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ABSTRACT

This work presents a first-principles study of the sodium intercalation process in a layered potassium birnessite (a layered manganese dioxide, δ -MnO₂) using hybrid-level density functional theory. Understanding the intercalation processes of δ -MnO₂ is a vital step in advancing its potential innovative applications. Using a formation energy formalism, we analyze the stability of the structure as sodium ions (Na⁺) are intercalated between layers. Simulated Raman spectra allow us to find relationships between the vibrational and structural properties of the material, i.e., we identify the most important vibrational modes and relate them to the structural/geometrical change. The diffusion of Na⁺ and K⁺ ions in birnessite is studied by transition state theory, determining the energy barriers to ion displacement in the interlayer. The symmetry and planar density of the system are characterized by simulated X-ray diffraction and geometrical analysis of the optimized structures. Through binding energy analysis, we also find that the Na⁺ ions are more loosely bound to the lattice as they reach the saturation limit. Finally, the electronic properties are studied via spin-polarized densities of states. As intercalants are added, the electronic properties are profoundly modified, resulting from modifications of Mn oxidation states, lattice distortions, and symmetry effects. Moreover, some of the intercalated structures behave as bipolar magnetic semiconductors with potential applications in spintronics devices. In other words, the bandgaps and magnetic behavior of the system can be controlled by intercalation. This work provides an overarching analysis of intercalated birnessite and describes the essential properties of potassium birnessite and co-intercalation with sodium as a next-generation energy, electronic, and spintronic material.

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I. INTRODUCTION

In a technology-driven world, there is a constant need for the development of low-cost, high-energy storage, and semiconducting materials. Among the materials studied in energy research, the layered birnessite manganese dioxide (δ -MnO₂) has emerged as a promising candidate for these technologies. Birnessite's two-dimensional structure, ability to store ions in the interlayer, high capacitance, and Mn³⁺/Mn⁴⁺ reversible redox activity make it an attractive material for next-generation energy storage and conversion systems. Its pseudocapacitive charge storage properties, high

power, and energy density qualify it as a potential material for supercapacitors and cathodic sodium-, lithium-, and magnesium-ion battery applications.^{1–3} In addition, its ion-exchange properties make it an effective material for water purification and heavy metal removal,⁴ while its strong catalytic activity allows it to play a crucial role in water splitting reactions for hydrogen (H₂) production.^{5,6}

Understanding the theoretical properties and intercalation processes of δ -MnO₂ is a vital step to advance its potential innovative applications. From a computational perspective, studies have revealed the structure and redox properties,⁶ the electronic structure in the presence of different cations,⁵ the defect properties of the

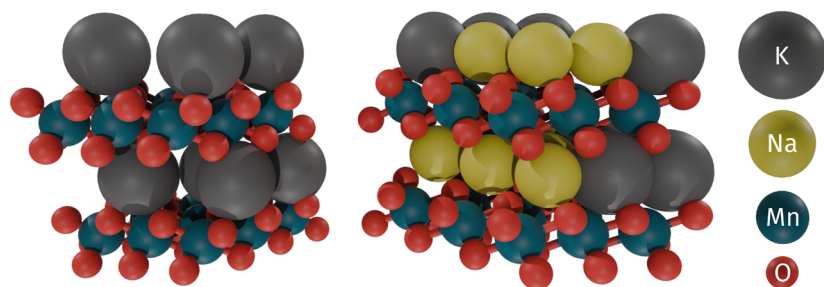


FIG. 1. 3D schematic depicting sodium (Na^+ , yellow atoms) intercalation in the potassium (K^+ , gray atoms) birnessite (KMO). The figure shows the KMO birnessite (left) and the Na^+ -intercalated KMO structure (right).

MnO_2 lattice,^{7–9} the selectivity of different facets for the formation of reactive oxygen species,¹⁰ the sorption selectivity,^{9,11} and a multitude of other properties and applications of this material.^{12–14} Although these studies have revealed many of the important properties of $\delta\text{-MnO}_2$, there are still shortcomings in the current state of the computational literature. For example, although Raman spectroscopy is one of the main experimental techniques for characterizing birnessite, not many calculated Raman spectra have been presented. The available calculated spectra explain how water affects the spectra;¹⁵ however, they do not address the progressive inclusion of ionic intercalants such as Na^+ and K^+ , which are common in layered MnO_2 structures. In addition, other properties of interest discussed in this work include formation energies, diffusion properties, structural features, and electronic structures during intercalation, which have yet to be fully described in the current state of the literature.

The present study constitutes a first-principles hybrid-level density functional theory (DFT) study of the Na^+ ion intercalation process in a layered birnessite with the formula given by $\text{K}_{1.33}\text{Mn}_3\text{O}_6$, i.e., $[\text{K}_{0.44}(\text{Mn}_{0.56}^{4+}\text{Mn}_{0.44}^{3+})\text{O}_2]$, or simply denoted as KMO in this work. This particular formula is chosen to resemble the experimental high pressure synthesis of potassium birnessite.¹⁶ Na^+ intercalation in the KMO structure is exemplified in Fig. 1. Furthermore, using a formation energy formalism, we analyze the stability of the structure as Na^+ ions are intercalated between layers. Through this analysis, we propose a Na^+ ion intercalation mechanism, which is further explored by analyzing the diffusion behavior of Na^+ ions in the structure. Raman spectra simulations also provide information about the system's vibrational properties, where we find a relationship between the mode shifts and structural/symmetry properties induced by Na^+ ion intercalation. Using X-ray diffraction (XRD) simulation and geometrical analysis, we describe the structure's evolution as Na^+ ions are incorporated, resulting in modifications in the system's lattice parameters and planar density. Finally, we describe the electronic properties of these systems via spin-polarized densities of states. This study aims to serve as a guide for experimental researchers performing electrochemical and structural analysis of KMO for pseudocapacitive energy storage, catalytic, and environmental purposes.

II. METHODOLOGY

A. Density functional theory

Computational calculations were performed within the hybrid DFT framework using the CRYSTAL23 package.¹⁷ Calculations were carried out by defining the electronic exchange–correlation

functional through the Heyd–Scuseria–Ernzerhof (HSE06) formulation.¹⁸ This hybrid functional was chosen due to its precision in predicting semiconductor materials' electronic properties^{19,20} (the semiconducting nature of $\delta\text{-MnO}_2$, predicted by HSE06, was verified through LDA+U²¹ calculations on VASP,^{22,23} which are shown in Table S1 of the [supplementary material](#)). Unrestricted wave functions were considered due to the partially filled 3d orbital electrons of the transition metal atoms in the structures. Grimme's third-order dispersion correction, D3, with Becke–Johnson damping was utilized throughout all calculations to account for van der Waals and London dispersion forces.^{24,25} Atomic orbitals for optimizations and frequency calculations were described using double- ζ valence with polarization (DZVP) quality basis sets, particularly pob-DZVP-rev2.²⁶ The electronic properties shown in the main paper were calculated with triple- ζ valence with polarization basis sets (TZVP), particularly pob-TZVP-rev2.²⁶ XRD simulations were constructed using the VESTA visualization software.²⁷ Raman simulations were achieved using the Coupled Perturbed Hartree–Fock/Kohn–Sham (CPHF/CPKS) methodology.^{28–30}

Integrations inside the first Brillouin zone were sampled on a Monkhorst–Pack k -mesh grid during both geometry optimizations and single-point energy calculations at a resolution of $\sim 2\pi/60 \text{ \AA}^{-1}$ ($a \cdot k_a = 40\text{--}60$, $b \cdot k_b = 40\text{--}60$, and $c \cdot k_c = 40\text{--}60$, where a , b , and c are the direct lattice vectors and k_a , k_b , and k_c are the integer shrinking factors). To calculate the density matrix and Fermi energy, a denser “Gilat net” sampling of k -points was carried out with a resolution of $\sim 2\pi/120 \text{ \AA}^{-1}$ ($k_G = 2k_{\text{max}}$, where k_G is the Gilat net shrinking factor and k_{max} is the largest shrinking factor among the previously defined k_a , k_b , and k_c).

