Unraveling the MnMoO₄ polymorphism: a comprehensive DFT investigation of α, β, and ω phases

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ABSTRACT

The MnMoO₄ is an environmentally friendly semiconductor material widely employed in technological devices. This material can be obtained on three different polymorphs, and although such phases were reported decades ago, some obscurity over their structure and properties is still perceived. Thus, this work provides a comprehensive DFT investigation of the α, β, and ω phases of MnMoO₄, analyzing their crystalline structure, stability, and electronic and magnetic properties. The results show that all phases of MnMoO₄ are stable at room conditions connected by pressure application or long-time high-temperature treatment. The MnMoO₄ phases are G-type antiferromagnetic with semiconductor bandgap and have enormous potential to develop magnetic, optical, and electronic devices and photocatalytic-based processes. The results also evidence potential antiviral and antibacterial activities of the three MnMoO₄ polymorphs.
Introduction

The manganese molybdate (MnMoO₄) is a powerful semiconductor material widely employed in developing supercapacitors found in several devices [1]. In current days, supercapacitors emerge as the best power source because of fast charging, minor maintenance required, high power density, elevated specific capacitance, and extremely high durability. In particular, the high efficiency of MnMoO₄ supercapacitors guarantees their application in portable devices, components of electric and hybrid vehicles, surrogate power sources, start engines, energy management, and others [1]. Furthermore, MnMoO₄ is also used in catalysts, optical and magnetic devices, electrochemistry, and batteries [2–8].

Notably, such high interest in this material comes from its abundance, low cost, wondrous mechanic and thermal stability, exciting properties, and environmental friend feature [9–11]. Thus, the MnMoO₄ was extensively investigated over the years being observed scientific reports focused on properties improvement [12, 13], creation of heterojunctions [14, 15], morphology-dependent properties [9, 16, 17], device performance evaluation [18, 19], graphene-mixed composites [20, 21], and hydrated MnMoO₄ crystals [22, 23]. Although the MnMoO₄ is a well-known material with a large amount of knowledge that has been previously published, the polymorphism observed for this material still represents a challenging task on MnMoO₄ materials development due to the different possible crystalline structures. In addition, some obscurity hovers over the poorly investigated polymorphism since the ω polymorph, the least evaluated phase, is erroneously treated as a subphase of α polymorph or amiss labeled as β polymorph [2].

The MnMoO₄ can be found on α, β, and ω polymorphs in pure form; the material crystallizes in a particular space group in hydrate form. The α-polymorph (Fig. 1a) is the most stable and investigated phase of MnMoO₄ and stands out by outstanding stability at room conditions [24]. This polymorph has tetrahedral Mn clusters and low-distorted octahedral Mo sites, being both observed in a C2/m space group forming low-distorted tetrahedral clusters [25–27]. This polymorph is frequently obtained from simple oxide mixtures or complex synthesis routes [1, 11, 25]. Another polymorph often reported is the β
phase (Fig. 1b), which presents a P2/c space group (existing in a wolframite structure) and Mn and Mo octahedral sites [28–30]. In this polymorph, both Mn and Mo cations occupy one-quarter of the interstitial position of the distorted polyhedral close packing [30, 31]. In particular, this polymorph is obtained from MoO$_3$ and MnO (or MnCO$_3$) under 900 °C and 6 GPa; further, the β polymorph can be transformed into α phase when heated for more than 48 h at 60 °C [23, 30]. This phase transition was also reported under 600 °C [28, 32]. The third polymorph of MnMoO$_4$, known as ω-phase (Fig. 1c), is isostructural to CoMnO$_4$ exhibiting a distorted C2/m space group where both Mn and Mo species occupy octahedral sites. Unlike the observed for the α phase, the Mo polyhedra are the most distorted within the structure [30]. This polymorph is poorly investigated, and few manuscripts have focused on it [8, 27–29, 31]. Finally, hydrated MnMoO$_4$ samples are found at different amounts; all the reports for this kind of material indicate a P1 space group [17, 33–36].

This work presents a careful density functional theory (DFT) investigation of α, β, and ω phases, presenting their electronic, optical, structural, and magnetic properties. Furthermore, phase transition and structural stability were evaluated by phonon dispersion calculations, bulk modulus, and vibrational simulations. The obtained results pave the way to end all the uncertainties on the structure and stability of MnMoO$_4$ polymorphs, depicting their properties carefully and opening up new applications such as material.

**Computational details**

DFT-based simulations were carried out using B3LYP exchange–correlation functionals implemented in CRYSTAL17 [37, 38]. The selected methodology was employed for elastic, vibrational, dielectric calculations, and electronic structure description. In all calculations, the Mn, Mo, and O atoms were described by 86-411d41G [39], HAYWSC-311(d31)G [40], and 86–4111(41D)G [41] localized Gaussian basis sets, respectively, considering the models at a vacuum condition and 0 K. All models have been fully relaxed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) second-order optimization algorithm available in CRYSTAL code. The energy self-consistent field (SCF) convergence criterion was defined as $10^{-8}$; the Mohnkhorst-Pack [42, 43] k points sampling was set to $8 \times 8 \times 8$, and the Coulomb and Hartree–Fock integrals were defined as $10^{-8}$ and $10^{-16}$, respectively. The SCF convergence was improved using the LEVSHIFT tool defined as 15 (0.15 Hartree).

