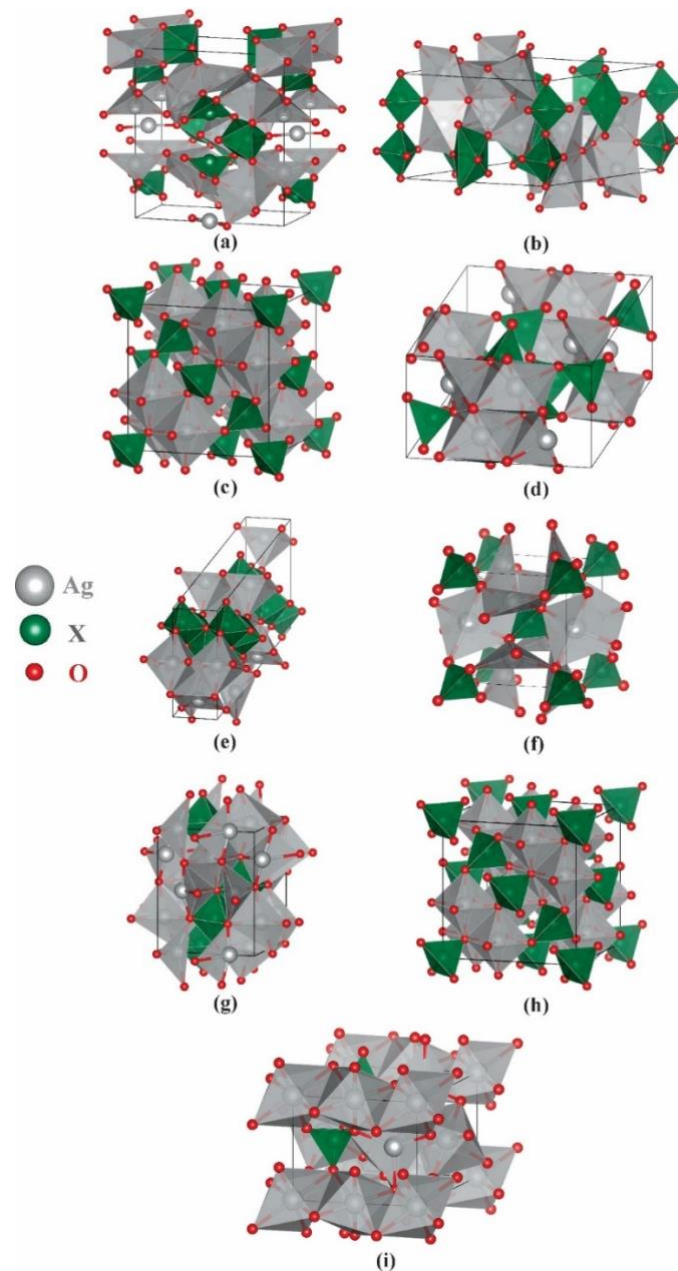
## 2. COMPUTATIONAL DETAILS

In this work, the photocatalytic potential of Ag-based semiconductors was evaluated by DFT simulations[51, 52]. The  $\alpha\text{-Ag}_2\text{WO}_4$ ,  $\beta\text{-Ag}_2\text{WO}_4$ ,  $\gamma\text{-Ag}_2\text{WO}_4$ ,  $\alpha\text{-AgVO}_3$ ,  $\beta\text{-AgVO}_3$ ,  $\alpha\text{-Ag}_2\text{MoO}_4$ ,  $\beta\text{-Ag}_2\text{MoO}_4$ , and  $\text{Ag}_2\text{CrO}_4$  were simulated using periodic models constructed from experimental crystalline data[11, 39, 42, 44, 49, 53]; these materials possess Pn2n, P63/m, Fd3m, Cd/c, Cm, Pbca, P4122, Fd-3m, and Pnma space groups, respectively. Figure 1 presents the unit cell for all investigated Ag-based materials.

The constructed models were fully optimized and discussed in terms of structural, electronic, and photocatalytic properties. The geometry was evaluated regarding the lattice parameters, bond-lengths, and  $[\text{AgO}_x]$  and  $[\text{MO}_x]$  clusters as building blocks of the  $\alpha\text{-Ag}_2\text{WO}_4$ ,  $\beta\text{-Ag}_2\text{WO}_4$ ,  $\gamma\text{-Ag}_2\text{WO}_4$ ,  $\alpha\text{-AgVO}_3$ ,  $\beta\text{-AgVO}_3$ ,  $\alpha\text{-Ag}_2\text{MoO}_4$ ,  $\beta\text{-Ag}_2\text{MoO}_4$ ,  $\text{Ag}_2\text{CrO}_4$ , and  $\text{Ag}_3\text{PO}_4$  materials. The electronic structure was analyzed from the total density of states (DOS) projections, band structure (BS) profiles, and the semiconductor type. The last one was estimated from the Fermi distribution on the top of the valence band (VB) and the bottom of the conduction band (CB). The DOS and BS analysis was performed for the last five bands of VB and the first five bands of CB, covering the band gap region. In turn, the photocatalytic properties were determined by the mobility of the charge carriers and the ability to oxidize or reduce  $\text{H}_2\text{O}$  and  $\text{O}_2$  molecules.

The simulations employ the density functional theory (DFT) allied to the B3LYP hybrid functional using the CRYSTAL17[54] package. The B3LYP functional employed in this work is the default version available on CRYSTAL code, including the Slater exchange correction combined with the fifth version of Vosko, Wilk, Nusair correlation description (SVWN5). This exchange-correlation functional offers an excellent

prediction of materials properties allied to a relatively low computational cost compared to other hybrid functionals such as HSE06 and WC1LYP.[55-57] Furthermore, the Grimme dispersion-corrections[58, 59] were also taken into account for all models since our previous report [60] evidences that such corrections are essential to better describe the Ag-based structural features. The calculations employ SCF convergence criteria established as  $10^{-8}$  and Mohnkhorst-Pack method[61, 62] for k points grid defined as  $8 \times 8 \times 8$ . The parameters above guarantee high reliability in the results, mainly for electronic structure prediction. The Ag, W, V, Mo, Cr, and O atoms were described by Gaussian-type basis sets reported in the references [63-68].