The convergence of the self-consistent field (SCF) energy, the root mean squared (RMS) forces, the maximum forces, the RMS atomic displacements, the maximum atomic displacements, and the convergence energies between geometries were established at $2.72 \times 10^{-6} \text{ eV}$, $1.54 \times 10^{-2} \text{ eV/\AA}$, $2.31 \times 10^{-2} \text{ eV/\AA}$, $6.35 \times 10^{-4} \text{ \AA}$, $9.53 \times 10^{-4} \text{ \AA}$, and $2.72 \times 10^{-6} \text{ eV}$, respectively. However, vibrational modes are highly sensitive to structural parameters, so we set a more rigorous convergence criterion for frequency calculations. The stricter thresholds for the convergence of the SCF energy, the RMS forces, the maximum forces, the RMS atomic displacements, the maximum atomic displacements, and the convergence energies between geometry were established at $2.72 \times 10^{-10} \text{ eV}$, $1.54 \times 10^{-3} \text{ eV/\AA}$, $2.31 \times 10^{-3} \text{ eV/\AA}$, $6.35 \times 10^{-5} \text{ \AA}$, $9.53 \times 10^{-5} \text{ \AA}$, and $2.72 \times 10^{-10} \text{ eV}$.

The Nudged Elastic Band (NEB) method^{31,32} as implemented in the Vienna *Ab initio* Simulation Package (VASP)^{22,23} was used to compute ion diffusion barriers. The Perdew–Burke–Ernzerhof

(PBE)³³ functional was used during these calculations along with Grimme's D3 dispersion corrections.²⁴ The projector-augmented-wave (PAW) pseudopotentials (potpaw.64) for PBE (K_pv, Mn_pv, O [standard], and Na_pv) were used.^{34,35} The cutoff energy during these calculations was 500 eV, and the k -mesh was set to a $6 \times 6 \times 6$ Monkhorst–Pack grid. For consistency with the rest of our work, the transition states geometries obtained with this method were then exported to CRYSTAL23, and single-point energy calculations were performed with HSE06 using these geometries to obtain the final energy values. Note that minor errors might be present due to the use of optimized geometries at the PBE-level to produce HSE06 energies due to self-consistency.

B. Defect formation energy formalism

The defect formation energies (DFEs) were obtained using the following equation:

$$\Delta E_F(\mu) = [E_D - E_H] + \sum n_i \mu_i. \quad (1)$$

Here, ΔE_F represents the resultant DFE, E_D is the energy of the structures with defects (intercalants), E_H is the energy of the host material (all structures previously fully optimized), and μ_i is the chemical potential of the species i involved in the formation of the material with defects.

Applying Eq. (1) to our KMO host material, with Na⁺-intercalated KMO as defect structures, we obtained the following equation:

$$\Delta E_F(\mu) = [E_D - E_{\text{K}_8\text{Mn}_{18}\text{O}_{36}}] + n_{\text{Na}} \mu_{\text{Na}}. \quad (2)$$

Through Eq. (2), we account for the variation in Mn, O, and Na as independent variables and the resulting formation energy of the defect structures as a dependent variable. Hence, to represent this equation in 3D, we take the variation of the chemical potential of Mn and O as a joint variable $\mu_{\text{Mn},\text{O}}$ considered on the x -axis; Na variation, μ_{Na} , on the y -axis; and the corresponding DFE, $\Delta E_F(\mu)$, on the z axis. The variation of sodium, n_{Na} , takes on negative integers for insertion and positive integers for removal. The energy range for $\Delta \mu_{\text{Na}}$ was defined from μ_{Na} (the energy per atom of bulk sodium) to $E_{\text{coh}}^{\text{Na}} = \mu_{\text{Na}} - E_{\text{Na atom}}$, where $E_{\text{Na atom}}$ is the energy of a sodium atom in vacuum.

III. RESULTS AND DISCUSSION

A. Construction and optimization of K- and Na-intercalated birnessite structures

We generate a potassium birnessite host structure for sodiation with the formula $\text{K}_8\text{Mn}_{18}\text{O}_{36}$ ($\text{K}_{1.33}\text{Mn}_3\text{O}_6$) by systematically adding K⁺ to a $3 \times 3 \times 2$ supercell of $\delta\text{-MnO}_2$. This K⁺-preintercalated structure was constructed based on the CIF file reported by Chu *et al.*,¹⁶ who investigated a potassium birnessite with the formula $\text{K}_{1.39}\text{Mn}_3\text{O}_6$. All combinations of K⁺ sites in this CIF file were systematically occupied to achieve the $\text{K}_8\text{Mn}_{18}\text{O}_{36}$ stoichiometry, and single-point calculations were performed to evaluate their relative stability. The lowest-energy configuration was subsequently fully optimized and selected as the preintercalated KMO structure.

The K⁺-intercalation process generally results in a symmetry change for the $\delta\text{-MnO}_2$ system: from $P\bar{3}m1$ (without K⁺ ions) to $C2/m$ ^{36,37} (fully intercalated with K⁺). However, computationally, the symmetry was reduced to $P1$ to achieve the desired partially intercalated $\text{K}_8\text{Mn}_{18}\text{O}_{36}$ stoichiometry.

Throughout our calculations, the MnO_2 layers were set to follow an out-of-plane antiferromagnetic order, typical of birnessite,⁶ as shown in Fig. 2. It is important to note that the partially intercalated KMO structure was chosen as a starting point because of synthesis feasibility in an experimental setting. After obtaining the initial structure of $\text{K}_8\text{Mn}_{18}\text{O}_{36}$, Na⁺ ions were inserted sequentially into the preintercalated structure. At each insertion step, all viable octahedral sites within the birnessite interlayer were evaluated, along with additional plausible insertion sites identified from geometric inspection given their spatial relationship to the K⁺ ions. The Na-intercalated structures are denoted Na_x , where x is the number of interstitial ions inserted. For Na_{1i} – Na_{10i} , the number of tested sites was 11, 8, 6, 6, 6, 4, 3, 2, 2, and 1.

Cell parameters for all Na⁺-intercalated structures are shown in Table S2, and volume change is observed in Fig. S1. The final stoichiometry of the fully co-intercalated Na⁺/K⁺ birnessite was $\text{Na}_{10}\text{K}_8\text{Mn}_{18}\text{O}_{36}$ ($\text{Na}_{1.66}\text{K}_{1.33}\text{Mn}_3\text{O}_6$), as shown in Fig. 2(b). We note that the K⁺ and Na⁺ ions are initially added as neutral atoms and are ionized when added to the system due to charge compensation. Furthermore, the structures presented here represent an ideal system, where the layered structure is free of defects, water, and external fields; therefore, some discrepancies with experimental analyses are expected.

