DGK Jahrestagung 2021



Contribution ID: 89

Type: Poster contribution

Proton motions in hydrogen bonds of hureaulite-type phosphatic oxyhydroxides

The peculiar hydrogen arrangement in the hureaulite-type manganese endmember $(Mn_5[(PO_4)_2(PO_3OH)_2](HOH)_4)$ comprises semihelical hydrogen bond chains along porous channels as well as framework HOH ligands in small cages. Results from extensive, complementary studies are presented to show (1) the time and length scales of local and long-range proton dynamics in the title compound and (2) contribute to the basic understanding of proton transport in confinement.

Diffuse difference Fourier maps around those hydrogen bond chains evaluated with X-ray single crystal and high-resolution neutron powder diffraction data adumbrate strong protonic disorder above 250 K together with fast rotating framework polyhedra. This temperature coincides with the onset of DC conductivity as probed by broadband dielectric spectroscopy. Neutron time-of-flight and backscattering spectroscopy revealed proton motions above room temperature with an activation energy of 0.39(1) eV and relaxation time of 11(2) ps. With a combined quasielastic neutron scattering data treatment, alongside geometrical considerations and ab initio molecular dynamics studies, these local motions were assigned to the rotations of HOH groups within the hydrogen bond chains. The vibrational density of states, collected with inelastic neutron scattering, was compared with experimentally obtained infrared and Raman spectra as well as simulated spectra based on electronic structure calculations.

As a result, we could elucidate lattice-dynamic-induced proton motions over the hydrogen bond network in this phosphatic oxyhydroxide. Such proton-phonon coupling is of great interest in the search for superprotonic conductors.

Primary author: Mrs HARTL, Anna (Ludwig-Maximilians-Universität München)

Co-authors: Prof. PARK, SoHyun (Ludwig-Maximilians-Universität München, Dept Earth & amp; Environ. Sciences, Section Crystallography); Dr JURANYI, Fanni (Paul Scherrer Institut); Dr KRACK, Matthias (Paul Scherrer Institut); Dr CHEPTIAKOV, Denis (Paul Scherrer Institut); Dr APPEL, Markus (Institut Laue-Langevin); Dr PAUL-MANN, Carsten (DESY); Dr ARAUZO, Anna (Universidad de Zaragoza); Dr LUNKENHEIMER, Peter (Universität Augsburg)

Presenter: Mrs HARTL, Anna (Ludwig-Maximilians-Universität München)

Session Classification: Energy materials: batteries, photovoltaics, etc.

Track Classification: Energy materials: batteries, photovoltaics, etc.