**Figure 1.** Schematic representation of 3D structures of (a)  $\alpha$ - $\text{Ag}_2\text{WO}_4$ , (b)  $\beta$ - $\text{Ag}_2\text{WO}_4$ , (c)  $\gamma$ - $\text{Ag}_2\text{WO}_4$ , (d)  $\alpha$ - $\text{AgVO}_3$ , (e)  $\beta$ - $\text{AgVO}_3$ , (f)  $\text{Ag}_3\text{PO}_4$ , (g)  $\alpha$ - $\text{Ag}_2\text{MoO}_4$ , (h)  $\beta$ - $\text{Ag}_2\text{MoO}_4$  and (i)  $\text{Ag}_2\text{CrO}_4$ . The  $[\text{AgO}_x]$  and  $[\text{MO}_x]$  clusters are depicted.

### 3. RESULTS AND DISCUSSION

#### 3.1. STRUCTURAL EVALUATION

The structural properties of the investigated Ag-based semiconductors were discussed in terms of lattice parameters, unit cell volume, and cluster description. The calculated values for the unit cell (Table 1) agree with experimental measurements[69-71], indicating the reliability of our methodology. As observed, the calculated lattice parameters and unit cell volumes are very similar to XRD results for all materials. Table 2 presents detailed information about the clusters within the structure, displaying the cation coordination numbers, Ag – O and M – O (M = W, V, Mo, Cr, and P) bond lengths, and the distortion degree ( $\Delta$ ) for each cluster (Table 2). The  $\Delta$  value for a cluster as expressed in Equation 1 relates the bond length ( $d_i$ ), the average bond distance ( $d_{ave}$ ), and the cation coordination number ( $C_n$ ).

**Table 1.** Lattice parameters and unit cell volume for investigated Ag-based semiconductors.

	Space group	Lattice Parameters							
		a (Å)	b (Å)	c (Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	V (Å <sup>3</sup> )	
$\alpha$ -Ag <sub>2</sub> WO <sub>4</sub>	This work	<b>Pn2n</b>	5.813	11.133	12.358	90	90	90	799.85
	Exp.[70]		5.92	10.89	12.03	90	90	90	775.56
$\beta$ -Ag <sub>2</sub> WO <sub>4</sub>	This work	<b>P63/m</b>	11.077	11.077	7.60	90	90	120	806.98
	Exp.[70]		11.09	11.09	7.54	90	90	120	803.71
$\gamma$ -Ag <sub>2</sub> WO <sub>4</sub>	This work	<b>Fd-3m</b>	9.496	9.496	9.496	90	90	90	846.47
	Exp.[69]		9.33	9.33	9.33	90	90	90	812.16
$\alpha$ -AgVO <sub>3</sub>	This work	<b>C2/c</b>	10.580	9.685	5.696	90	101.21	90	568.46
	Exp.[70]		10.44	9.90	5.53	90	99.7	90	563.30
$\beta$ -AgVO <sub>3</sub>	This work	<b>Cm</b>	17.942	3.537	8.270	90	103.70	90	509.88
	Exp.[70]		18.11	3.58	8.04	90	104.40	90	504.70
$\alpha$ -Ag <sub>2</sub> MoO <sub>4</sub>	This work	<b>P4122</b>	7.115	7.115	7.115	90	90	90	455.54
	Exp.[71]		7.01	7.01	7.01	90	90	90	424.93
$\beta$ -Ag <sub>2</sub> MoO <sub>4</sub>	This work	<b>Fd-3m</b>	9.533	9.533	9.533	90	90	90	866.28
	Exp.[70]		9.32	9.32	9.32	90	90	90	808.80
Ag <sub>2</sub> CrO <sub>4</sub>	This work	<b>Pnma</b>	10.152	6.968	5.555	90	90	90	393.00
	Exp.[70]		10.07	7.02	5.54	90	90	90	391.79
Ag <sub>3</sub> PO <sub>4</sub>	This work	<b>P-43n</b>	6.064	6.064	6.064	90	90	90	222.99
	Exp.[70]		6.00	6.00	6.00	90	90	90	216.43

**Table 2.** Coordination number, bond lengths, total energy ( $E_T$ ), and distortion degree ( $\Delta$ ) for  $[\text{AgO}_x]$  and  $[\text{MO}_x]$  clusters ( $M = \text{W}, \text{V}, \text{Mo}, \text{Cr}, \text{and P}$ ) for the Ag-based semiconductors. The number in parentheses indicates the number of repetitions of a bond length.

	Cluster	Bond lengths ( $\text{\AA}$ )	$\Delta$ ( $10^{-4}$ )	$E_T$ (Hartree)
$\alpha$ - $\text{Ag}_2\text{WO}_4$	$[\text{AgO}_7]$	2.33, 2.43, 2.50, 2.64, 2.65, 2.89, 3.04	49.13	$-4.8021 \cdot 10^3$
	$[\text{AgO}_6]$	2.33, 2.43, 2.50, 2.64, 2.65, 2.89	46.16	
	$[\text{AgO}_4]$	2.29 (2), 2.34 (2)	0.98	
	$[\text{AgO}_2]$	2.13 (2)	0	
	$[\text{WO}_6]$	1.75 (2), 1.82, 1.92, 2.32, 2.33	158.72	
	$[\text{WO}_6]$	1.75 (2), 1.85 (2), 2.39 (2)	198.44	
	$[\text{WO}_6]$	1.74 (2), 1.84 (2), 2.38 (2)	198.46	
$\beta$ - $\text{Ag}_2\text{WO}_4$	$[\text{AgO}_6]$	2.37 (3), 2.51 (3)	5.32	$-4.8033 \cdot 10^3$
	$[\text{AgO}_5]$	2.32, 2.43, 2.57, 2.59, 2.89	55.85	
	$[\text{WO}_4]$	1.76 (2), 1.77, 1.78	0.21	
	$[\text{WO}_5]$	1.80 (3), 1.90 (2)	408.99	
$\gamma$ - $\text{Ag}_2\text{WO}_4$	$[\text{AgO}_6]$	2.55 (6)	0	$-1.2006 \cdot 10^3$
	$[\text{WO}_6]$	1.77 (4)	0	
$\alpha$ - $\text{AgVO}_3$	$[\text{AgO}_6]$	2.33 (2), 2.40 (2), 2.57 (2)	17.57	$-5.2621 \cdot 10^3$
	$[\text{AgO}_6]$	2.24 (2), 2.54 (2), 2.72 (2)	62.37	
	$[\text{VO}_4]$	1.65, 1.66, 1.80, 1.81	18.62	
$\beta$ - $\text{AgVO}_3$	$[\text{AgO}_6]$	2.35 (2), 2.44 (4)	3.03	$-5.2621 \cdot 10^3$
	$[\text{AgO}_5]$	2.42 (2), 2.46 (2), 2.54	3.07	
	$[\text{AgO}_4]$	2.31 (2), 2.74 (2)	74.11	
	$[\text{VO}_6]$	1.66, 1.70, 1.88 (2), 2.24, 2.33	171.18	
	$[\text{VO}_6]$	1.66, 1.72, 1.85 (2), 2.12, 2.46	196.98	
$\alpha$ - $\text{Ag}_2\text{MoO}_4$	$[\text{AgO}_4]$	2.21 (2), 2.94 (2)	202.66	$-3.2233 \cdot 10^3$
	$[\text{AgO}_6]$	2.38 (2), 2.54 (2), 2.76 (2)	37.78	
	$[\text{AgO}_6]$	2.47 (2), 2.58 (2), 2.74 (2)	18.92	
	$[\text{MoO}_6]$	1.90 (2), 2.00 (2), 2.09 (2)	14.88	
$\beta$ - $\text{Ag}_2\text{MoO}_4$	$[\text{AgO}_6]$	2.54 (6)	0	$-1.3200 \cdot 10^3$
	$[\text{MoO}_4]$	1.81 (4)	0	
$\text{Ag}_2\text{CrO}_4$	$[\text{AgO}_6]$	2.35 (2), 2.38 (2), 2.60 (2)	21.52	$-6.5476 \cdot 10^3$
	$[\text{AgO}_6]$	2.30 (2), 2.42 (2), 2.49 (2)	10.93	
	$[\text{CrO}_4]$	1.65, 1.65 (2), 1.67	0.24	
$\text{Ag}_3\text{PO}_4$	$[\text{AgO}_4]$	2.39 (4)	0	$-2.1592 \cdot 10^3$
	$[\text{PO}_4]$	1.56 (4)	0	