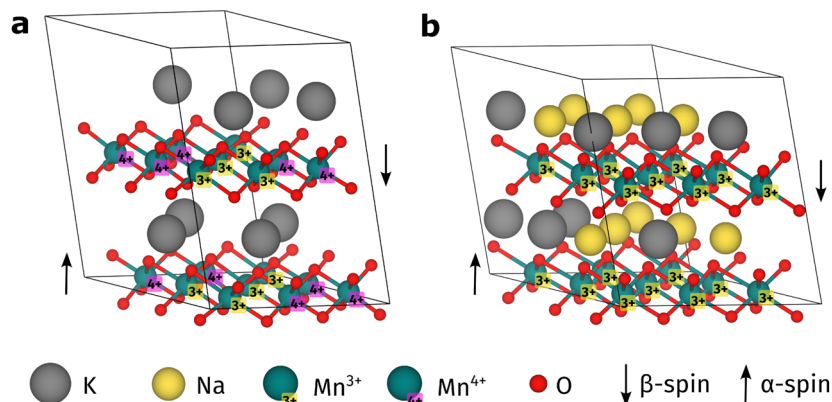


FIG. 2. (a) KMO birnessite with the formula $\text{K}_8\text{Mn}_{18}\text{O}_{36}$ and (b) fully Na⁺-intercalated birnessite with the formula $\text{Na}_{10}\text{K}_8\text{Mn}_{18}\text{O}_{36}$.

Spin-difference ($\alpha - \beta$) Mulliken Population Analysis (MPA) was used to estimate the valence state of each Mn atom present in our KMO structures. It is important to note that even though MPA gives a qualitative indication of the transition metal valence states, it is known to yield inaccurate results for the number of unpaired electrons because of an overestimation of the bonds' covalent character. Thus, magnetic moment calculations would be necessary to accurately estimate the magnetic moment for each atom in the system. Nevertheless, by combining bond analysis and MPA, we were able to estimate the oxidation states. As shown in Fig. 2(a), the relationship $\text{Mn}^{3+}/\text{Mn}^{4+}$ matches the stoichiometry of the material, i.e., the number of Mn^{3+} is equivalent to the amount of intercalated K^+ ions. This relationship is consistent after complete interlayer saturation with Na^+ ions [Fig. 2(b)].

B. Formation and binding energies

To understand the KMO sodiation process, the stepwise Na^+ -insertion process was studied through a defect formation energy formalism based on chemical potential³⁸ (see Sec. II B). We select this method because our KMO structures are non-stoichiometric; therefore, they cannot be directly compared through total energies. Within this formalism, structures with varying amounts of interstitial atoms can be compared through their change in relative energy in a given range of chemical potential where crystal growth can occur.³⁹ We note that, while the DFE reflects the thermodynamic stability of a given Na^+ concentration relative to the reference state, the energy associated with an individual Na^+ insertion step can be obtained from the difference between consecutive DFE values.

1. Proposed sodium ion intercalation mechanism and stability of defect structures

To propose a Na^+ -intercalation mechanism, we analyze potential sites for the introduction of this species to find preferential configurations. First, we model a Na_K substitution by testing all potential substitution sites (all sites with preintercalated K^+) via single-point calculation. The lowest energy structure was chosen and then fully optimized in lattice parameters, cell angles, and atomic positions. This optimized structure resulted in a higher relative energy than that of the host material by 1.37 eV in Na-rich conditions and 4.19 eV in Na-poor conditions. The increase in energy upon substitution occurs because the Na_K energy accounts for both the removal of a K^+ and the insertion of a Na^+ . Therefore, substitutions were excluded for the rest of the analysis, and Na^+ ions were incorporated into the KMO structure without removing any pre-intercalated K^+ .

After systematically inserting Na^+ into the KMO structure, we confirmed the progressive reduction of the remaining Mn^{4+} to Mn^{3+} . Once the available high-symmetry octahedral lattice positions are full, the structure is considered saturated, as the addition of more Na^+ would result in steric and Coulombic repulsions. The Na_{11i} configuration was optimized and resulted in DFE values of -25.08 eV in Na-rich conditions and 5.94 eV in Na-poor conditions. These are higher than Na_{10i} by 1.48 eV in Na-rich conditions and 4.3 eV in Na-poor conditions. This indicates that, without taking into account Na^+/K^+ substitutions, the acceptance limit of the Na^+ ions in the birnessite structure is equivalent to the Mn^{4+} available in the rigid

layers. In the case of our KMO structure, a maximum of 10 Na^+ ions are accepted. Based on our stepwise Na^+ insertion, we suggest that the barriers of ion insertion will determine the stability of the resulting structures.

Figure 3(a) shows the relative stability of the eleven optimized structures, from the initial KMO Na_{0i} to Na_{10i} . Each plane represents the structures' stability at different chemical potentials. Chemical potentials are varied to evaluate the stability of different degrees of intercalation at different sodium growth conditions. Here, a lower defect formation energy is associated with greater stability. The change in the chemical potential of Mn/O does not impact stability because their stoichiometry is unchanged from one structure to the next, as observed in Fig. 3(b). Rather, the stability is mediated by the sodium chemical potential, as the amount and position of sodium atoms change between the investigated structures. The 3D planes were projected onto the x, y ($\Delta\mu_{\text{Mn},\text{O}}, \Delta\mu_{\text{Na}}$) plane, constructing a 2D defect stability diagram that exclusively shows the most stable structures and their chemical potential range [see Fig. 3(c)]. As shown, the fully saturated structure with 10 Na^+ is the most stable, even in regions near the Na^+ -poor chemical potential limit. In the Na^+ -poor limit, it can be observed that the most stable structures are Na_{2i} and Na_{0i} . Finally, in Fig. 3(d), we show stability lines (plane projections on the E_f vs $\Delta\mu_{\text{Na}}$ axes) with varying Na chemical potential. Under conditions rich in Na^+ , the stability is directly correlated with the number of Na^+ ions inserted into the material, i.e., more Na^+ intercalants lead to greater stability. This trend is consistent through most of the chemical potential range. However, near Na^+ -poor conditions, the stability lines cross (see the inset), allowing Na_{2i} and Na_{0i} to be the most stable in this range. Thus, the thermodynamic stability is governed by the chemical potential, except at the Na^+ -poor limit.

2. Binding energy

While the defect formation energy is used to compare the stability of structures under different growth conditions (in this case, different Na content), the binding energy gives physical insight into the binding strength between the ions and the layers. To further understand the energetics of the Na-intercalated KMO, we calculate the binding energy of our defect structures using the following equation:

$$\frac{E_B}{n} = -\frac{E_{\text{Structure}} - E_{\text{Layer}} - E_{\text{Ions}}}{n}. \quad (3)$$

Here, E_B/n is the binding energy per intercalated sodium ion. $E_{\text{Structure}}$ is the energy of the complete structure with sodium intercalants. E_{Layer} is the energy of the structure without sodium intercalants (note that this energy includes pre-intercalated K^+ and retains the geometry of $E_{\text{Structure}}$ except for the removal of sodium). E_{Ions} is the energy of the Na^+ ions by themselves without the KMO lattice and in the same positions as in $E_{\text{Structure}}$. Finally, n is the number of sodium intercalants in that structure. The results of the calculated binding energies are shown in Fig. 4.