In this work, the three known polymorphs of MnMoO$_4$ were investigated by periodic models constructed according to the crystalline structure previously reported by experimental efforts [24, 30, 31]. In all polymorphs, the Mn atoms present magnetism due to unpaired electrons into the 3d orbitals. Thus, the magnetic features of investigated materials were evaluated through the Ising model, a theoretical tool to determine magnetic coupling constant (J) and the magnetic ground state of solid-state materials from evaluating all possible magnetic states. The mathematical representation of the Ising model is expressed in Eq. 1 and Eq. 2, where N refers to the number of magnetic cations in the unit cell, Z is the number of magnetic neighbors, and $S_x$ represents the spin-
charge for each magnetic atom. Three-dimensional spin densities also evaluated the magnetic properties of MnMoO₄ polymorphs.

\[ \Delta E_T = E_{T,FM} - E_{T,AFM} \]

(1)

\[ \Delta E_T = -N \cdot Z \cdot S_1 \cdot S_2 \cdot J \]

(2)

The structural stability of \( \alpha, \beta, \) and \( \omega \) polymorphs was studied from a joint discussion of lattice parameters, the *bulk modulus* obtained from the Birch–Murnaghan equation of state \([44, 45]\), frequency calculations \([46]\), and phonon dispersions \([47]\).

Finally, the electronic properties for all polymorphs were discussed by the density of states (DOS) projection and band structures (BS), considering the bandgap region. The optical properties were examined from bandgap prediction and charge carriers stability predicted by the effective mass method. Furthermore, coupled-perturbation calculations were performed to predict the dielectric features of the investigated materials.

## Results and discussion

### Structural evaluation and polymorphs stability

First, the structural properties of the three polymorphs of MnMoO₄ are discussed in terms of lattice parameters, unit cell volume, bond lengths, and cluster distortion degree (\( \Delta \)). In particular, the \( \Delta \) values quantify the distortion on crystalline sites and can be obtained from Eq. 3, where \( d_i \) refers to Cation –O bond length, \( d_{ave} \) is the average value for bond distance in each site, and the \( X \) refers to the number of bonds in the cluster. The obtained results for MnMoO₄ phases compose Tables 1 and 2.

\[ \Delta = \frac{1}{X} \sum \left( \frac{(d_i - d_{ave})^2}{d_{ave}} \right) \]

(3)

The results for lattice parameters of MnMoO₄ polymorphs obtained by our simulations agree with experimental data at room conditions \([24, 27, 28, 48, 49]\) and other theoretical calculations \([2]\). Meanwhile, there were not reported data for bond lengths and distortion degree in the literature for evaluated polymorphs. In particular, the results provide essential information on Mo and Mn clusters distortion in the three polymorphs. As observed, there are two different Mn clusters in \( \alpha \) polymorph, being such polyhedra more distorted than Mo clusters. In the case of the \( \beta \) polymorph, different from that observed for \( \alpha \) and \( \omega \) polymorphs, there is only one type of [MnO₆] and [MoO₆] clusters within the structure; the Mo cluster is more distorted than Mn sites. The high distortion degree comes from the increased decentralization of the Mo sites of the central position of the octahedral clusters. As observed in Fig. 1, the structure of this polymorph is very different compared to the other two pure phases of MnMoO₄.

The \( \omega \) polymorph, firstly reported by Abrahams and Reddy, is the least investigated structure and the reason behind the obscurity over manganese