$$\Delta = \frac{1}{c_n} \sum_i \left\{ \frac{(d_i - d_{ave})^2}{d_{ave}} \right\} \quad \text{Equation 1}$$

First of all, the  $\text{Ag}_2\text{WO}_4$  polymorphs were discussed; the  $\alpha$  polymorph presents four different  $[\text{AgO}]$  clusters, where the  $c_n$  for Ag is 2, 4, 6, and 7 and three different distorted  $[\text{WO}_6]$  octahedra. The  $\beta$  polymorph for  $\text{Ag}_2\text{WO}_4$  exhibits  $[\text{AgO}_6]$ ,  $[\text{AgO}_5]$ ,  $[\text{WO}_5]$ , and  $[\text{WO}_4]$  clusters, being the penta-coordinated sites more distorted, mainly for  $[\text{WO}_5]$ . In contrast, non-distorted  $[\text{AgO}_6]$  and  $[\text{WO}_6]$  clusters are observed in the gamma

phase. It is essential to highlight that the  $\beta$  and  $\gamma$  phases are metastable.[11, 20] As observed for  $\gamma$ - $\text{Ag}_2\text{WO}_4$ , the  $\text{Ag}_3\text{PO}_4$  presents perfect tetrahedral sites composed of Ag and P.

In the case of  $\text{AgVO}_3$  materials, the  $\alpha$  polymorph presents two distinct  $[\text{AgO}_6]$  clusters and one type of  $[\text{VO}_4]$  cluster; both clusters show a high distortion degree. The  $\beta$  polymorph possesses two different distorted  $[\text{VO}_6]$  sites and also distorted  $[\text{AgO}_6]$ ,  $[\text{AgO}_5]$ ,  $[\text{AgO}_6]$  clusters. In contrast to  $\text{Ag}_2\text{WO}_4$ , both polymorphs of  $\text{AgVO}_3$  are stable and synthesized from different approaches. The  $\text{Ag}_2\text{MoO}_4$  materials were also investigated, and the obtained results indicate the existence of perfect  $[\text{AgO}_6]$  and  $[\text{MoO}_4]$  clusters in the  $\beta$  phase. Thus, the  $\alpha$  polymorph exhibits highly distorted  $[\text{AgO}_4]$  tetrahedra, two different types of distorted  $[\text{AgO}_6]$  and distorted  $[\text{MoO}_6]$  clusters. Finally, the  $\text{Ag}_2\text{CrO}_4$  possesses slightly distorted tetrahedral Cr sites and two distinct six-folded Ag sites with high distortion.

Another relevant discussion is the role of the different  $[\text{AgO}_x]$  and  $[\text{MO}_x]$  clusters in forming the crystal structure and classified as structure formers or structure modifiers.[72] The structure formers are the clusters responsible for creating the crystalline network; these clusters are usually composed of chemical bonds with more pronounced covalent behavior.[73] In turn, the structure modifiers refer to those clusters responsible for connecting different crystalline structures, enabling polymorphism, and are commonly composed of chemical bonds with major ionic character.[74] In the case of Ag-based semiconductors, Botelho *et al.*[75], Longo *et al.*[17], and Gouveia *et al.*[43] stated that the  $[\text{AgO}_x]$  clusters act as structure modifiers in  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_2\text{MoO}_4$  materials. Similarly, the structural results presented in this work point out that such clusters also play the role of modifier for  $\text{Ag}_2\text{WO}_4$ ,  $\text{AgVO}_3$ , and  $\text{Ag}_2\text{CrO}_4$  due to the high distortion degree in the  $[\text{AgO}_x]$  polyhedra. Further, the different Ag coordination observed in different polymorphs corroborates the role of  $[\text{AgO}_x]$  as a structure modifier, whereas the  $[\text{MO}_x]$  clusters behave as structure formers in the investigated Ag-based materials.

Furthermore, from the evaluation of structural features, it is possible to access essential insights into materials properties since Ag and M species existence in different chemical environments leads to different electronic structures and stability. The comparison between distortion degrees (Table 2) and band gap values (Table 4) indicates that the polymorphs with high distortion degrees present narrowed band gap values. A similar observation was reported for  $\text{CdGa}_2\text{S}_4$ ,  $\text{CdGa}_2\text{Se}_4$ ,  $\text{CdGa}_2\text{Te}_4$ , and Na-doped



CuInS<sub>2</sub> materials.[76, 77] The distortion degree for [AgO<sub>x</sub>] and [MO<sub>x</sub>] clusters is also connected to the polymorphs energies, being higher total energies (E<sub>T</sub>) found for high-distorted systems. The stability predicted from E<sub>T</sub> disagreed with the experimental reports for the polymorphs; however, the proper prediction of polymorph stability requires phonon calculations and phase transitions investigations which are far from the focus of this work.