Binding energies can be interpreted as the energy required to separate a Na^+ ion from the rest of the structure. Furthermore, because of the negative sign at the beginning of the equation, positive binding energies are favorable and indicate stronger interactions,

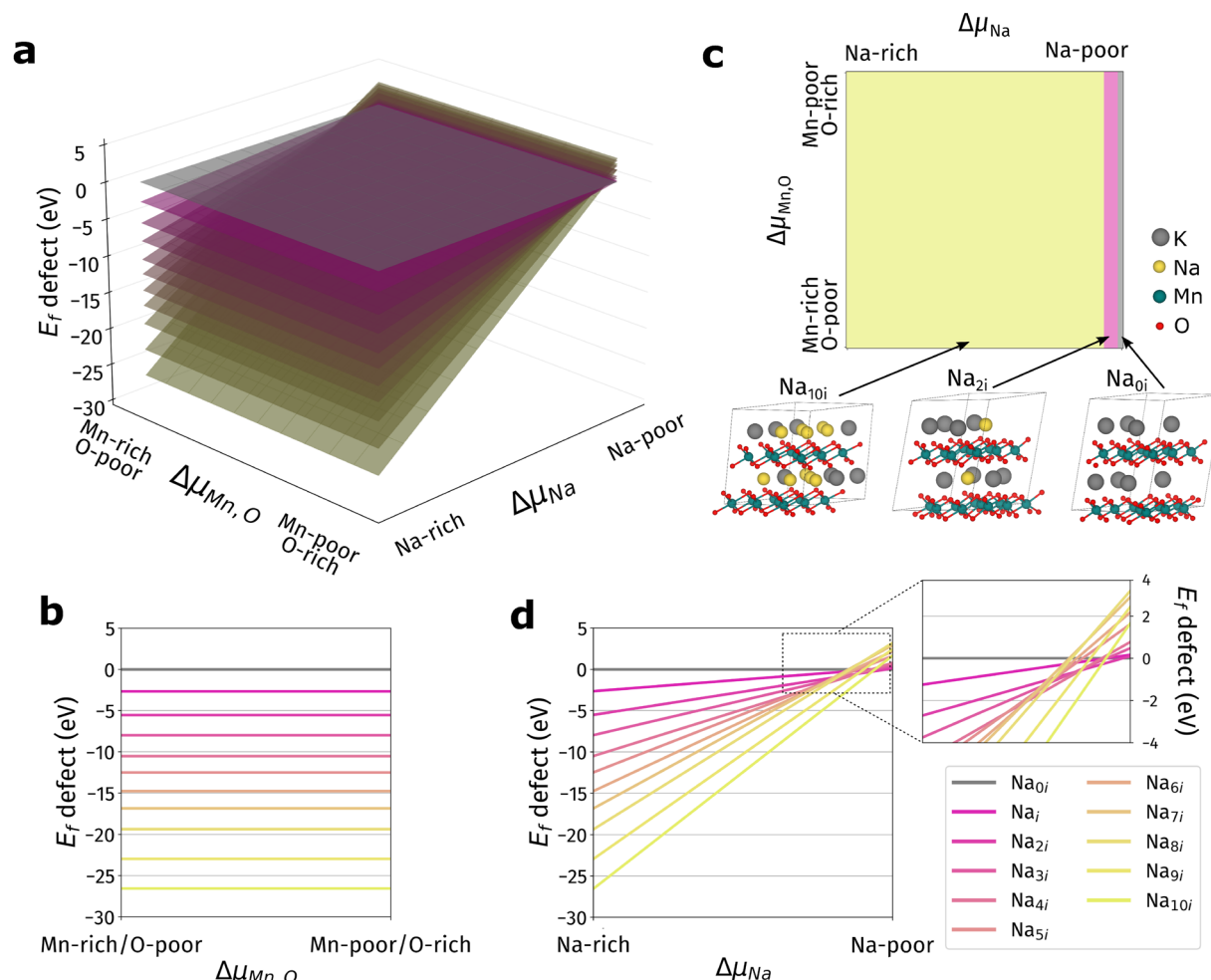


FIG. 3. Defect formation energy (DFE) as Na^+ ions are intercalated in the KMO birnessite. (a) 3D DFE plot, considering the change in Mn, O, and Na growth conditions. (b) Stability diagram (2D projection) showing the most stable structures. (c) View along the Mn, O growth conditions, cross section at Na^+ -rich conditions. (d) View along the Na growth conditions, cross section at Mn-rich/O-poor conditions.

whereas negative binding energies are unfavorable. In our particular structure, the introduction of one Na^+ ion has a high binding energy of 2.5 eV and is strongly bound to the structure. However, a second Na^+ intercalant is enough to lower the binding energy below 1.5 eV. The binding energies reduce as more Na^+ is inserted into the structure. This reduction in binding energy is mainly due to (I) steric and Coulombic repulsions due to the presence of more interlayer ions and (II) weaker electrostatic interactions due to the reduction of Mn^{4+} to Mn^{3+} . The final structure (KMO-Na_{10i}) has a binding energy of 0.42 eV. Based on this analysis, we conclude that Na^+ ions are readily removable in structures with a higher degree of saturation. In other words, it is likely that, during the de-intercalation process, the first Na^+ would be removed, while some sodium ions would remain in the interlayer.

C. Diffusion analysis

After analyzing the stability and binding energies of the Na^+ -intercalation process, we examined ion diffusion at the interlayer by calculating the energy barriers present in the minimum energy pathway (MEP) to gain insight into the intercalation/deintercalation process. To achieve this, we performed Nudged Elastic Band (NEB) calculations. We are particularly interested in the difference between Na^+ vs K^+ intercalation within the KMO structure, since ion dynamics are important descriptors of electrochemical processes. In this case, the calculations (see Fig. 5 and CIF files in the [supplementary material](#)) represent the movement of an ion from an octahedral site, which is the lowest-energy position, to another adjacent octahedral site, passing through an intermediate position corresponding to the transition state. We note that the configuration chosen for this

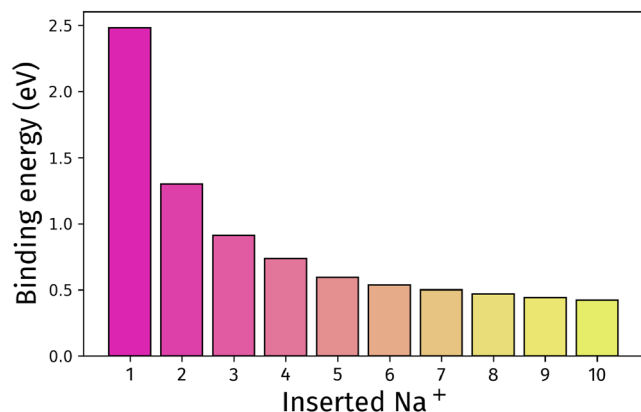


FIG. 4. Binding energies as Na⁺ ions are intercalated in the KMO birnessite.

analysis is a simplified version, where all intercalants in the KMO structure are stripped out except for one. This simplified model is necessary because of the complexity of a partially intercalated structure, where there is likely a significant geometry rearrangement during intercalation, making it difficult to find the true lowest-energy and transition state positions.