| Lattice Parameters for \( \alpha, \beta, \) and \( \omega \) polymorphs of MnMoO₄ obtained from DFT/B3LYP calculations |
|---------------------------------------------------------------|
| Lattice Parameters |
| a (Å) | b (Å) | c (Å) | \( \alpha \) (°) | \( \beta \) (°) | \( \gamma \) (°) | V (Å³) |
|---------------------------------------------------------------|
| \( \alpha \) (C2/m) |
| This work | 10.646 | 9.567 | 7.275 | 90 | 107.054 | 90 | 706.05 |
| Exp. [24] | 10.488 | 9.532 | 7.150 | 90 | 106.31 | 90 | – |
| Exp. [48] | 10.911 | 9.529 | 7.157 | 90 | 106.33 | 90 | – |
| Theor. [2] | 10.64 | 9.70 | 7.25 | 90 | 105.77 | 90 | 720.30 |
| \( \beta \) (P2/c) |
| This work | 4.868 | 5.829 | 5.035 | 90 | 89.938 | 90 | 142.88 |
| Exp. [28] | 4.818 | 5.759 | 4.965 | 90 | 90.82 | 90 | 137.75 |
| Exp. [49] | 4.821 | 5.740 | 4.999 | 90 | 90.861 | 90 | – |
| \( \omega \) (C2/m distorted) |
| This work | 10.105 | 9.250 | 7.787 | 90 | 113.527 | 90 | 667.36 |
| Exp. [27] | 10.469 | 9.516 | 7.143 | 90 | 106.17 | 90 | – |
| Theor. [2] | 10.08 | 9.18 | 7.86 | 90 | 113.5 | 90 | 667.40 |
molybdate polymorphism. In this work, we present a detailed description of this phase. Within this structure are observed octahedral Mn and Mo sites with high distortion degree, which arise from a fourth bond length in both sites indicating that the cations are more shifted from the central position of the polyhedral. Moreover, as observed for $\alpha$-MnMoO$_4$, two different Mn and Mo sites lead to particular magnetic properties. Finally, the main differences between $\alpha$ and $\omega$ structures lie in the coordination number and distortion degree of the Mo clusters since the $\omega$ structures exhibit more distorted [MoO$_6$] clusters.

Next, the thermodynamic stability of such structures is evaluated from harmonic frequency calculations assuming room conditions (298.15 K and 1 atm). This kind of calculation provides the Gibbs energy ($\Delta G$), enthalpy ($\Delta H$), and entropy ($\Delta S$) values for the three polymorphs. The $\Delta G$ calculated results (Table 3) evidence that the $\alpha$ polymorph is the most stable as well known in the literature [24], followed by the $\omega$-phase that possesses a similar structure and the $\beta$ polymorph. The prediction of solid-state materials from $\Delta G$ values analysis is a simple tool that provides reliable results that agree with experimental evaluations and theoretical approaches based on $\Delta H$ values determined from precursor compounds [50–52].

The stability of all polymorphs was also evaluated by bulk modulus calculations aiming to determine the stiffness of the solid material when compressed in an isotropic regime at constant T. The results (Table 3) indicate that $\beta$ polymorph is the more resistant MnMoO$_4$ phase to isostatic pressure application, followed by $\alpha$ and $\omega$ phases. The energy vs. pressure behavior of the $\alpha$, $\beta$, and $\omega$ polymorphs was investigated from the Birch–Murnaghan equation of state, enabling the prediction of underpressure phase transitions. The obtained curves compose Fig. 2 and indicate that a phase transition from $\beta$ to $\omega$ polymorph is expected at a pressure of 6.5 GPa; and also, a phase transition from $\alpha$ to $\omega$ phase is observed at a volume of 9.5 GPa. In particular, the analysis of Fig. 2 also suggests that the $\alpha$ and $\beta$ are not connected by only pressure application. In the light of experimental evidence [28, 30, 32], it is possible to state that such transition can occur only at temperatures of 60 °C; meanwhile, the DFT calculations performed in this work do not include temperature effects on phase transition. The Poisson ratio was also

### Table 2

| Bond lengths and cluster distortion degree (Å) for $\alpha$, $\beta$, and $\omega$ polymorphs of MnMoO$_4$ obtained from DFT/B3LYP calculations |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Cations         | O$_1$           | O$_2$           | O$_3$           | O$_4$           | O$_5$           | O$_6$           | $\Delta$ (10$^{-4}$) |
| $\alpha$ (C2/m) | $\text{[MnO}_6\text{]}$ | 2.105           | 2.169           | 2.285           | –               | –               | –               | 11.611           |
|                 | $\text{[MoO}_4\text{]}$ | 2.112           | 2.133           | 2.223           | –               | –               | –               | 4.987            |
| $\beta$ (P2/c)  | $\text{[MnO}_6\text{]}$ | 2.098           | 2.168           | 2.295           | –               | –               | –               | 13.901           |
|                 | $\text{[MoO}_4\text{]}$ | 1.810           | 1.919           | 2.219           | –               | –               | –               | 76.080           |
| $\omega$ (C2/m distorted) | $\text{[MnO}_6\text{]}$ | 2.083           | 2.120           | 2.122           | 2.368           | –               | –               | 33.201           |
|                 | $\text{[MoO}_4\text{]}$ | 2.077           | 2.128           | 2.333           | –               | –               | –               | 25.779           |

### Table 3

| Bulk modulus (GPa) | Poisson ratio (GPa) | Thermodynamic properties |
|--------------------|---------------------|-------------------------|
|                    |                     | G (kJ.mol$^{-1}$) | H (J.mol$^{-1}$) | S (J.mol$^{-1}$ K$^{-1}$) |
| $\alpha$           | 75.87               | 0.337                  | –             | 67.498             | 21.796            | 481.573        |
| $\beta$            | 127.30              | 0.359                  | –             | 49.815             | 17.437            | 396.684        |
| $\omega$           | 48.43               | 0.324                  | –             | 58.536             | 20.360            | 440.976        |
calculated; this analysis measures the material deformation in a direction perpendicular to the applied pressure indicating the hardness of a material and how much pressure can be suffered without phase transition. The values agree with the stability predicted by bulk modulus evaluation.