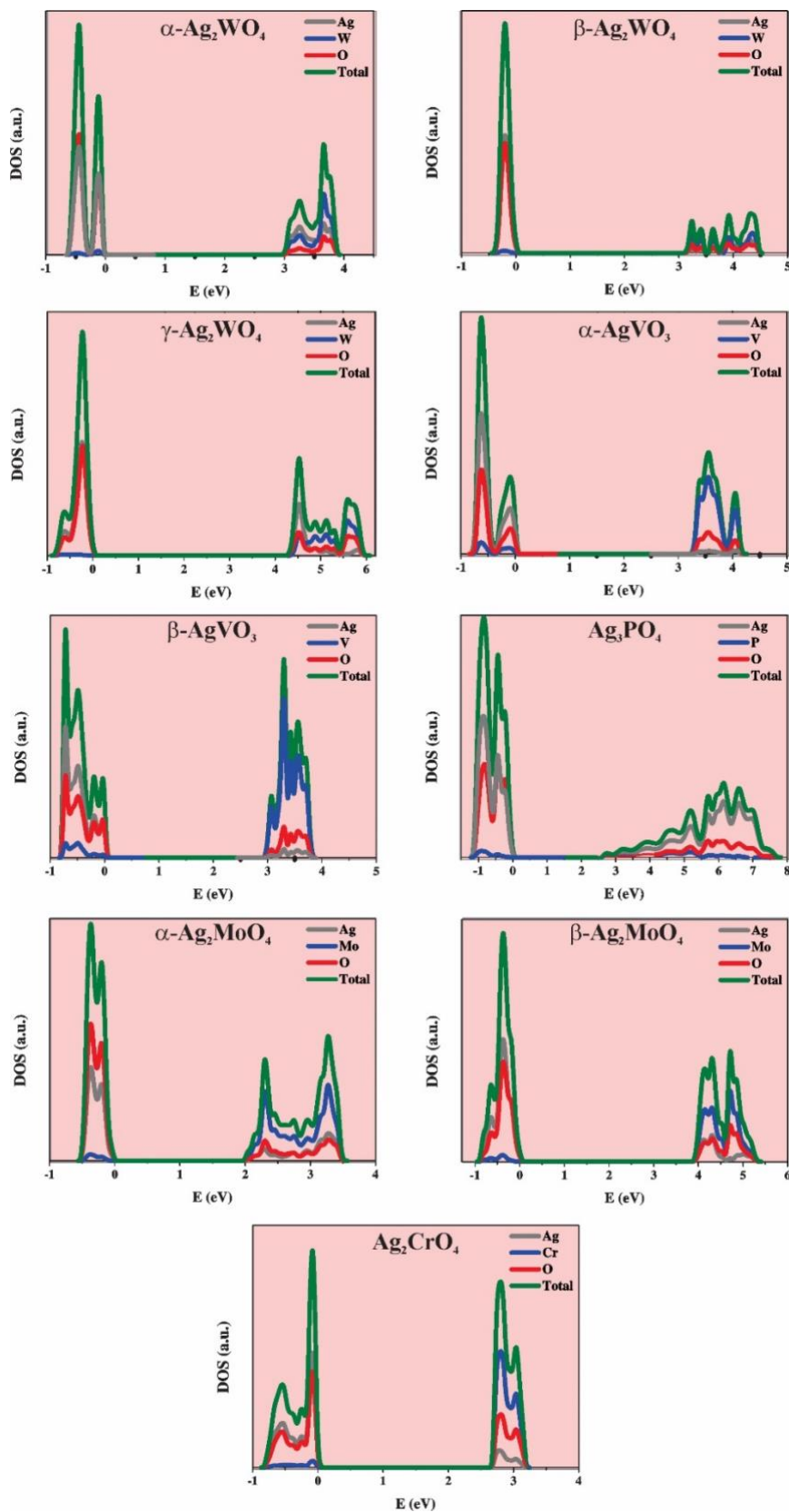
The theoretical results presented in this work also offer important insights into the crystalline structure of Ag-based semiconductors previously synthesized by our group. The previous manuscripts[11-24, 26, 32, 37-47, 50, 60, 75, 78-89] focused on describing the lattice parameters allied to cluster coordination. Thus, this work provides a complete description of the crystalline structures, discussing cluster coordination and its quantitative distortion degree, lattice parameters, bond lengths, and structure formers and modifiers.

### 3.2. ELECTRONIC STRUCTURE

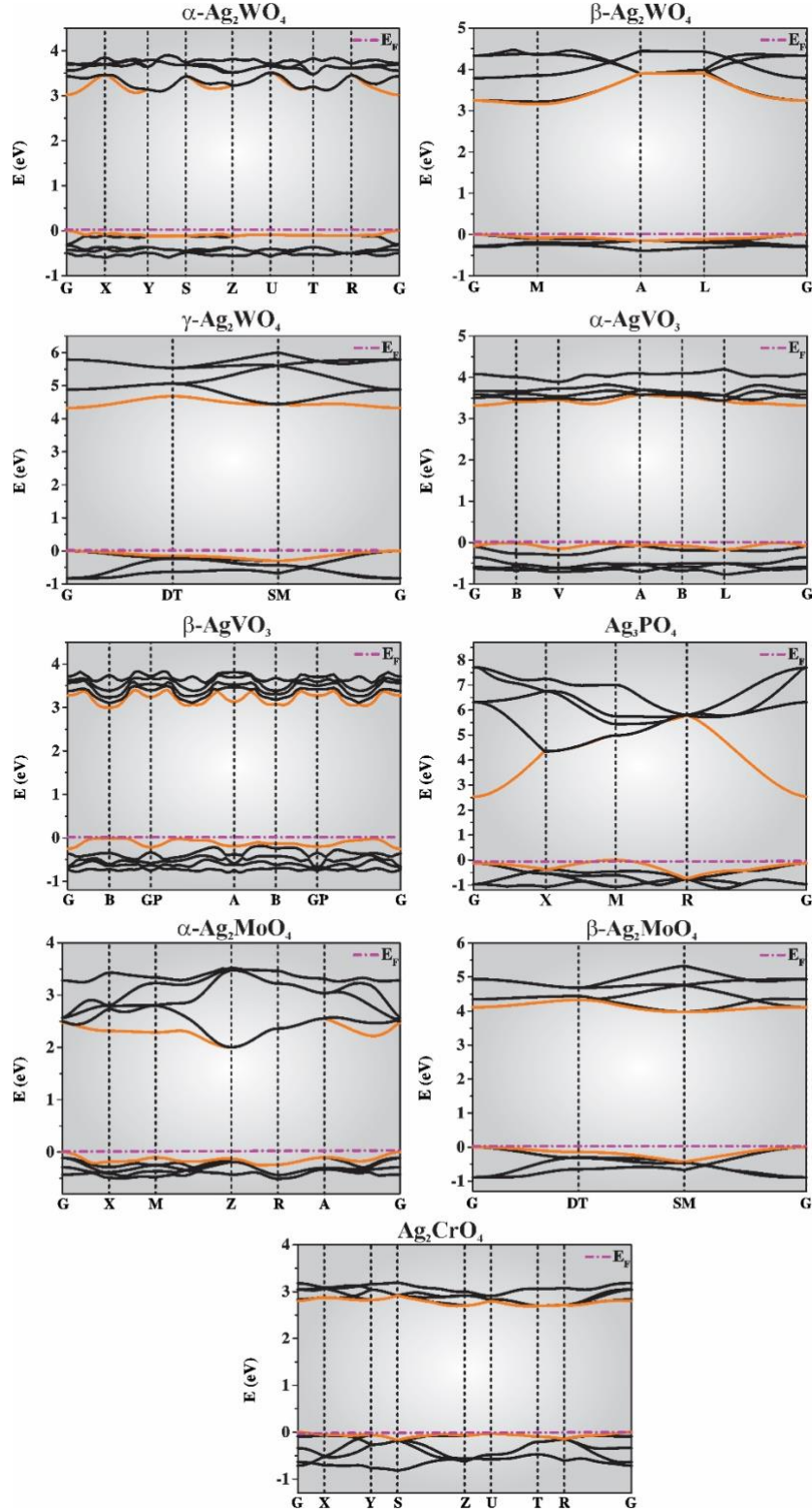
The electronic properties of Ag-based semiconductors investigated in this manuscript were described from the total DOS projection, BS, and electron-hole charge carriers properties. The DOS data (Figure 2) for all semiconductors indicate that, despite the polymorphism, the chemical elements contribute similarly to the VB and CB. The W atoms have a reasonable contribution to VB states and substantial participation in the formation of CB; the V atoms contribute to VB energy levels and, more significantly, to CB. The Mo species compose the VB by a small contribution and are responsible for forming the CB. The Cr atoms also contribute to both regions, but the participation on CB is more pronounced. Meanwhile, the P species possess little contribution to VB and CB. In particular, the O atoms show a regular contribution to all investigated Ag-based semiconductors since they are relevantly involved in forming VB and CB energy levels, being the highest participation to the VB states. Finally, the Ag atoms also present a regular contribution to both energy regions on all investigated systems; for such atoms, a high contribution to VB is observed allied to a minor contribution to CB.