The results of our simplified model (shown in Fig. 5) demonstrate that the activation barrier for Na⁺ diffusion is lower than that of K⁺ by 0.03 eV (~10%). Although this value is close to the DFT uncertainty range, yet the trend should hold, thus this result suggests that K⁺ ions could present reduced mobility throughout the birnessite interlayer, while Na⁺ could preferentially diffuse in an electrochemical environment. If this is the case, we propose that K⁺ ions act as anchoring separators for the layers. Moreover, we expect the system to have higher Na⁺ mobility as the intercalation number is increased, since binding energies are drastically reduced at higher Na⁺ content (Fig. 4). Further calculations (finite temperature dynamics, such as *ab initio* molecular dynamics and mean squared displacements) would be required to confirm the diffusion roles of K⁺ and Na⁺ during intercalation.

D. Raman spectroscopy simulation

Raman spectra were simulated to further understand the characteristic vibrational modes of the birnessite KMO structure and the impact of Na⁺ introduced into the lattice (Fig. 6). We note that experimental results can be affected by the presence of water in the birnessite interlayer. However, the main peaks in the presence of water have been shown to remain at 490 and 560 cm⁻¹ wavenumbers.¹⁵ Given that the present calculations were performed without the inclusion of water, the results should be interpreted primarily in terms of the birnessite rigid structure and ionic interlayer. The characteristic peaks were identified by analyzing the vector displacements in the vibrational patterns and comparing these to the ideal characteristic modes as defined from experiments and the pristine MnO₂ calculation.

First, a pure δ -MnO₂ structure was simulated to determine the position and intensity of the main birnessite modes and compare them with the experimental literature results [Fig. 6(a)]. In experimental studies, two distinctive birnessite peaks are found. One mode occurs at 646 cm⁻¹, which can be viewed as the symmetric stretching vibration (Mn–O) of the MnO₆ octahedral groups (A_{1g} mode), and another at around 575 cm⁻¹, related to the stretching vibration (Mn–O) in the basal plane of (MnO₂) sheets (E_g mode).⁴⁰ Similarly, we found that only two signals appeared in the MnO₂ spectrum: the A_{1g} mode at 656 cm⁻¹ (labeled ν_1 in Fig. 6) and the E_g mode at 558 cm⁻¹ (labeled ν_2 in Fig. 6). This close value from our quantum calculations to the experimental results validates the method used for our calculations.

As there are no previous reports of DFT simulated Raman spectra for our particular co-intercalated structure, we used this initial calculation as a set point for the progressive ion intercalation analysis of the following structures.

The KMO (Na_{0i}), Na_{4i}, Na_{7i}, and Na_{10i} structures were selected due to their distinctive crystallographic structures, as identified from our XRD results (see Sec. III E), and were considered an appropriate representation of the gradual intercalation of Na⁺. Consistent with experimental studies, a significant number of signals appear in the simulated spectra when ionic species are present in the interlayer,^{40,41} compared to pure MnO₂. Structural symmetry,

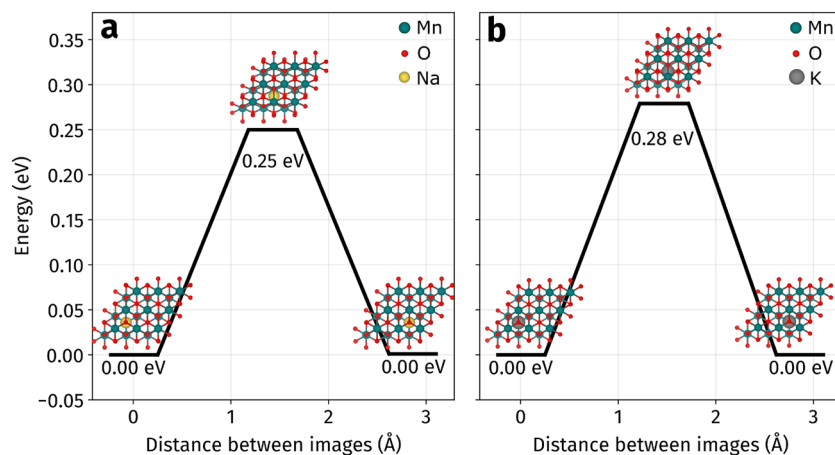


FIG. 5. Diffusion analysis (activation barriers) calculated with NEB for (a) Na⁺ and (b) K⁺ in the KMO structure.

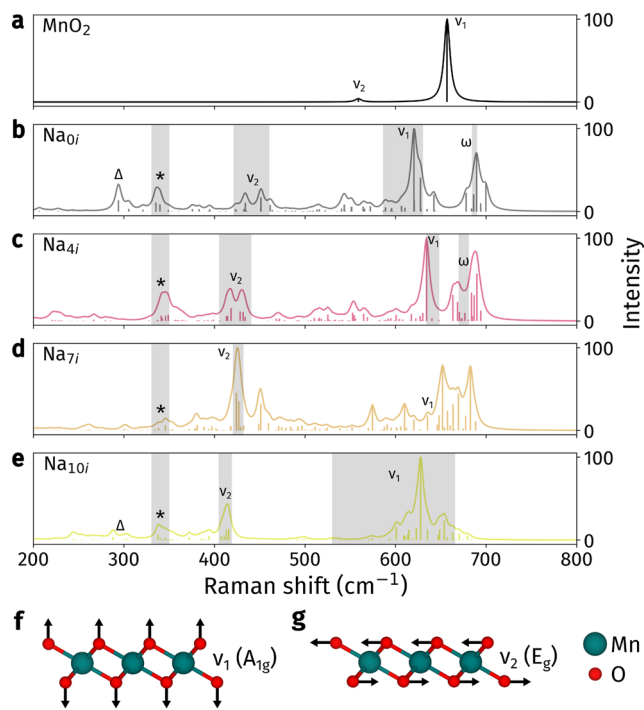


FIG. 6. Simulated Raman spectra using the HSE06 functional and CPHF/CPKS method for (a) the pristine δ -MnO₂, (b) potassium intercalated KMO Na_{0i}, (c) partially intercalated Na_{4i}, (d) partially intercalated Na_{7i}, and (e) fully intercalated Na_{10i} structures. The two characteristic birnessite vibrational modes are shown in (f) v_1 (A_{1g} mode) and (g) v_2 (E_g mode).

driven by sodium insertion, appears to play a major role in the activity of vibrational modes: the more symmetric the structure—both in the rigid lattice and the interlayer—the fewer active modes are observed.

When visualizing the atomic displacements for each computed mode, two general spectral regions were found across the four intercalated structures [Figs. 6(b)–6(e)]: Region I, hosting modes associated with potassium/sodium ions at wavenumbers below 300–370 cm^{-1} ; and region II, hosting modes that correspond exclusively to the rigid lattice, at wavenumbers above 400 cm^{-1} . The A_{1g} and E_g modes [see Figs. 6(f) and 6(g)] can be identified in region II. Although in the pure MnO₂ spectrum these characteristic modes appear as sharp, localized frequencies, the intercalated spectra exhibit near-symmetric vibrations with noticeable distortions and extend through a range of wavenumbers rather than at a specific value. We note that, in Na_{7i}, these distortions hindered the recognition of characteristic vibrational modes. We attribute this to a pseudosymmetry transition that occurs at this intercalation step (see Sec. III E).