The phase transitions between the three different polymorphs of MnMoO$_4$ can be justified by modifying [MnO$_x$] and [MoO$_x$] clusters (Fig. 3). The less stable polymorph (β) comprises high-distorted six-folded Mn and Mo clusters. When the phase transition occurs, the ω polymorph achieved presents higher stability and [MnO$_6$] and [MoO$_6$] clusters with distortion degrees drastically increased. Finally, the pressure applied on the ω phase gives rise to the most stable polymorph of the MnMoO$_4$, the α phase. Such structure is formed by low-distorted [MnO$_6$] and [MoO$_4$] clusters. Therefore, these results suggest that reducing the distortion degree in the Mn and Mo clusters is the driving force for under pressure phase transition reaching more stable structures due to little distorted clusters.

Finally, to provide a deep investigation of MnMoO$_4$ polymorphs stability, we have performed phonon dispersion calculations from quasi-harmonic approximation (QHA). As observed in Fig. 4, no soft modes are found for any polymorphs, except that observed at G symmetry points. Thus, thermodynamic instability is not expected for the investigated MnMoO$_4$ polymorphs. The phonon dispersion curves also suggest the dispersion of high-frequency phonon modes (higher than 10,000 cm$^{-1}$) in α and ω structures. The high-frequency phonon modes can be connected to higher stability of the polymorphs; thereby, the polymorphs stability order is observed following $\alpha > \omega > \beta$ under room conditions. The phonon dispersion curves agree with the stability trend predicted by G, H, and S. Furthermore, the phonon dispersion curves evaluation also provides essential insights into the nature of chemical bonds found on molecular groups in MnMoO$_4$ polymorphs. As expected, the molecular groups with dominant covalent bond nature are responsible for phonon modes in high frequencies, while minor frequency modes are related to groups in which an ionic nature dominates [53]. Thus, from valence charge density data (Figure S2), it is possible to state that the low frequencies come from the [MnO$_6$] clusters, and high frequencies are attached to [MoO$_4$] or [MoO$_6$] clusters.

Therefore, the results indicate that all phases of MnMoO$_4$ are stable at room conditions, showing that the main route to control which one will be obtained is the right choice of precursors and the synthesis route, particularly for ω polymorph. Furthermore, the phase transition results, allied to experimental
evidence found in the literature [23, 30], indicate that the three phases of MnMoO$_4$ are connected by pressure application or long-time high-temperature treatment.

**Magnetism**

The MnMoO$_4$ materials are semiconductors that have gained large notoriety due to their magnetic behavior. However, to the best of our knowledge, only the $\alpha$-polymorph magnetism was observed from experimental efforts [26, 54–56], while the magnetism of $\beta$ and $\omega$ phases has not been reported yet. Thereby, the present manuscript provides novel information about the magnetic features of the three polymorphs and represents the first theoretical investigation focusing on such properties for MnMoO$_4$. The magnetic properties are then discussed in terms of $J$ magnetic coupling constant, total and local magnetic moment ($\mu_B$), magnetic ground state, Néel temperature prediction ($T_N$), and three-dimensional spin densities.

As previously mentioned in the Computational Details section, the magnetic features of solid-state systems are usually analyzed using the Ising model (Eq. 1 and Eq. 2). To adequately reproduce the magnetic properties, it is mandatory to consider all the possible magnetic states. Thus, the models for magnetic states were constructed aiming to depict: (i) the interaction between magnetic Mn cations composing the first kind of [MnO$_6$] octahedral ($J_{\text{Mn}(A)-\text{Mn}(A)}$); (ii) interaction between magnetic Mn cations occupying the second type of Mn clusters ($J_{\text{Mn}(B)-\text{Mn}(B)}$), and (iii) the interaction between Mn cations in different clusters ($J_{\text{Mn}(A)-\text{Mn}(B)}$) within the structure. Then, in addition to the ferromagnetic (FM) model ($\uparrow\uparrow\uparrow\uparrow\uparrow$), three ferrimagnetic (FeM) models were simulated assuming the magnetic orderings as follows: $\uparrow\uparrow\uparrow\uparrow J_{\text{Mn}(A)-\text{Mn}(A)}$, $\uparrow\uparrow\downarrow\downarrow J_{\text{Mn}(B)-\text{Mn}(B)}$ and $\uparrow\downarrow\downarrow\downarrow J_{\text{Mn}(A)-\text{Mn}(B)}$, where the first two spin arrows represent Mn atoms in the first [MnO$_6$] cluster type, while the Mn cation composing the second type of cluster was represented by the third and fourth spin arrow. Finally, a final model was determined as the magnetic ground state based on the obtained results. In particular, since the $\beta$ polymorph possesses only one type of [MnO$_6$] clusters, the $J_{\text{Mn}(B)-\text{Mn}(B)}$ and $J_{\text{Mn}(A)-\text{Mn}(B)}$ were not taken into account. Thus, for $\alpha$ and $\omega$ polymorphs, five different magnetic states were evaluated, while three different magnetic states were calculated for the $\beta$ polymorph. The reliability of this representation for magnetic materials can be found in other references [50, 57–60].