The BS profiles (Figure 3) are also discussed, featuring the band gap region. The results indicate that the VB energy levels are located in a low energy range, being observed close to each other in terms of energy whereas the energy levels for CB are well-spaced from each other. The energy separation is more accentuated in  $\beta$ -Ag<sub>2</sub>WO<sub>4</sub>,  $\alpha$ -

$\text{Ag}_2\text{MoO}_4$ , and  $\text{Ag}_3\text{PO}_4$ , where the investigated CB levels cover a more comprehensive energy range.



**Figure 2.** The total density of states projection for Ag-based materials.



**Figure 3.** Band structure for Ag-based materials. The coordinates for high-symmetry points for  $\alpha\text{-Ag}_2\text{WO}_4$  are G (0.0 0.0 0.0), X (0.5 0.0 0.0), Y (0.0 0.5 0.0), Z (0.0 0.0 0.5), U (0.5 0.0 0.5), T (0.0 0.5 0.5), R (0.5 0.5 0.5); for  $\beta\text{-Ag}_2\text{WO}_4$  are G (0.0 0.0 0.0), M (0.5 0.0 0.0), A (0.0 0.0 0.5), L (0.5 0.0 0.5); for  $\gamma\text{-Ag}_2\text{WO}_4$  are G (0.0 0.0 0.0), DT (0.5 0.0 0.0), SM (0.5 0.5 0.0); for  $\alpha\text{-AgVO}_3$  are G (0.0 0.0 0.0), B (0.5 0.0 0.0), V (0.5 0.5 0.0), A (0.0 0.0 0.5), B (0.5 0.0 0.5), L (0.5 0.5 0.5); for  $\beta\text{-AgVO}_3$  are G (0.0 0.0 0.0), B (0.5 0.0 0.0), GP (0.5 0.5 0.0), A (0.0 0.0 0.5), B (0.5 0.0 0.5), GP (0.5 0.5 0.5); for  $\text{Ag}_3\text{PO}_4$  are G (0.0 0.0 0.0), X (0.5 0.0 0.0), M (0.5 0.5 0.0), R (0.5 0.5 0.5); for  $\alpha\text{-Ag}_2\text{MoO}_4$  are G (0.0 0.0 0.0), X (0.5 0.0 0.0), M (0.5 0.5 0.0), Z (0.0 0.0 0.5), R (0.5 0.0 0.5), A (0.5 0.5 0.5); for  $\beta\text{-Ag}_2\text{MoO}_4$  are G (0.0 0.0 0.0), DT (0.5 0.0 0.0), ST (0.5 0.5 0.0); for  $\text{Ag}_2\text{CrO}_4$  G (0.0 0.0 0.0), X (0.5 0.0 0.0), Y (0.0 0.5 0.0), S (0.5 0.5 0.0), Z (0.0 0.0 0.5), U (0.5 0.0 0.5), T (0.0 0.5 0.5), R (0.5 0.5 0.5).

DOS analysis for Ag-based semiconductors allows estimating the charge carrier concentration through the Fermi distribution, which considers the temperature influence on the number of electrons and holes.[5, 90] Mathematically, the Fermi distribution is represented by Equations 2-3, which relate the Boltzmann constant ( $k_b$ ), temperature ( $T$ ), electronic DOS per unit cell volume ( $D(\varepsilon)$ ), Fermi energy level ( $\varepsilon_F$ ), maximum VB energy value ( $\varepsilon_{VBM}$ ) and minimum CB energy value ( $\varepsilon_{CBM}$ ). This methodology assumes that the presence of dilute defects does not essentially affect the DOS and, consequently, the charge carrier density. From the obtained values, the semiconductor type can be determined. Thus, n-type semiconductors (electrons as predominant charge carrier) are associated with a higher number of states in CB. Likewise, an increased number of states in VB regions indicates a high possibility of photogenerated electrons, indicating a p-type semiconductor. The reliability of charge carriers density obtained from Fermi distribution is evidenced in the references [91-95]. In this work, the charge carrier density was determined at 300 K, 600 K, and 900K, and computed results compose Table 3.