In region I, the spectra display fewer signals, and their intensities decrease as sodiation takes place. All intercalated structures show a characteristic signal at around 330–350 cm^{-1} (labeled * in Fig. 6), seemingly related to the presence of ionic species in the interlayer. However, there was no clear symmetric vibration that could be associated with it. Another signal at 294–295 cm^{-1} (labeled Δ in

Fig. 6) can be clearly identified in the Na_{0i} spectrum and is faintly visible in the Na_{10i} spectrum; for this mode, intensity is the only observable difference between structures hosting exclusively K⁺ and those incorporating sodium.

We now focus on region II. The A_{1g} mode (v_1) initially redshifts when going from MnO₂ to Na_{0i}, which is attributed to the symmetry breakdown of the MnO₆ octahedra caused by Jahn–Teller distortion due to the presence of K⁺.⁴² Following this, v_1 generally shifts toward higher wavenumbers with progressive Na⁺ intercalation. In Na_{0i}, the mode spans 586–630 cm^{-1} , while in Na_{4i}, it narrows and shifts to 634–648 cm^{-1} . In Na_{7i}, a slight trace is visible at 635 cm^{-1} , but its relatively low intensity reveals it is not the dominant signal (which occurs at 651 cm^{-1}). Finally, in Na_{10i}, the mode extends broadly through 530–663 cm^{-1} , a range that we attribute to the enhanced pseudosymmetry achieved at full sodiation. The E_g mode (v_2) also shows a strong initial redshift from MnO₂ to Na_{0i}. Moreover, v_2 tends to shift to lower and more localized wavenumbers with increasing sodiation. In Na_{0i}, two distinct signals are observed that span 422–461 cm^{-1} , resulting from MnO₆ symmetry breaking.⁴² In Na_{4i}, the mode is displayed as vibrations located in layers between 405 and 438 cm^{-1} , with successive wavenumbers along this range activating vibrations in alternating layers. In Na_{7i}, the signals around 417–432 cm^{-1} are consistent with the expected vibration; however, high spectral noise prevents a definitive assignment. Finally, in Na_{10i}, the mode is compressed into an individual, well-resolved signal at 407–415 cm^{-1} as the pseudosymmetry is regained. Pseudosymmetry recovery in Na_{10i} also eliminated many of the non-totally symmetric (disorder-induced) modes that were present in partially intercalated structures along the 450–550 cm^{-1} range in Na_{0i}, Na_{4i}, and Na_{7i}.

The Na_{0i} and Na_{4i} spectra show an unidentified signal at wavenumbers above 660 cm^{-1} [labeled ω in Figs. 6(b) and 6(c)]. In Na_{0i}, this signal displays a symmetric vibration at 685–690 cm^{-1} seemingly along the basal plane, while in Na_{4i}, a similar vibration is observed around 670–680 cm^{-1} . In Na_{7i}, neither this symmetric movement nor any other pattern is clearly identified, although a signal is present. These signals appear to redshift with increasing sodiation, seemingly converging with the A_{1g} mode as saturation is reached in Na_{10i}.

Furthermore, along the spectra, several vibrational modes appear in pairs at adjacent wavenumbers. Each pair corresponds to the same atomic displacements but occurs in alternating layers. For example, the E_g mode (v_2) in Na_{10i} appears at 413 and 415 cm^{-1} [Fig. 6(e)]. This splitting is attributed to subtle geometric and electronic variations between layers, arising from the nature and position of the ions between layers and the resulting Mn³⁺/Mn⁴⁺ ratio.

E. XRD simulation and geometry analysis

As we modeled the systematic insertion of sodium ions in the KMO structure, we noticed a transformation in the overall unit cell of the structure, expressed as a deformation and an apparent increase in the crystalline order. To analyze this trend, we performed XRD simulations and geometry analysis.

Figure 7(a) shows a 3D visualization of the XRD patterns as sodium ions were intercalated in the structure. We first notice considerable peak shifts and intensity changes in the 2θ range of 25–45°,

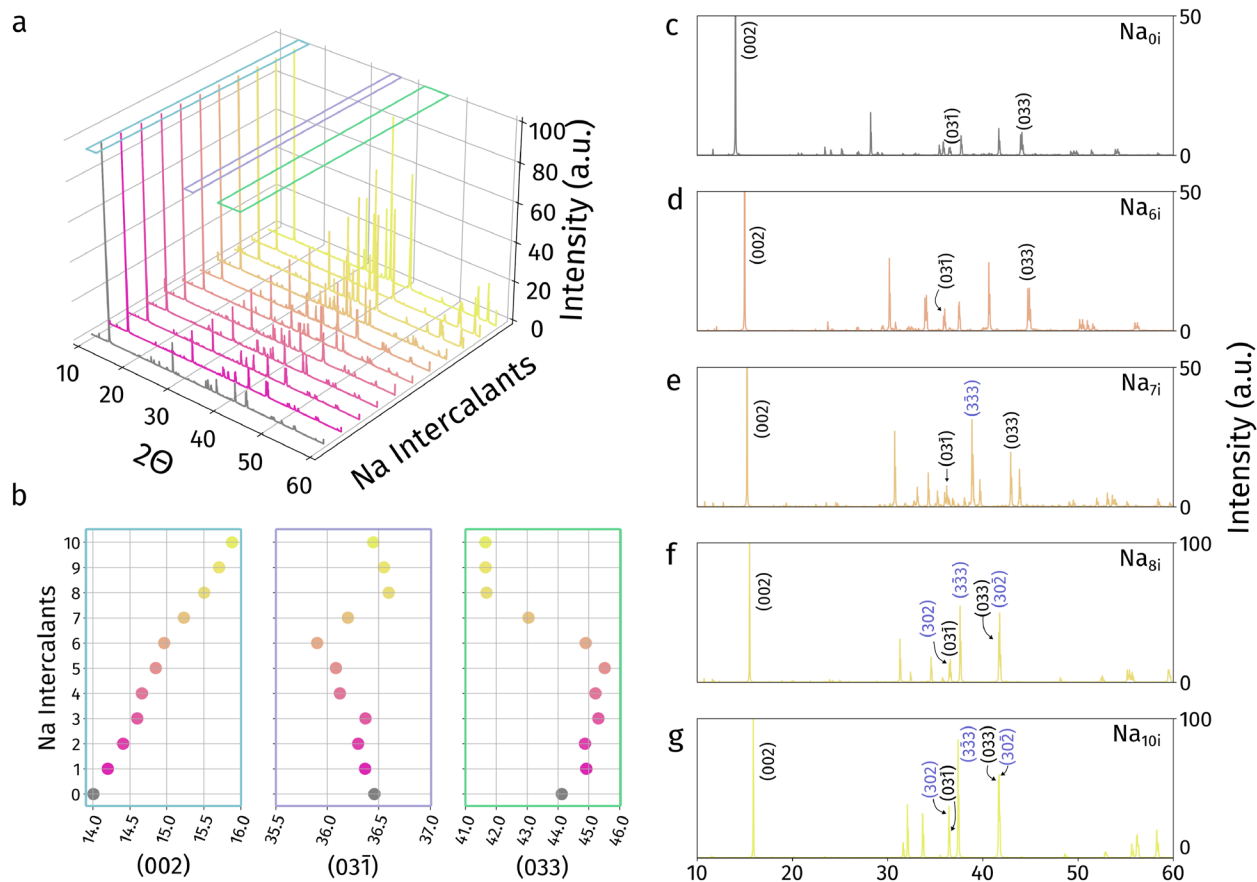


FIG. 7. Simulated XRD patterns with increasing intercalated Na^+ . (a) 3D figure showing all of the simulated XRD patterns. Blue, lavender, and green rectangles show the areas of interest for (002), (031), and (033) peaks, respectively. (b) Projections along peaks of interest. [(c)–(g)] Individual diffractograms for selected structures. Peaks that are maintained throughout the entire sodium intercalation process are labeled in black. Blue labels correspond to the largest peaks in the fully saturated structure (g). These peaks also appear in configurations Na_{7i} , Na_{8i} , and Na_{9i} .

indicating plane distortion and the emergence of new diffracting planes, with an increase in intensity suggesting higher symmetry and atomic density. The blue, purple, and green rectangles show the areas of interest for the peaks corresponding to the (002), (031), and (033) planes. The projection of these peaks is shown in Fig. 7(b).