The calculated results (Table 4) suggest that the three polymorphs of MnMoO$_4$ present an antiferromagnetic (AFM) ground state, as evidenced by negative values of the $J$ coupling constant. As observed, the values of the $J$ coupling constant for $\alpha$ indicate a little AFM coupling between magnetic species, which probably comes from a significant FM interaction between neighboring Mn cations with opposite ordering (easily observed in Fig. 5a). Such FM interaction is not strong enough to overcome the AFM interaction, being responsible only for minimizing $J$ values. This behavior was previously reported by Ehrenberg et al. [54] and Lautenschläger et al. [56].
through experimental analysis. Similarly, the same behavior is expected for \( \omega \) polymorph due to similar structure and J values and the existence of Mn sites neighbored by other Mn with opposite spin directions. In particular, the J value for the \( b \) phase of MnMoO\(_4\) indicates that the influence of such FM interaction decreases. It is important to highlight that all polymorphs of MnMoO\(_4\) present G-type antiferromagnetism since each magnetic cation is surrounded by magnetic sites oriented along a contrary spin direction.

Once all investigated MnMoO\(_4\) polymorphs present AFM ground states, the stability of such magnetic ordering should be determined. In this case, the Néel temperature \( (T_N) \) (defined as the maximum temperature at an AFM ordering is vanished giving rise to paramagnetism) was predicted for each system by using the mean-field approximation \([61, 62]\) in Eq. 4.

\[
T_N = \frac{2}{3k_B} \left(-2J_{AA} + 4J_{BB} - 4J_{AB}\right)
\]

Moreover, the total and local magnetic moments \( (\mu_B) \) for MnMoO\(_4\) phases were investigated (Table 5). The calculated values indicate a null total \( \mu_B \) for all polymorphs as characteristic for AFM materials. The local \( \mu_B \) values for Mn suggest five unpaired electrons in each Mn cation, as expected for Mn\(^{2+}\) cations. Small values are found in Mo and O sites; this spin contamination is usually observed in DFT investigations. Moreover, it is observed that the local \( \mu_B \) for Mn atoms slightly increases in the order \( \beta < \omega < \alpha \).

Finally, the \( \mu_B \) results are corroborated by three-dimensional representations of spin densities (Fig. 5). For all phases, the spherical shape of Mn spin density denotes that the five 3d orbitals present unpaired electrons. Similarly, the absence of spin densities around Mo and O atoms proves that the small local \( \mu_B \) values refer to spin contaminations.

### Table 4

|          | \( J_{\text{Mo(A)-Mo(A)}} \) (K) | \( J_{\text{Mo(B)-Mo(B)}} \) (K) | \( J_{\text{Mo(A)-Mo(B)}} \) (K) | Magnetic ground state | \( T_N \) (K) |
|----------|---------------------------------|---------------------------------|---------------------------------|----------------------|--------------|
| \( \alpha \) | -1.225                          | -1.771                          | -0.579                          | AFM                  | 7.900        |
| \( \beta \)  | -4.088                          | -                               | -                               | AFM                  | 5.451        |
| \( \omega \)  | -1.736                          | -1.908                          | -0.874                          | AFM                  | 9.734        |

**Figure 5** Three-dimensional spin densities for \( \alpha \) (a), \( \beta \) (b), and \( \omega \) (c) polymorphs of MnMoO\(_4\). The structures correspond to the primitive unit cell of each polymorph.
Electronic structure

This section discusses the electronic properties of $\alpha$, $\beta$, and $\omega$ polymorphs from DOS projection, band structure (BS), semiconductor type, charge carriers mobility, valence band (VB) and conduction band (CB) edge potentials. The DOS projection takes into account the contribution of each species to compose the top of the VB and the bottom of CB regions so that the bandgap region is featured. In turn, the band structure was calculated considering the same region along the high-symmetry points of the Brillouin zone for each space group. Figure 6 presents the DOS and BS for the investigated MnMoO$_4$ polymorphs.

The DOS analysis indicates that the contribution of the three species is the same for all crystalline phases. The Mn species are the main ones responsible for forming the VB region and significantly contribute to CB levels; in both cases, the 3d orbitals are involved. Similarly, the Mo cations have a minor contribution to VB energy levels and a major contribution to CB with 4d orbitals. Meanwhile, the O atoms strongly contribute by 2p orbitals to VB and CB levels. In particular, in $\beta$ polymorph, the O atoms contribute to VB, being the most responsible for forming this energy range surpassing the Mn contribution.

