

## Ab initio structure determination of two new titanium phosphates synthesized via molten salt synthesis.

H. Petersen<sup>1</sup>, N. Stegmann<sup>1</sup>, M. Fischer<sup>2,3</sup>, B. Zibrowius<sup>1</sup>, W. Schmidt<sup>1</sup>, M. Etter<sup>4</sup>, C. Weidenthaler<sup>1</sup>

<sup>1</sup>Max-Planck-Institut für Kohlenforschung, Heterogeneous Catalysis, Kaiser-Wilhelm-Platz 1 45470 Mülheim, Germany,

<sup>2</sup>Crystallography/Geosciences, University of Bremen, Klagenfurter Straße 28359 Bremen, Germany,

<sup>3</sup>MAPEX Center for Materials and Processes, University of Bremen, 28334 Bremen, Germany,

<sup>4</sup>Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85 22607 Hamburg, Germany

petersen@kofo.mpg.de

The class of transition metal phosphates (TMPs) shows a wide range of chemical compositions, variations of valence states and respective crystal structures. Among TMPs, VO(P<sub>2</sub>O<sub>7</sub>) and LiFePO<sub>4</sub> are of special interest as the only commercially used heterogeneous catalyst for the selective oxidation of butane to maleic anhydride [1] and cathode material in rechargeable batteries [2]. Due to their structural features, TMPs are considered as proton exchange-membranes in fuel cells, working in the intermediate-temperature range [2, 3]. We report on the successful ab initio structure determination of two novel titanium pyrophosphates, NH<sub>4</sub>Ti(III)P<sub>2</sub>O<sub>7</sub> and Ti(IV)P<sub>2</sub>O<sub>7</sub>, from X-ray powder diffraction data. Both compounds were synthesized via a new molten salt synthesis route. The low symmetry space groups P2<sub>1</sub>/c (NH<sub>4</sub>TiP<sub>2</sub>O<sub>7</sub>) and P-1 (TiP<sub>2</sub>O<sub>7</sub>) complicate the structure determination, making the combination of spectroscopic, diffraction, and computation techniques mandatory. In NH<sub>4</sub>TiP<sub>2</sub>O<sub>7</sub>, titanium ions (Ti<sup>3+</sup>) occupy the TiO<sub>6</sub> polyhedron, coordinated by five pyrophosphate groups, one as a bi-dentate ligand. This secondary coordination causes the formation of one-dimensional six-membered ring channels with a diameter d<sub>max</sub> of 514(2) pm, stabilized by ammonium ions. Annealing NH<sub>4</sub>TiP<sub>2</sub>O<sub>7</sub> in inert atmospheres results in the formation of the new TiP<sub>2</sub>O<sub>7</sub>, showing a similar framework consisting of [P<sub>2</sub>O<sub>7</sub>]<sup>4-</sup> units and TiO<sub>6</sub> octahedra as well as an empty one-dimensional channel (d<sub>max</sub> = 628(1) pm). The structures can be related to the high-voltage pyrophosphate cathode material Li<sub>2</sub>FeP<sub>2</sub>O<sub>7</sub> also crystallizing in P2<sub>1</sub>/c [4]. Li<sub>2</sub>FeP<sub>2</sub>O<sub>7</sub> consists of a three-dimensional arrangement of undulating [Fe<sub>4</sub>P<sub>8</sub>O<sub>32</sub>]<sub>∞</sub> layers [4] building a channel system that is occupied by Li<sup>+</sup> ions. The structural relation to Li<sub>2</sub>FeP<sub>2</sub>O<sub>7</sub> implies a good proton conductivity of NH<sub>4</sub>Ti(III)P<sub>2</sub>O<sub>7</sub> and Ti(IV)P<sub>2</sub>O<sub>7</sub>. Both newly synthesized phosphates, NH<sub>4</sub>Ti(III)P<sub>2</sub>O<sub>7</sub> and Ti(IV)P<sub>2</sub>O<sub>7</sub>, show a proton conductivity based on the Grotthus mechanism. The activation energy of the proton migration of NH<sub>4</sub>Ti(III)P<sub>2</sub>O<sub>7</sub> belongs to the lowest which has been reported for this class of materials and indicates its potential application as a proton electrolyte in the intermediate temperature range. *In situ* X-ray diffraction study of the transformation of NH<sub>4</sub>TiP<sub>2</sub>O<sub>7</sub> to TiP<sub>2</sub>O<sub>7</sub> reveals a two-step mechanism, the decomposition of ammonium ions coupled with the oxidation of Ti<sup>3+</sup> to Ti<sup>4+</sup> and subsequent structural relaxation.

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**Keywords: structure determination, transition metal phosphates, proton conductivity, in-situ investigation**

*We acknowledge DESY (Hamburg, Germany) a member of the Helmholtz Association HGF, for the provision of experimental facilities. Parts of this research were carried out at PETRA III, beamline P02.1. We thank ZBT (Duisburg, Germany) for the possibility of Protonconductivity measurements.*