The shift of the (002) peaks [leftmost plot in Fig. 7(b)] to higher diffraction angles confirms a decrease in the interplanar distance, expressed as a distortion in the c lattice parameters from 12.64 to 11.34 Å. Although individual ions are more loosely bound to the structure as the interlayer is saturated (see Sec. III B 2), the decrease in interlayer distance suggests an increased force of attraction between the MnO_2 and intercalated ion layers. Moreover, the (002) peak shows a change in its shift trend, starting from the configuration with seven Na^+ intercalants. We attribute this trend/slope change to a modification of the system's symmetry. This observation is further reinforced by changes in the shift slopes of the (031) and (033) peaks [center and right plots in Fig. 7(b)], where we observe an even more drastic modification of the general trend of these lines, also starting with the Na_{7i} configuration.

The peak shifts shown in Fig. 7(b) demonstrate a pseudo-symmetry recovery at the fully intercalated limit. During the intercalation process, the introduction of potassium and sodium intercalants initially breaks down the pristine birnessite symmetry ($P\bar{3}m1$) to $P1$, as explained in Sec. III A. In the fully intercalated structure, the disorder introduced by the presence of two co-intercalated species preserves $P1$ symmetry; however, the underlying structure (i.e., if all intercalants were the same) has $C2/m$ symmetry.

Next, we analyze the lengths of the Mn–O bonds during the stepwise reductions of $\text{Mn}^{4+}/\text{Mn}^{3+}$, as shown in Table I. With each $\text{Mn}^{4+}/\text{Mn}^{3+}$ reduction, the average Mn–O bond length increases due to symmetry breaking, which confirms the Jahn–Teller distortion of the MnO_6 octahedra. This distortion also explains the expansion of the layers along the $[110]$ direction, as evidenced by the increase in the lattice parameters a and b .

As the lattice parameters change, the $(\bar{3}\bar{3}4)$, $(30\bar{3})$, $(\bar{3}\bar{3}0)$, and (301) planes are converted into the $(\bar{3}\bar{3}3)$, $(30\bar{2})$, $(\bar{3}\bar{3}1)$, and (302) planes, respectively; all of these planes intersect Mn, O, and

TABLE I. Mn–O bond-length variation as a consequence of Mn⁴⁺/Mn³⁺ reduction.

Structure	Mn ⁴⁺ /Mn ³⁺ ratio	Mn–O bond-length average (Å)	Variance of Mn–O bond-length (%)
KMO (Na _{0i})	10/8	1.951	1.09
Na _{5i}	5/13	2.009	2.46
Na _{10i}	0/18	2.084	4.79

interlayer atoms. The increased intensities of these planes, together with that of the (400) plane, indicate improved atomic accommodation and higher symmetry due to the higher planar density of the interlayer.

F. Electronic density of states (DOS)

The spin-polarized, atom-projected densities of states (DOS) of all KMO structures are plotted and compared in Fig. 8

(see Fig. S2 for Mn *d*-orbital contributions). The experimental pristine birnessite (δ -MnO₂) has a reported bandgap of 2.23 eV.⁴³ Our pristine birnessite has a bandgap of 3.5 eV, similar to previous HSE06 calculations.⁶ Our KMO model (Na_{0i}) presents spin-up and spin-down bandgaps of 2.22 and 2.25 eV, respectively. The fully saturated structure (Na_{10i}) presents a bandgap of ~3.1 eV, and intermediate structures have varied bandgap values.

All structures exhibit either semiconducting or insulating behavior. Although Na⁺ ions do not appear to be prevalent contributors to DOS around the Fermi level, it is evident that there are electronic effects that arise as a result of the introduction of sodium into the structure. The difference in electronic properties arises primarily due to the modification of the Mn⁴⁺/Mn³⁺ oxidation states as Na⁺ is intercalated, which in turn causes lattice distortions (previously analyzed in Table I) and symmetry effects (as analyzed by XRD).

The interplay between rigid MnO₂ layers and Na⁺ intercalants results in a distinct electronic pattern. Structurally, the Na⁺ ions intercalate in opposite interlayers. This results in a reduction of