In turn, the BS for $\alpha$ polymorph indicates that the energy levels in VB are largely spaced in energy, whereas the CB levels are close together. Also, the levels change considerably according to the high-symmetry point of the Brillouin zone. For $\beta$-MnMoO$_4$, the BS drastically changes since the energy difference between the energy levels of VB increases. A similar increase is observed in energy levels spacing for CB. This polymorph also presents energy levels strongly dependent on high-symmetry points of the Brillouin zone. Finally, the features of the BS for $\omega$ polymorph are very similar to those calculated for $\alpha$-MnMoO$_4$.

Other important information about the MnMoO$_4$ not reported nowadays is the semiconductor type obtained from Fermi distribution in DOS analysis. This approach presents very reliable results for other semiconductor materials representing a suitable tool that considers the influence of temperature on charge carrier concentrations [64–68]. The calculated charge carrier densities at 300 K, 600 K, and 900 K compose Table 6. The results indicate a significant increase in charge carrier number as temperature increases, as expected for semiconductors. It can be observed that
the electrons are the major charge carrier for \( \alpha\)-MnMoO\(_4\), indicating an \( n\)-type semiconductivity. On the other hand, in the \( \beta\) and \( \omega\) phases, a higher concentration of holes suggests a \( p\)-type semiconductivity. The change of semiconductor type can be attributed to the higher contribution of O species on VB for \( \beta\) and \( \omega\) polymorphs, as evidenced by DOS analysis.

Therefore, the electrons are the driving force of the conduction process occurring in \( \alpha\)-MnMoO\(_4\) while the conduction process in \( \beta\) and \( \omega\)-MnMoO\(_4\) is majorly dependent on holes. Once the concentration of charge carriers is known, substantial pieces of information on their stability can be accessed from the effective mass method [69–72]. The study of the stability of electrons and holes is crucial to adequately predict photocatalytic activity because a good photocatalyst presents a low charge carrier recombination rate [73–76]. In other words, the high stability of charge carriers is responsible for the migration of e\(^-\) and h\(^+\) and, consequently, by inhibiting the recombination process. The stability of charge carriers is also desired for thermoelectric applications [77–80]. In this work, the stability of the charge carriers was depicted from the values of the ratio between hole and electron effective masses \((m_h/m_e)\) being the desired values lower than 0.5 or higher than 1.5 [73, 74, 81, 82]. The obtained results (Table 7) suggest that \( \alpha\) and \( \omega\) are favorable candidates for photocatalytic-based applications due to the good stability of charge carriers. Thus, a low rate of electron–hole pair recombination is expected for such polymorphs. Otherwise, the values for \( \beta\)-MnMoO\(_4\) refer to a fast recombination process non-desired for photocatalysis, excluding this polymorph as a candidate. Furthermore, it is essential to highlight that the models computed in this work did not consider lattice defects, which act as strong electron–hole

**Figure 6** Density of states (DOS) and band structure for \( \alpha\) (a), \( \beta\) (b), and \( \omega\) (c) polymorphs of MnMoO\(_4\). For \( \alpha\) and \( \omega\), the high symmetry points of Brillouin zone are G (0.0 0.0 0.0), B (0.5 0.0 0.0), LD (0.0 0.5 0.0), V (0.5 0.5 0.0), A (0.0 0.0 0.5), B (0.5 0.0 0.5), U (0.0 0.5 0.5), and L (0.5 0.5 0.5); whereas for \( \beta\) polymorph, the points are G (0.0 0.0 0.0), Y (0.5 0.0 0.0), Z (0.0 0.5 0.0), C (0.5 0.0 0.0), C (0.0 0.0 0.5), A (0.5 0.0 0.5), D (0.0 0.5 0.5), and E (0.5 0.5 0.5).

**Table 6** Charge carrier densities and semiconductor type for \( \alpha\), \( \beta\), and \( \omega\) polymorphs of MnMoO\(_4\) investigated in this work at different temperatures

|            | Charge carrier density \( \left(10^{20} \text{ cm}^{-3}\right)\) |
|------------|---------------------------------------------------------------|
|            | 300 K  | 600 K  | 900 K  |
|            | Holes  | Electrons | Holes  | Electrons | Holes  | Electrons |
| \( \alpha\) | 70.448 | 73.091   | 72.297 | 74.918    | 76.508 | 79.386    | \( n\) |
| \( \beta\)  | 340.498| 340.310  | 348.974| 348.611   | 369.895| 369.631   | \( p\) |
| \( \omega\) | 68.728 | 68.707   | 70.446 | 70.417    | 74.648 | 74.626    | \( p\) |

The models computed in this work did not consider lattice defects, which act as strong electron–hole
centers, promoting the charge carrier recombination [64]. Surface models presenting lattice defects should be calculated to predict the charge carrier recombination rate more precisely. However, this kind of investigation is far from the scope of this work.

