ESRF	**Experiment title:** Structural Investigations of Topotactic Solid State Reactions of Calcium Phosphates by Means of Powder Diffraction	**Experiment number:** CH-267
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Report:

High temperature diffraction studies in the system $CaO\text{-}P_2O_5\text{-}H_2O$ have been carried out at the powder beamline BM 16. Our research focused on the dehydration reactions of $\alpha\text{-}Ca_2[P_4O_{12}] \cdot 4H_2O$ (a calcium cyclotetraphosphate) and $Ca[H_2PO_4]_2 \cdot H_2O$. Earlier measurements [1] showed that in both cases the solid state reaction proceeds via several intermediate phases to the same $\beta\text{-}(Ca_2[PO_3]_4)_x$ (a calcium polyphosphate). The transformation process of $\alpha\text{-}Ca_2[P_4O_{12}] \cdot 4H_2O$ has been discussed on the basis of a topotactic solid state reaction. A other presumable topotactic reaction is the thermal transformation of CaP_4O_{11} [2] leading to the formation of the same $\beta\text{-}(Ca_2[PO_3]_4)_x$ as mentioned above. The knowledge of the structures of the intermediate phases can be used to understand the mechanism of the transformation steps in these reactions.

The in situ measurements have been done in transmission mode with 1.0 mm quartz capillaries using a wavelength of 0.63346 Å from the double monochromator and a nine-crystal analyser stage was used as detector. Data were collected in continuous mode and afterwards converted to equal step size in 28 of 0.005". A hot air blower was used for heating with heating rates of 1°/min. Short Scans of 10 min duration monitored the ongoing solid state reaction.

Despite using open capillaries on one side to allow the escape of water the dehydration of

α-$Ca_2[P_4O_{12}] \cdot 4H_2O$ led via another route of intermediate phases to the formation of the known β-$(Ca_2[PO_3]_4)_x$. The main intermediate crystalline phase formed at about 220°C is $CaH_2P_2O_7$. There are entries for this compound in the ICCD database but no crystallographic data have been determined up to now. Very recently, we were successful to solve ab initio the structure of this phase using a long scan from the in situ measurements. It can be assumed that the pressure of the evaporated water within the capillary led to the hydrolysis of the cyclotetraphosphate.

The compound γ-$(Ca_2[PO_3]_4)$ (another calcium polyphosphate) which is formed as intermediate phase during the dehydration of $Ca[H_2PO_4]_2 \cdot H_2O$ was measured at RT and despite the presence of β-$(Ca_2[PO_3]_4)$ as minor phase the structure was successfully solved from a powder pattern as given in Fig. 1. The Rietveld refinement of the structure model of γ-$(Ca_2[PO_3]_4)$ and inclusion of the β-polyphosphate as second phase led to a good convergence (R_{wp} = 11.6% and R_I = 3.6% for the main phase). Some more details about this structure are given in [3].

No single crystals of a second modification of the calcium cyclophosphate β-$Ca_2[P_4O_{12}] \cdot 4H_2O$ could be prepared and therefore a powder pattern of this complex compound has been collected. We hope to solve this structure also ab initio from powder data.

[1] Schneider, M. & Jost, K. H. (1990) *Z. anorg. allg. Chem. 580,* 175-180.

[2] Schneider, M.; Buschmann, J. & Luger, P. (1994) Z. *anorg. allg. Chem.* **620**, 766-770.

[3] Trommer, J., Schneider, M., Worzala, H. & Fitch, A. ***N.*** (1998) *Z. Kristallogr. Suppl.,* in press.

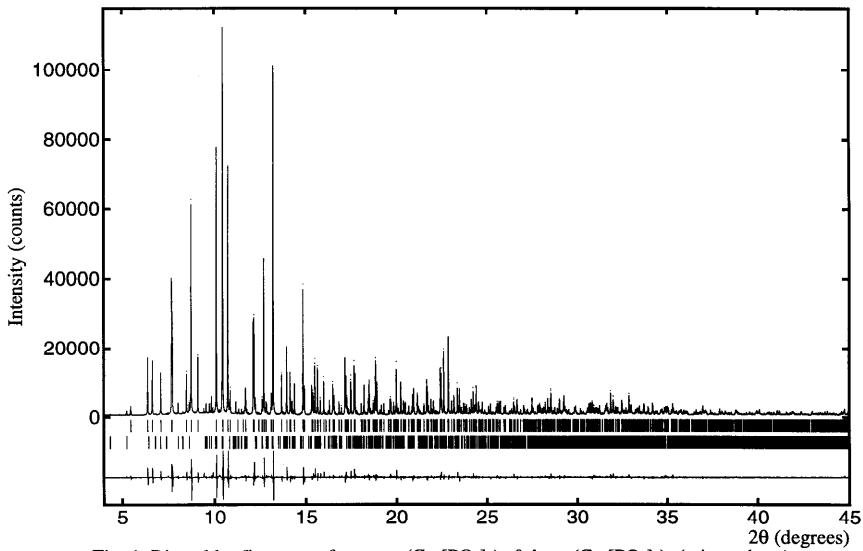

Fig. 1 Rietveld refinement of gamma-$(Ca_2[PO_3]_4)_x$ & beta-$(Ca_2[PO_3]_4)_x$ (minor phase)