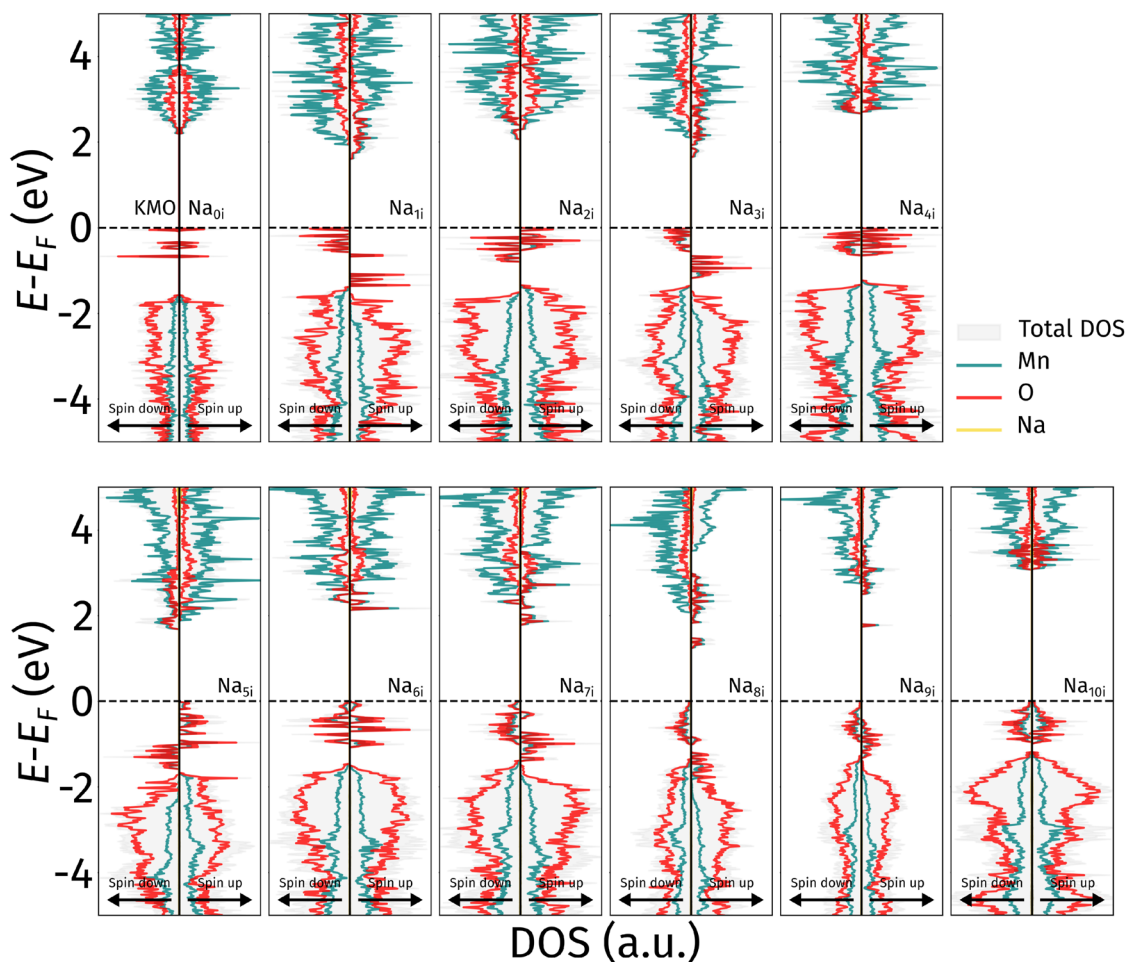


FIG. 8. Electronic density of states for the pristine and intercalated KMO birnessite structures as Na⁺ ions are added to the lattice, calculated with HSE06 and pob-TZVP-rev2 basis sets.

Mn⁴⁺ to Mn³⁺ in opposite rigid layers. Due to the initial antiferromagnetic spin alignment, a decompensation/compensation effect is observed as Mn is reduced, leading to distinct spin-polarized states. In particular, when a Na⁺ is introduced, the reduced Mn³⁺ sites have one extra electron, which aligns with the layer and decompensates the antiferromagnetic arrangement. This is in agreement with previous studies showing that K⁺ intercalants induce small polarons in birnessite, resulting in energy-split conduction band edges between the two spin-polarized states.⁶ Similarly, we observe a spin-polarized effect in the DOS around the Fermi level (CBM and VBM), which is particularly strong for odd intercalation numbers, since these have one extra unpaired electron in the layers. The exception being Na_{8i}, since the ground state for this structure resulted in two uncompensated Mn³⁺ atoms in a single layer. This results in spin-down polarized states directly below the Fermi level and spin-up polarized states directly above it.

We note that the structures Na_{7i}, Na_{3i}, Na_{5i}, Na_{7i}, Na_{8i}, and Na_{9i} all present a spintronic DOS profile resembling that of bipolar magnetic semiconductors. These materials have spin-polarized VBM and CBM in opposing spin directions.⁴⁴ By controlling the position of the Fermi level, for example via a gate voltage, it is possible to access fully spin-polarized conducting states at the valence/conduction band. This opens the possibility of using co-intercalated birnessite as a spin filter with bipolar field effect, field effect spin valve, or to detect and separate entangled electrons from superconductors.⁴⁵

Table S3 shows the bandgap for all Na⁺-intercalated structures. The bandgaps span a range of values, from 1.91 to 3.11 eV; thus, it is possible to systematically fine-tune the bandgap depending on the number of intercalants. The minimum bandgap (1.91 eV) occurs at 5 Na⁺ intercalants in the alpha channel (spin-up). In general, structures with strong spin polarization (odd intercalation number and Na_{8i}) are observed to have lower bandgaps (in one of their spin channels) than structures with fully compensated antiferromagnetic oxidation/spin patterns. The maximum bandgap within our structures (3.11 eV) is reached when the intercalation sites are completely saturated. Here, the structure returns to being fully spin compensated, with an even distribution of spin-up and spin-down electrons, where additionally all MnO₆ octahedra have Jahn–Teller distortions.

IV. CONCLUSION

In conclusion, we provide a systematic analysis of the structural, energetic, diffusional, vibrational (Raman), and electronic/spintronic properties of a sodium-intercalated potassium birnessite. We begin with a systematic addition of K⁺ to δ -MnO₂ birnessite to find the ground state of a potassium birnessite structure with K_{1.33}Mn₃O₆ stoichiometry. This particular stoichiometry was chosen due to the previously reported experimental synthesis feasibility. We take this as our starting point and incorporate sodium until we reach a stoichiometry of Na_{1.66}K_{1.33}Mn₃O₆, with fully intercalated layers. Our findings include the following: (1) The most stable structures are the fully intercalated Na_{10i}, partially intercalated Na_{2i}, and Na_{0i} structures in different regions of the Na chemical potential. (2) Binding energies indicate that Na⁺ ions are more loosely bound to the lattice, especially near the saturation limit. (3) The diffusion of Na⁺ is slightly more energetically

favorable than that of K⁺; thus, we propose that K⁺ ions serve as spacers, while Na⁺ diffuses quickly through the structure. (4) Characteristic Raman peaks are shifted when sodium and potassium are added to the structure. In addition, the number of peaks is reduced as the structure regains symmetrical features when fully saturated. (5) The XRD patterns show a change in symmetric order at Na_{7i}, indicated by a change in the trend of the characteristic peaks. Furthermore, at Na_{10i}, we observe a pseudosymmetry recovery when the interlayer is fully saturated. (6) DOS plots reveal that the bandgaps and magnetic behavior of the system can be controlled by intercalation. Some of the spin-polarized structures behave as bipolar magnetic semiconductors, with potential application in spintronics devices. Furthermore, bandgaps seem to depend on the number of intercalants. This work provides an overarching analysis of intercalated birnessite and can serve as an enriching complement to current and future experimental and theoretical studies.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for additional data supporting the findings of this study. Table S1 shows the bandgaps calculated for the pristine and Na⁺-intercalated KMO structures using the LDA+U functional. Table S2 lists the parameters of the crystal unit cell for the pristine and Na⁺-intercalated KMO structures. Table S3 reports the calculated bandgaps of the KMO and of all Na⁺-intercalated structures using the HSE06 functional. Figure S1 shows the volume evolution as Na was incorporated into the structure. Figure S2 shows the *d*-orbital projected density of states for all Na⁺-intercalated KMO structures. The [supplementary material](#) also provides crystallographic information files (.cif) for the pristine KMO structure (Na_{0i}), the KMO structures with one through nine Na⁺ intercalants (Na_{1i}–Na_{9i}), the fully intercalated structure with ten Na⁺ intercalants (Na_{10i}), and the transition-state structures for K⁺ and Na⁺ intercalation.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

A.L.P. and D.M.-L. contributed equally to this work.

All authors have read and agreed to the published version of the article.

Adriana Lee Punaro: Data curation (equal); Formal analysis (equal); Investigation (equal); Visualization (equal); Writing – review & editing (equal). **Daniel Maldonado-Lopez:** Data curation (equal);

Formal analysis (equal); Investigation (equal); Methodology (equal); Visualization (equal); Writing – review & editing (equal). **Jorge L. Choluta-Díaz**: Supervision (supporting). **Marcelo Videia**: Conceptualization (lead); Supervision (equal); Writing – review & editing (equal). **Jose L. Mendoza-Cortes**: Conceptualization (lead); Formal analysis (equal); Funding acquisition (lead); Investigation (equal); Methodology (equal); Project administration (lead); Resources (lead); Software (lead); Supervision (lead); Visualization (equal); Writing – original draft (equal); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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