Combining the results for charge carriers effective masses and semiconductor type, it is possible to predict the efficiency of semiconductor material in the conduction process. Usually, high-efficiency conduction processes are found when the predominant charge carrier possesses a low effective mass [64]. Thereby, the only MnMoO$_4$ polymorph that reaches such a condition is the ω structure because the predominant charge carrier (holes) has a minor effective mass.

To better describe the photocatalytic potential of materials and also estimate their antiviral and bactericide potential once such species can kill pathogens directly through oxidative damage to biological compounds or indirectly by non-oxidative paths such as autophagy or T-lymphocyte responses [87–94]. Thus, a good antiviral and bactericide material must present a high ROS concentration, guaranteeing a long-time activity to eliminate several kinds of viruses and even drug-resistant bacteria [91]. The obtained results (Fig. 7) indicate that all MnMoO$_4$ polymorphs can interact with visible and ultraviolet radiation to generate different kinds of ROS, being expected antiviral and antibacterial activities for these materials. Furthermore, the results praise the MnMoO$_4$ polymorphs as outstanding candidates for antiviral and antibacterial purposes such as masks, cloths, gloves, other health devices, inks, and other surface protection. It is important to highlight that this kind of property emerges as vital to current human society due to different viruses and bacteria that can spread worldwide fast; in this context, the SARS-CoV-2 (COVID-19) stands out because of the pandemic situation started in 2020 [95, 96].

Finally, since the electronic properties and charge carrier features were carefully discussed, one mandatory point is the bandgap values of MnMoO$_4$ polymorphs. As presented in Table 7, all polymorphs have bandgap values typically observed for semiconductor materials, indicating a broad potential for developing several electronic, optical, electro-optical, and other technological applications. In particular, the ω polymorph stands out as the most suitable material for photocatalytic-based purposes due to its bandgap value (within the visible range) and charge carrier stability.

The results in this section remark that the MnMoO$_4$ polymorphs are exciting applicants for several technological purposes. The potential of such materials increases even more due to their environmentally

### Table 7

| Bandgap (eV) | Effective masses |
|-------------|-----------------|
|             | $m_e/m_0$       | $m_e/m_0$ | $m_e/m_0$ |
| α           | 3.670 (A–G)     | 17.592   | 43.524   | 2.471   |
| β           | 2.590 (Z–D)     | 18.661   | 16.602   | 0.890   |
| ω           | 2.889 (G–G)     | 46.911   | 101.441  | 2.162   |

Figure 7 Calculated valence (black) and conduction (blue) band edge potential for α, β, and ω polymorphs of MnMoO$_4$ investigated in this work. The dotted lines indicate the potential (V) for generating reactive oxygen species (ROS).
friendly behavior and low cost, making \( \alpha \), \( \beta \), and \( \omega \) polymorphs of manganese molybdate more attractive. Our previous manuscript focused on how surface and morphological properties of \( \alpha \)-MnMoO\(_4\) have evidenced the photocatalytic, electronic, magnetic, and biocide features of this polymorph through surface and morphology evaluation [97].

**Dielectric properties**

The dielectric properties of MnMoO\(_4\) polymorphs were determined from Coupled-Perturbed Kohn–Sham (CPKS) and harmonic frequency calculations. The first approach provides all the dielectric tensors within the crystalline structure and their dielectric constant and polarizability, while the second effort offers the static dielectric constant value. In summary, the dielectric constant measures the amount of electric potential energy stored in a given material exposed to an external electric field; in other words, this constant determines the charge storage capacity of the material. The polarizability measures how polarized a given material is when exposed to an external electric field, indicating how much the electronic density stored within the crystalline structure can be controlled. Meanwhile, the static dielectric constant refers to those values obtained under constant electric fields.

For MnMoO\(_4\) polymorphs, the three features above exhibit an anisotropic behavior due to non-center symmetric structures. The calculated values (Table 8) indicate that all polymorphs possess a high charge storage capacity at variable electric fields (dielectric constant values) and constant electric fields (static dielectric constant values), being both mainly observed in \( xx \), \( yy \), and \( zz \) tensors. Similarly, all polymorphs present high polarizability values, proving that the charge stored in the MnMoO\(_4\) material can be highly controlled by electric field application. Notably, the \( \beta \) phase possesses the most exciting dielectric properties among the investigated polymorphs. Furthermore, both dielectric constants and polarizability of \( \omega \) polymorph are higher than that detected in the \( \alpha \) phase; such increase can be justified by the high distortion degree observed in the \( \omega \) phase.

From the obtained values, it is possible to state that all manganese molybdate polymorphs are excellent candidates for capacitors, optical fibers, radiofrequency transmission lines, sensors for environmental monitoring, and batteries [98, 99]. Furthermore, the similarity of the dielectric features indicates that \( \beta \) and \( \omega \) polymorphs are also potential alternatives to the development of supercapacitors, being this the main application of the \( \alpha \)-MnMoO\(_4\).

