

Synthesis and Proton Conductivity of Acid Tantalum Phosphate

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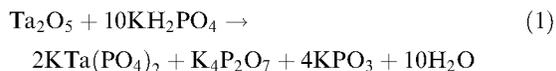
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A new method of tantalum phosphate acid dehydrate synthesis has been proposed and the structure and two-dimensional proton conductivity is described.

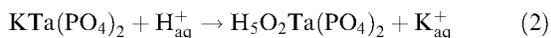
Deniard-Courant and co-workers, and ourselves, have recently synthesized acid antimony phosphate dihydrate^{1,2} with a conductivity of 2×10^{-3} Sm cm⁻¹. In the fine crystalline materials involved proton transfer mostly takes place on the microcrystalline surface and is characterised by the substantial dependency of conductivity on humidity. This paper is devoted to the synthesis and investigation of high crystalline acid tantalum phosphate.

Chernorukov and coworkers have prepared the material required by lengthy warming of a tantalum oxide and HF mixture with an excess of phosphoric acid.³ The substance thus obtained was finely crystalline with substantial broadening of the X-ray powder peaks. This was the reason for synthesizing acid tantalum phosphate by ion-exchange from the K form. $\text{KTa}(\text{PO}_4)_2$ was obtained from initial tantalum oxide and potassium dihydrophosphate at 1270 K according to reaction (1):



The reactants' proportions were calculated so as to give along with the main product, a mixture of meta- and pyrophosphates in a ratio corresponding to a double eutectic. The reaction should be carried out in a melt in order to either provide depth of the reaction or growth of the crystals.

The mixture obtained was treated with a mixture of hydrochloric and phosphoric acids (anion concentration *ca.* 1 M) under steady-state then flow conditions. As a result an ion-exchange process takes place, reaction (2):



According to chemical analysis (thermogravimetry for water, titrimetry for protons, gravimetry for phosphate anion and tantalum oxide content) the resulting compound has the composition $\text{H}_5\text{O}_2\text{Ta}(\text{PO}_4)_2$. Cell parameters were refined by a least-squares procedure from powder diffraction data collected with a diffractometer (Stoe, $\lambda_{\text{CuK}\alpha}$).

$\text{KTa}(\text{PO}_4)_2$ and $\text{H}_5\text{O}_2\text{Ta}(\text{PO}_4)_2$ crystallize in orthorhombic syngony. The lattice parameters are given in Table 1. In the case of $\text{KTa}(\text{PO}_4)_2$ the data are in agreement with the literature,⁴ though we did not observe a symmetry decrease to monoclinic.

The structure of the substances involved comprises layers

Table 1 Unit cell parameters for $\text{KTa}(\text{PO}_4)_2$ and $\text{H}_5\text{O}_2\text{Ta}(\text{PO}_4)_2$.

Compound	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å
$\text{KTa}(\text{PO}_4)_2$	8.610(1)	5.2156(6)	8.420(1)
$\text{H}_5\text{O}_2\text{Ta}(\text{PO}_4)_2$	8.826(3)	5.212(3)	9.505(3)

of $\text{Ta}(\text{PO}_4)_2$, which are built up of TaO_6 octahedra and PO_4 tetrahedra linked together *via* vertices so that three of the four anion oxygen atoms take part in tantalum polyhedron formation. The other oxygen atoms are considered to be either part of the coordination sphere of K^+ or to form hydrogen bonds with proton-containing groups.

The IR study was carried out with a Perkin-Elmer

spectrometer at 4000–400 cm⁻¹ in hexachlorobutadiene and vaseline oil suspensions. Since an HOH bending vibration band at 1740 cm⁻¹ is observed, it is suggested the proton is hydrated (H_5O_2^+). The increase in the *c* cell parameter, parameters *a* and *b* being constant, confirms the formation of (H_5O_2^+). Stretching vibration bands with maxima at 2825 and 3350 cm⁻¹ correspond to hydrogen bonds O–H...O of length 2.58 and 2.73 Å.⁵ The high value of the former is in accord with the substantial shift of the central proton in (H_5O_2^+) to one of the oxygen atoms of water.

The proton conductivity study was carried out on an alternative current bridge P568 with a two-contact technique at frequencies between 10² and 10⁵ Hz under a 10–30 mV potential on a right-angled pressed pellet with carbon electrodes. The high texture of the crystals leads to a

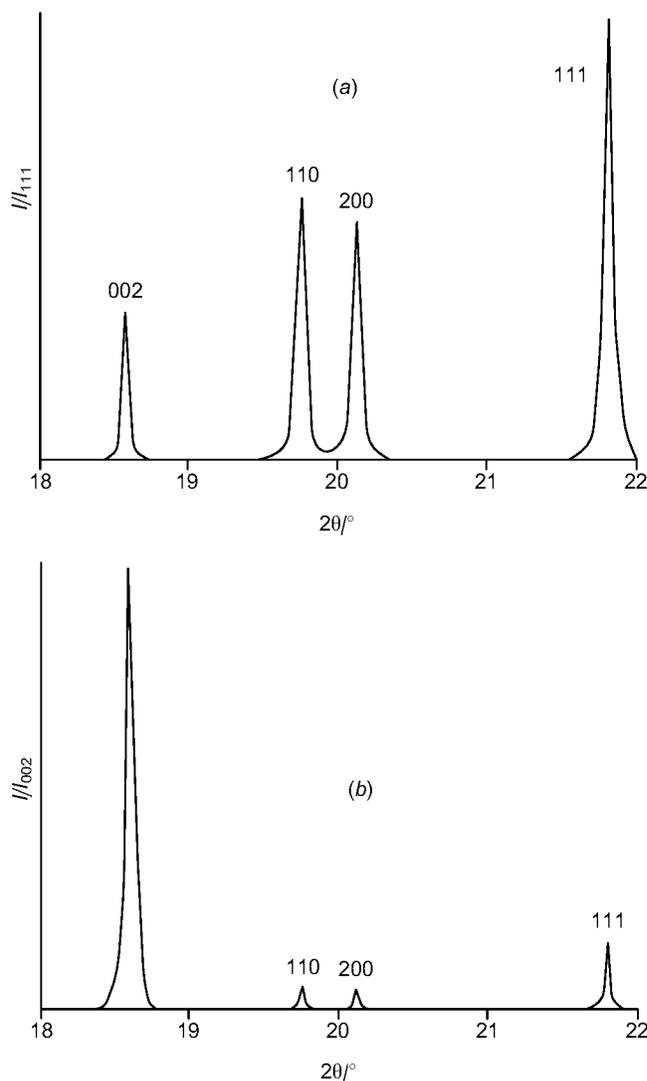


Fig. 1 Diffractograms of $\text{KTa}(\text{PO}_4)_2$ fragments: (a) powder, (b) pellet pressed in the direction parallel to the pressure plane.

difference in electroconductivity readings both perpendicular and along the pressure axis. The former is *ca.* $1.0(1) \times 10^{-3}$ Sm cm⁻¹ at 298 K, which is among the best for known low temperature proton conductors. The conductivity in the perpendicular plane is two orders lower. The powder diffraction spectra along the pressure axis, Fig. 1(b), contain extremely intense 001 peaks. Thus, we can conclude that proton transport takes place in the *ab* plane.

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