$$p = \int_{-\infty}^{\varepsilon_{VBM}} D(\varepsilon) \frac{1}{\exp[(\varepsilon_F - \varepsilon)/k_B T] + 1} d\varepsilon \quad \text{Equation 2}$$

$$n = \int_{\varepsilon_{CBM}}^{\infty} D(\varepsilon) \frac{1}{\exp[(\varepsilon - \varepsilon_F)/k_B T] + 1} d\varepsilon \quad \text{Equation 3}$$

In summary, the results indicate an n-type semiconductor behavior for  $\alpha$ - and  $\beta$ - $\text{Ag}_2\text{MoO}_4$  and a p-type semiconductor for the other evaluated materials. Moreover, the calculated values suggest a significant increase in charge carrier number as temperature increases, as expected for semiconductors. Although the materials discussed in this work have already been investigated in the literature, to the best of our knowledge, the semiconductor type was not determined by experimental or theoretical analysis. Therefore, our results represent the first evaluation of charge carrier concentration for  $\alpha$ - $\text{Ag}_2\text{WO}_4$ ,  $\beta$ - $\text{Ag}_2\text{WO}_4$ ,  $\gamma$ - $\text{Ag}_2\text{WO}_4$ ,  $\alpha$ - $\text{AgVO}_3$ ,  $\beta$ - $\text{AgVO}_3$ ,  $\text{Ag}_4\text{V}_2\text{O}_7$ ,  $\alpha$ - $\text{Ag}_2\text{MoO}_4$ ,  $\beta$ - $\text{Ag}_2\text{MoO}_4$ ,  $\text{Ag}_2\text{CrO}_4$ , and  $\text{Ag}_3\text{PO}_4$  materials.

**Table 3.** Charge carrier concentration (expressed in  $10^{22} \text{ cm}^{-3}$ ) for Ag-based semiconductors at 300 K, 600 K, and 900 K.

	Semiconductor type	300 K		600 K		900 K	
		holes	electrons	holes	electrons	holes	electrons
$\alpha$ -Ag <sub>2</sub> WO <sub>4</sub>	p	9.244	4.354	9.474	4.462	10.040	4.473
$\beta$ -Ag <sub>2</sub> WO <sub>4</sub>	p	2.134	1.228	2.191	1.258	2.322	1.333
$\gamma$ -Ag <sub>2</sub> WO <sub>4</sub>	p	1.302	1.131	1.334	1.159	1.414	1.228
$\alpha$ -AgVO <sub>3</sub>	p	2.164	1.630	2.218	1.671	2.351	1.770
$\beta$ -AgVO <sub>3</sub>	p	2.177	1.867	2.232	1.914	2.365	2.028
$\alpha$ -Ag <sub>2</sub> MoO <sub>4</sub>	n	1.940	2.243	1.988	2.299	2.107	2.434
$\beta$ -Ag <sub>2</sub> MoO <sub>4</sub>	p	1.311	1.228	1.344	1.258	1.424	1.333
Ag <sub>2</sub> CrO <sub>4</sub>	p	2.554	2.379	2.617	2.439	2.774	2.584
Ag <sub>3</sub> PO <sub>4</sub>	p	4.855	4.402	4.977	4.511	5.273	4.781

Further, the electronic structure has also been discussed regarding band gap values (Table 4), which suggest all materials as typically semiconductors with a band gap in the visible range of the electromagnetic spectrum (1.6 eV to 3.3 eV), but  $\beta$ -Ag<sub>2</sub>MoO<sub>4</sub> that has a band gap in the ultraviolet region. The band gap values agree with some previously reported experimental results, evidencing the theoretical methodology's reliability employed in this work.[20, 22, 41, 42, 46, 47, 69, 82, 87] The prediction of the band gaps from DFT simulation is always challenging since the obtained values might be far from the experimental values. For instance, LDA and PBE functionals usually provide metallic or conductor band gaps for semiconductor materials.[55, 60] This failure can partially be avoided using the Hubbard parameter (U) that corrects the band gap description. Another alternative approach is the employment of hybrid exchange-correlations functionals.[51, 52] Thus, the chosen DFT/B3LYP methodology in this work has been used successfully in other studies and adequately predicted the band gap of the semiconductor materials.[1, 96, 97]

Furthermore, the reliability of the other analysis performed in this work is corroborated by our other works employing a similar theory level[60, 95, 98, 99] or manuscripts from other authors[91-93, 100, 101]. In particular, the results of band edge potential for Ag-based semiconductors are also strong evidence of the reliability of the calculations since they agree with experimental reports.

**Table 4.** Bandgap values and effective mass for charge carriers for investigated Ag-based semiconductors.

	Band-gap (eV)		Effective mass		
	This work	Exp.	$m_{h^*}/m_o$	$m_{e^*}/m_o$	$m_{h^*}/m_{e^*}$
$\alpha$ -Ag <sub>2</sub> WO <sub>4</sub>	3.02 (G – G)	3.10 [20]	0.65	0.41	0.64
$\beta$ -Ag <sub>2</sub> WO <sub>4</sub>	3.16 (G – M)	3.10 [22]	30.88	10.07	0.33
$\gamma$ -Ag <sub>2</sub> WO <sub>4</sub>	4.32 (G - SM)	3.21 [69]	29.57	35.26	1.19
$\alpha$ -AgVO <sub>3</sub>	3.31 (B – G)	2.80 [41]	25.67	64.35	2.51
$\beta$ -AgVO <sub>3</sub>	3.00 (B – B)	2.04 [82]	48.00	23.06	0.48
$\alpha$ -Ag <sub>2</sub> MoO <sub>4</sub>	2.00 (G – Z)	1.26 [42]	7.90	9.24	1.17
$\beta$ -Ag <sub>2</sub> MoO <sub>4</sub>	3.98 (G – G)	3.41[46]	28.74	13.53	0.47
Ag <sub>2</sub> CrO <sub>4</sub>	2.69 (G – Z)	1.80 [47]	30.35	45.27	1.49
Ag <sub>3</sub> PO <sub>4</sub>	2.54 (M – G)	2.45 [87]	0.29	0.11	2.64

Finally, from the band structure profiles, it is possible to determine the mobility of the charge carriers and the efficiency of the conduction process[5] using the effective mass method[102-105]. This method relates the mass of holes ( $m_{h^*}$ ), electrons ( $m_{e^*}$ ) and the invariant electron mass( $m_o$ ), being the mobility of the charge carrier predicted from the evaluation of the electron ( $m_{h^*}/m_o$ ) and hole ( $m_{e^*}/m_o$ ) effective masses. A qualitative evaluation of both charge carrier values can elucidate the efficiency of the materials in the conduction process if the dominant charge carrier presents low minor effective mass value.[5] Further, the ratio between charge carrier effective masses ( $m_{h^*}/m_{e^*}$ ) enables to predict the recombination rate of the photogenerated electron-hole pairs; in general, a good photocatalytic activity is found in materials with  $m_{h^*}/m_{e^*}$  minor than 0.5 or higher than 1.5.[106-109] The calculated results (Table 4) suggest an outstanding charge carrier mobility for Ag<sub>3</sub>PO<sub>4</sub> allied to a moderate efficiency on the conduction process because of high mobility for electrons instead of holes. The same limited efficiency is observed for  $\alpha$ -AgVO<sub>3</sub>, which possesses moderated mobility of charge carriers. The other semiconductors investigated present moderated mobility associated with good efficiency in the conduction process since the predominant charge carrier is significantly more mobile than the other charge carrier.