Herein, the three manganese molybdate polymorphs have extensively been investigated, showing broad applicability to different purposes as confirmed by some reported experimental data [2, 54, 56]. Besides, the reliability of the employed

| Tensors | \( xx \) | \( xy \) | \( xz \) | \( yx \) | \( yy \) | \( yz \) | \( zx \) | \( zy \) | \( zz \) |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| \( \alpha \) Polarizability | 461.001 | 0.570 | – 40.382 | – | 426.361 | 0.891 | – | – | 463.098 |
| Dielectric constant (Bohr\(^3\)) | 3.403 | 0.0 | – 0.210 | 0.0 | 3.223 | 0.005 | 0.0 | 0.0 | 3.414 |
| Static dielectric constant (Bohr\(^3\)) | 8.245 | 0.039 | – 0.707 | 0.039 | 7.781 | – 0.064 | – 0.497 | – 0.069 | 7.819 |
| \( \beta \) Polarizability | 327.975 | – | – 2.202 | – | 277.392 | – | – | – | 379.530 |
| Dielectric constant (Bohr\(^3\)) | 5.274 | 0.0 | – 0.029 | 0.0 | 4.615 | 0.0 | 0.0 | 0.0 | 5.946 |
| Static dielectric constant (Bohr\(^3\)) | 15.088 | 0.0 | – 0.307 | 0.0 | 11.650 | 0.0 | – 0.279 | 0.0 | 21.153 |
| \( \omega \) Polarizability | 517.518 | 0.328 | – 45.123 | – | 507.374 | 0.931 | – | – | 626.136 |
| Dielectric constant (Bohr\(^3\)) | 3.888 | 0.001 | – 0.252 | 0.0 | 3.831 | 0.005 | 0.0 | 0.0 | 4.494 |
| Static dielectric constant (Bohr\(^3\)) | 10.195 | 0.036 | – 0.589 | 0.034 | 10.201 | – 0.058 | – 0.337 | – 0.063 | 12.467 |
methodology has also been evidenced in previous works [50, 60, 100].

**Thermoelectric properties**

The thermoelectric properties of MnMoO₄ polymorphs were also calculated using the Boltzmann transport approach [101, 102] available on CRYSTAL code. The thermoelectric properties are then discussed in terms of three parameters: (i) the Seebeck coefficient (S), which measures the average entropy carried by a charge in the material, being a high value connected to a high heat-electricity conversion rate; (ii) the thermal conductivity (κ); and (iii) electrical conductivity (σ). An ideal thermoelectric possesses high S and σ values allied to low values of κ; when such condition is found and is expected a significant reduction of Joule heating and the prevention of thermal short-circuiting, as indicated by the values of σ and κ, respectively [103]. Further, the evaluation of the Seebeck coefficient also shows the primary charge carrier involved in transport properties, being positive and negative values attached to holes and electrons.

As found in Figure S3 (Supplementary material), the MnMoO₄ polymorphs present increased values for Seebeck coefficient, like those observed for the best room temperature thermoelectric material, the Bi₂Te₃ [104]. The Seebeck graphs for all polymorphs are very similar and it is possible to observe a slight difference on charge carriers contribution to transport properties. The results agree with that predicted from charge carrier concentration (Table 6). The evaluation of electron conductivity also suggests high values of σ for all calculated polymorphs. Meanwhile, the thermal conductivity of MnMoO₄ is less than that found for Bi₂Te₃ [102].

Therefore, the obtained results strongly indicate the MnMoO₄ polymorphs as powerful thermoelectric material, being observed a high heat-electricity conversion rate allied to a diminutive possibility of Joule heating thermal short-circuiting.

**Conclusion**

The manganese molybdate (MnMoO₄) is an environmentally friendly semiconductor material widely employed in developing high-efficiency supercapacitors, catalysts, electrochemistry applications, and optical and magnetic devices.

This work provides a careful DFT investigation and demonstrates that all phases of MnMoO₄ are stable at room conditions, being the synthesis of a polymorph mainly controlled by precursor species and, in the particular case of the ω polymorph, the synthesis route. The phase transition results, allied to reported experimental evidences, indicate that the three phases of MnMoO₄ are connected by pressure application or long-time high-temperature treatment. Moreover, the phase transition mechanism is driven by modifications on [MnOₓ] and [MoOₓ] clusters. The magnetic and electronic properties of MnMoO₄ polymorphs were also calculated, being observed antiferromagnetic materials with bandgaps typically observed for semiconductors. Furthermore, the charge carriers features were extensively discussed. The results also suggest an exciting photocatalytic and antiviral activity for MnMoO₄ polymorphs.

In summary, the results presented in this work put an end to the obscurity over MnMoO₄ polymorphs, offering a deep description of each phase. Further, the results remark the MnMoO₄ polymorphs as exciting alternatives for several technological purposes. The potential of such materials increases even more due to their environmentally friendly behavior and low cost, making α, β, and ω polymorphs of manganese molybdate more attractive.

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