

MS17 Minerals, materials and polymorphs

Chairs: Håkon Hope, Elisa Nauha

MS17-P1 Re-determination of four CsCoPO₄ crystal structures from single-crystal X-ray diffraction data

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The crystal structures of the four known CsCoPO₄ polymorphs have been reported by P. Henry [1] and H. Kawaji [2]. The structures were determined using synchrotron (phase 1-4) and neutron powder diffraction (phase 3) methods. Although the reported structures are correct and are in good agreement with known structural analogues, for example, CsZnPO₄, isotropic displacement parameters of some atoms seem to be questionable. For example, B_{iso} of P1 of the phase 4 exhibits very low value of 0.3(1) Å². In order to understand the nature of low displacement parameters and to obtain more precise structural information for CsCoPO₄ polymorphs, a single crystal diffraction study has been performed. The compound undergoes three phase transitions at following temperatures: 280, 210, 30°C. It adopts two orthorhombic phases crystallizing in space group *Pnma* (phase 1) and *Pn2₁a* (phase 2), and two monoclinic phases, space group *P12₁/a1* (phase 3) and *P12₁/1* (phase 4). New structural data of all four polymorphs with anisotropically refined displacement parameters will be presented and compared with known powder diffraction data. **KEYWORDS** Phosphates, Polymorphism, Crystal structure, Structure solution, Single-crystal diffraction

[1] P. Henry, E. Hughes, M. T. Weller, J. Chem. Soc., Dalton Trans., 2000, 555-558

[2] H. Kawaji, Y. Ishihara, A. Nidaira, et al., J. Therm Analys. 92 2008, 451-455

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Keywords: Phosphates, Polymorphism, Crystal structure, Structure solution, Single-crystal diffraction

MS17-P2 2D and 3D Titanium Phosphate Materials: Crystal Structure and Properties

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In 1990 Christensen *et al.* proposed the structure of titanium compound, Ti(PO₄)(H₂PO₄)₂·2H₂O, according with Clayden, but later the combined SS-NMR and powder synchrotron X-ray diffraction data showed a different cell [1]. In 1995, the γ-ZrP was solved by Poojary *et al.*, confirming the model reported by Christensen. Later, the β-TiP showed that the structure of the γ-type layer is retained in the anhydrous compound. Layered titanium phosphate compounds intercalated with amines may be used as precursors in pillaring reactions [2]. Despite the many potential applications of these materials, including the synthesis of organic-inorganic nanotubes [3], their detailed structural features have remained poorly understood. In the last decade, we have combined chemical information, NMR spectroscopy and powder XRD data, and chemical modeling studies to describe the alkylamine templated γ-titanium phosphates, including the (C₂H₅NH₂)[Ti(H₂PO₄)(PO₄)₂·H₂O pseudotridimensional porous structure (fibrous morphology) that shows an unusual and very strong interlayer-hydrogen bond [4].

Layered α-Ti(HPO₄)₂·H₂O (α-TiP) and its propylamine intercalation product, α'-Ti(HPO₄)₂·2C₃H₇NH₂·H₂O, have been synthesized and characterized, their sorption capacity for europium(III) was investigated, and structure of α-[Eu(H₂O)₉]₂Ti(PO₄)₂·(H₂O)_{11/3}, has been proposed by DFT calculations. Tri-dimensional Ti₂O(PO₄)₂·2H₂O polymorphs (ρ-TiP and π-TiP) were prepared hydrothermally. The crystal structure of Π-phase was solved *ab initio* from synchrotron data, and the thermal transformation of ρ-Ti₂O(PO₄)₂·2H₂O to ρ-Ti₂O(PO₄)₂ was monitored by HT-PXRD. The coordination environment of the hydrated titanium changes from octahedral to distorted tetrahedral, which explains the measurable thermally activated nitrogen-adsorption observed for the anhydrous phase. To our knowledge, the process described here constitutes the first example of nitrogen-fixation by an inorganic material far above room temperature.

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References [1] S. García-Granda, et al., *Inorganic Chemistry* 49 (2010) 2630-2638; [2] L. Mafra, et al., *Chemistry of Materials* 17 (2005) 6287-6294;; [3] J.A.