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Defect chemistry of layered manganese oxides

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Semiconducting minerals like birnessite, a layered Mn(IV) oxide, harness and transfer energy throughout natural systems, catalyzing nominally slow redox reactions and facilitating biogeochemical cycling. Charge transport underpins the dynamic redox behavior of birnessite, but the details of the atomic and electronic structure and mobility of charge carriers remain elusive. Structural defects include reactive Jahn-Teller-distorted Mn(III) octahedra, Mn vacancies, foreign interlayer cations, and Frenkel defects coupled with disproportionation of displaced Mn(III), among others. Treating the inherently coupled defects individually enables the exploration across a complicated defect landscape. In this study, we employ density functional theory (DFT) to investigate the defect chemistry of birnessite and, in turn, understand the formation and structural relationships between atomic and electronic defects. Chalcophanite ($ZnMn_3O_7·3H_2O$) is utilized as an analogue for biogenic birnessite, particularly since the structure contains Mn(IV) vacancies and interlayer cations. In addition to Zn, the alkali earth elements and Mn^{2+} were also evaluated as possible interlayer cations. The enthalpy of formation for chalcophanite containing alkali earth elements were linearly correlated with ionic radius based on the equation y = -1.5x-1.64 with a R^2 of 0.997, while the enthalpies of formation for the chalcophanite containing Zn and Mn^{2+} were *ca.* 0.2 eV higher than the alkali earth fitted line. To further evaluate the onset of defect formation in birnessite, $MnO_2·nH_2O$ systems were constructed containing charged and neutral point defects. We calculate the formation energies for charged and neutral point defects in the $MnO_2·nH_2O$ system to construct energy level diagrams and identify the most thermodynamically favorable defects. Subsequent analyses probed the atomic and electronic structures of the identified defects. Our findings offer insight into the complex defect landscape of birnessite, laying the groundwork for further evaluation of defect formation, structure, and the impact on charge transport.