ESRF	**Experiment title:** Ab-initio structure determination and refinement of two new three-dimensional phosphates: α-$CsTi_3P_5O_{19}$ and the first with ionic exchange properties, $Ti_2P_2O_{11}H_4$	**Experiment number:** CH-253
Beamlme: BM16	**Date of experiment:** from: **26-2-97** to: **28-2-97**	**Date of report:** **28-7-97**
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Report:

Titanium(IV) phosphates have received a considerable attention in the last decades by their properties as ion exchangers, sorbents and convenient matrices for chemical modification. In recent years, new types of titanium(IV) phosphate based materials have been synthesized by high temperature solid state reactions and by hydrothermal methods under mild conditions. The latter approach is of a special interest because it allows the synthesis of metastable phases that could exhibit ion exchange and catalytic properties.

A sample with the empirical formula, $Ti_2H_4P_2O_{11}$, was obtained hydrothermally from titanium(IV) chloride in phosphoric acid solutions. The reaction mixture was sealed and heated at 190°C for 10 days. On the other hand three-dimensional compounds can be obtained by thermal treatment of ion-exchange phases of lamellar phosphates. Heating at 900°C γ-$Ti(Cs_{0.5}H_{1.5}PO_4)\cdot nH_2O$ gives rise to the compound α-$CsTi_3P_5O_{19}$.

The crystal structure of $Ti_2H_4P_2O_{11}$ was *ab initio* determined from synchrotron X-ray powder diffraction data. The X-ray data were collected on the beam line BM16. A finely ground sample of $Ti_2H_4P_2O_{11}$ was loaded in a 1.0 mm borosillicate capillary and mounted in a rotatory goniometer. Room-temperature data were collected using an incident wavelength of **0.62992 Å up** to 35°2θ.

Integrated intensities were extracted from the synchrotron data using the program FULLPROF[1]. After careful optimization of the appropriate profile parameters and the intensities themselves, 947 F^2 values were extracted from the raw data; The F^2 data were used as the starting data for the direct-methods program **SHELXS-86**[2]. A plausible solution was found assuming the space group $P\bar{1}$ showing the positions of all non-hydrogen atoms. Using this model, a Rietveld refinement against the synchrotron powder X-ray data was carried out. Successful convergence was accomplished, $R_{wp} = 13.3$, $\chi^2 = 18.6$. The H-atom positions were determined by Fourier Difference Synthesis, using constant-wavelength neutron powder diffraction data ($\lambda = 1.594$ Å).

The structure consists of a three-dimensional network of $Ti0_6$ octahedra and PO_4 tetrahedra linked by vertex sharing. The two independent titanium atoms are connected by an oxo bridge and two independent water molecules are linked to one type of Ti atoms. The topology of this structure consists of a Ti/P/O framework enclosing two principal channels running parallel to the ***a*** axis, into which the H atoms of the water molecules project, one different molecule by channel. All the hydrogen atoms participates in weak hydrogen bonds. No hydrogen bonding occurs between two water molecules.

Determination of hydrogen sites confirms that the structural formula is $Ti_2O(PO_4)_2(H_2O)_2$ rather than $Ti_2O(OH)(HPO_4)(PO_4)$ and this fact explains the low activity of this compound as ionic exchanger.

1. Rodriguez-Casvajal, J. *FULLPROF: A Program for Rietveld Refinement and Pattern Matching Analysis;* XV Congress of the IUCr, Toulouse; France, 1990,127.

2. Sheldrick, G.M. *SHELXS-86 User Guide.* University of Guttingen, Germany, 1986.

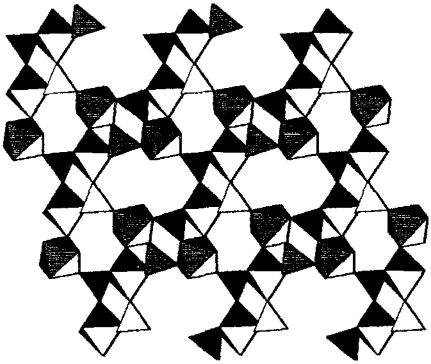

Figure. Polyhedral plot of $Ti_2O(PO_4)_2(H_2O)_2$ along *a*. *c* across, *b* down.