### 3.3. PREDICTION OF PHOTOCATALYTIC, ANTIBACTERIAL, AND ANTIVIRAL ACTIVITIES

Semiconductor photocatalysts are powerful alternatives to degrade water contaminants using solar radiation without generating other hazardous species, being used for such purposes for several decades. Usually, the photodegradation process catalyzed by semiconductors includes the following steps: i) sunlight absorption creates photogenerated electron-hole pairs; ii) charge carrier separation and electron transfer with chemical molecules absorbed on semiconductor surfaces; iii) charge carrier participation in oxidation/reduction process on the surface to generate reactive oxygen species (ROS), and iv) recombination of charge carriers in bulk or surface of the semiconductor.[110] Thus, the photocatalytic potential of semiconductor materials depends on the thermodynamics and kinetics of the process mentioned above and adequate band gap values (desired in the visible range) allied to good stability of charge carriers.[106-109]

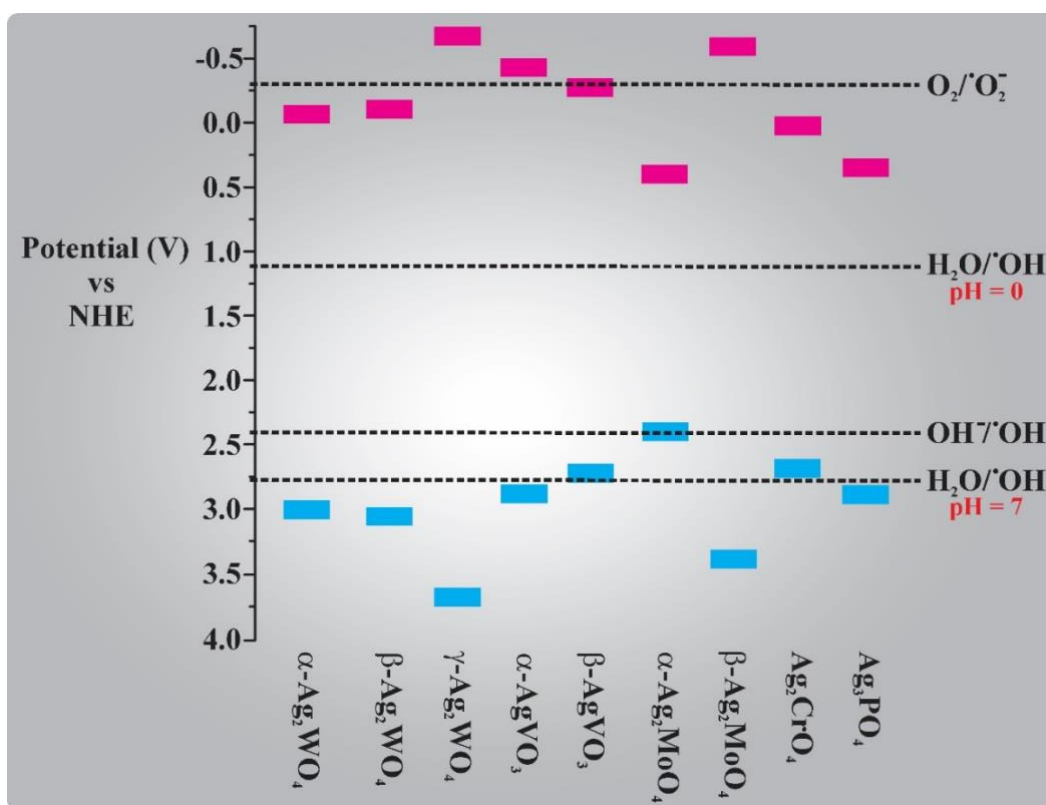
For the Ag-based semiconductors investigated in this work, the results (Table 3) suggest that  $\text{AgWO}_4$ ,  $\text{AgVO}_3$ ,  $\text{Ag}_3\text{PO}_4$ , and  $\text{Ag}_2\text{CrO}_4$  possess an exciting combination of band gap and charge carriers stability; consequently, such semiconductors are potential candidates for photocatalytic-based purposes. Among such materials, the  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_2\text{CrO}_4$  are highlighted since they possess band gaps similar to that value considered as the most efficient for photodegradation and water splitting processes (2.40 eV). Some works support this information showing that this band gap value is related to a minimum efficiency of 10% in the use of incident solar radiation.[111, 112] As well as, previous results reported by our group evidences both materials as potential photocatalysts.[87, 113]

The insights on Ag-based semiconductors with photocatalytic potential can be expanded from the VB and CB edge potential analyses, which enables verifying whether an inorganic semiconductor can split  $\text{H}_2\text{O}$  molecules generating the hydroxyl radicals ( $\bullet\text{OH}$ ) and/or reduce the  $\text{O}_2$  to superoxide radical ( $\bullet\text{O}_2^-$ ). Similarly, the comparison with the potential of forming hydroxyl radicals from  $\text{OH}^-$  ions ( $\text{OH}^-/\bullet\text{OH}$ ) indicates the possibility of generating this ROS. The CB and VB edges can be calculated from a well-known set of equations (Equations 4 and Equation 5) which relates the Mulliken electronegativity ( $\chi$ ) of the semiconductor, the normal hydrogen electrode potential ( $E_e$ , NHE = 4.5 eV), and the band gap value ( $E_{gap}$ ).[100, 101]

