

**o.m.5.o5** Structure-conductivity correlations in monoclinic bronze phases  $H_xMoO_3$ . St. Adams, *MKI, Universität Göttingen., Germany. Email: sadams@gwdg.de*

Notes

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Hydrogen molybdenum bronzes  $H_xMoO_3$  are consistently described as low-dimensional mixed conductors. Their properties are controlled by a complex interplay between structural or microstructural effects of the  $H^+$  intercalation into the layered  $MoO_3$ , the accompanying electron transfer to the host as well as by the  $H^+$  distribution and ordering.

Crystal structures of all four stable  $H_xMoO_3$  phases have been determined and Rietveld-refined from powder XRD data, utilising structure models obtained by molecular mechanics simulations of the hydrogen intercalation process<sup>1,2</sup>. The distortion within the double layers of  $MoO_6$  octahedra in the bronzes imposes strong constraints on the band topology near the respective Fermi level and consequently determines the electronic and ionic conductivity of the bronzes. In contrast to earlier findings<sup>2</sup> that proton ordering should act as the driving force for the metal-to-semiconductor transition as well as the host structure modulation in  $H_{0.3}MoO_3$ , Extended Hückel tight-binding band structure calculations identify a Fermi surface nesting as the origin of the observed  $2b \times 2c$  superstructure in phase III ( $H_{1.6}MoO_3$ ).

Bond valence sum calculations state a significant difference between the valence states of the crystallographic distinct Mo atoms, e.g. in the refined  $2c$  superstructure of phase II ( $H_{0.9}MoO_3$ )<sup>1</sup>. Moreover hydrogen bond-valence maps have been employed to model the proton rearrangement during intercalation and potential long-range  $H^+$  migration pathways.  $H^+$  diffusion mechanisms in the bronzes are discussed based on a combination of bond-valence pseudopotentials with molecular dynamics simulations. For  $H_2MoO_3$ , the bond-valence analysis of the refined structure suggests that a  $H^+$  ordering on fully occupied interlayer sites is avoided by the occupation of a second type of interlayer sites.

As expected for solid state reactions under mild conditions, the hydrogen intercalation causes strong deviations from equilibrium, which give rise to a variety of metastable states and prominent hysteresis effects depending on the microstructure of the samples. The formation of one of the metastable phases ( $0.6 < x < 0.8$ ) is investigated by a time-resolved XRD study for the oxidation of phase II. The structure determination of the metastable phase reveals its crucial role for the hydrogen rearrangement between the two types of intercalation sites. Strong differences between the anisotropic thermal expansion of the bronzes can be related to the respective hydrogen distribution.

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