$$E_{CB} = \chi - E_e - 0.5E_{gap} \quad \text{Equation 4}$$

$$E_{VB} = E_{CB} + E_{gap} \quad \text{Equation 5}$$

The comparison of VB and CB edge potentials with the corresponding potentials of  $\text{H}_2\text{O}/\bullet\text{OH}$  (2.72 V at pH = 7, and 1.23 V at pH = 0),  $\text{OH}^-/\bullet\text{OH}$  (2.40 V), and  $\text{O}_2/\bullet\text{O}_2^-$  (-0.33 V) composes Figure 4. The results for VB edge potentials indicate that the  $\text{Ag}_2\text{WO}_4$ ,  $\alpha\text{-AgVO}_3$ ,  $\beta\text{-Ag}_2\text{MoO}_4$ , and  $\text{Ag}_3\text{PO}_4$  can produce hydroxyl radicals from water molecule splitting at pH = 7. On the other hand, all investigated materials can generate the same radical under pH = 0. Similarly, all simulated materials can oxidize  $\text{OH}^-$  ions to  $\bullet\text{OH}$ . The evaluation of CB edge values indicates that the photogenerated charge carriers in  $\alpha\text{-Ag}_2\text{WO}_4$ ,  $\alpha\text{-AgVO}_3$ , and  $\beta\text{-Ag}_2\text{MoO}_4$  materials reduce  $\text{O}_2$  molecules to  $\bullet\text{O}_2^-$ . Such theoretical results are in agreement with the photocatalytic potential reported for  $\text{Ag}_2\text{CrO}_4$ [49],  $\text{Ag}_2\text{WO}_4$  [11, 23, 26],  $\beta\text{-Ag}_2\text{MoO}_4$ [46], and  $\text{Ag}_3\text{PO}_4$ [34, 60, 87]. In particular, the efficiency of  $\text{Ag}_2\text{CrO}_4$  as photocatalyst for Rhodamine B degradation under visible radiation was proven by Assis et al. reporting the relation between high photocatalytic activity and morphological properties for such material.[113] Meanwhile, the photocatalytic potential of the other investigated Ag-based semiconductors represents a novel contribution to the literature and potential alternatives to photocatalytic-based goals.



**Figure 4.** Calculated valence (blue) and conduction (purple) band edge potentials for  $\alpha\text{-Ag}_2\text{WO}_4$ ,  $\beta\text{-Ag}_2\text{WO}_4$ ,  $\gamma\text{-Ag}_2\text{WO}_4$ ,  $\alpha\text{-AgVO}_3$ ,  $\beta\text{-AgVO}_3$ ,  $\alpha\text{-Ag}_2\text{MoO}_4$ ,  $\beta\text{-Ag}_2\text{MoO}_4$ ,  $\text{Ag}_2\text{CrO}_4$ , and  $\text{Ag}_3\text{PO}_4$  materials.



Besides photocatalytic activity, the ability of semiconductor materials to generate ROS is strongly connected to antiviral and antibacterial behavior.[114, 115] It comes from the biocide mechanism observed in semiconductors surfaces where the photogenerated ROS are responsible for killing pathogens through oxidative damage to biological compounds or non-oxidative ways, such as autophagy or T-lymphocyte responses.[116-123] Thus, a high concentration of ROS, resulting from the ability of semiconductors to produce such species from reaction with H<sub>2</sub>O and O<sub>2</sub> molecules, guarantees a significant antiviral feature as well as a long-time antibacterial activity.[96, 124, 125] In this work, the biocide activity was accessed from comparing the valence and conduction band edge potentials (Figure 4) and the potentials to ROS formation; this approach have successfully predicted the biocide properties of MnMoO<sub>4</sub>. [98] The results indicate that a good biocide activity is expected for the evaluated Ag-based materials. The biocide activity of some silver semiconductors has previously been evidenced by our group, as observed for  $\alpha$ -Ag<sub>2</sub>WO<sub>4</sub>[14, 23],  $\alpha$ -AgVO<sub>3</sub>[37, 39, 41],  $\beta$ -Ag<sub>2</sub>MoO<sub>4</sub>[45, 46], and Ag<sub>3</sub>PO<sub>4</sub>[41] materials. In front of this scenario, the present manuscript represents the first theoretical investigation demonstrating, from ab initio calculations, the ability of these systems to produce ROS and, consequently, to exhibit antiviral and bacterial features found experimentally.

#### 4. CONCLUSIONS

This manuscript presents a careful DFT/B3LYP investigation of  $\alpha$ -Ag<sub>2</sub>WO<sub>4</sub>,  $\beta$ -Ag<sub>2</sub>WO<sub>4</sub>,  $\gamma$ -Ag<sub>2</sub>WO<sub>4</sub>,  $\alpha$ -AgVO<sub>3</sub>,  $\beta$ -AgVO<sub>3</sub>,  $\alpha$ -Ag<sub>2</sub>MoO<sub>4</sub>,  $\beta$ -Ag<sub>2</sub>MoO<sub>4</sub>, Ag<sub>2</sub>CrO<sub>4</sub> and Ag<sub>3</sub>PO<sub>4</sub> materials. The structural and electronic features of these semiconductors were extensively depicted, and potential antiviral and antibacterial properties were found for materials bulk. The main conclusions can be summarized as follows:

- i) The structural evaluation indicates that the [AgO<sub>x</sub>] clusters are structure modifiers in the investigated Ag-based materials, while the [BO<sub>x</sub>] clusters behave as structure formers.
- ii) DOS and band structure analysis point out all materials as visible-range semiconductors, but  $\beta$ -Ag<sub>2</sub>MoO<sub>4</sub>, which has a band gap in the ultraviolet region.

- iii) The charge carrier features were calculated. The density of holes and electrons suggests that the  $\alpha$ -Ag<sub>2</sub>MoO<sub>4</sub> is an n-type semiconductor, while the other investigated materials exhibit a p-type semiconductor behavior.
- iv) The effective masses evaluation for investigated materials indicates good stability of electron and hole charge carriers for  $\alpha$ -Ag<sub>2</sub>WO<sub>4</sub>,  $\beta$ -Ag<sub>2</sub>WO<sub>4</sub>,  $\alpha$ -AgVO<sub>3</sub>,  $\beta$ -AgVO<sub>3</sub>,  $\beta$ -Ag<sub>2</sub>MoO<sub>4</sub>, Ag<sub>2</sub>CrO<sub>4</sub>, and Ag<sub>3</sub>PO<sub>4</sub> materials
- v) The conduction band and valence band edge potentials indicate exciting photocatalytic, antiviral, and antibacterial properties for Ag-based semiconductors in the bulk phase. Thus, additional surface calculations are required to prove the existence of such features.

Finally, the theoretical results for Ag-based semiconductors depicted in this work represent a relevant contribution to the knowledge of the structural and electronic features of these semiconductors and can also help materials science researchers to choose potential candidates for novel devices and technologies.

## **ELECTRONIC SUPPLEMENTARY MATERIAL**

Additional information of the relative errors observed on the determination of the structural parameters of Ag-based semiconductors can be found in Electronic Supplementary Material.

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