Experimental report

17/12/2019

Proposal: EASY-399 **Council:** 10/2018

Title: An unprecedented hydride-substituted apatite

Research area: Chemistry

This proposal is a new proposal

Main proposer: Nathalie KUNKEL

Experimental team:

Local contacts: Clemens RITTER

Samples: Sr5(PO4)3D

Instrument	Requested days	Allocated days	From	To
D2B	4	4	09/07/2019	10/07/2019

Abstract:

Mixed - anionic hydrides are currently a very important field of research. In search of new hydride materials, we prepared an unprecedented strontium apatite compound. While recent publications describe that mixtures of hydroxide and hydride anions could be found in such compounds, we have now successfully replaced fluoride/hydroxide completely by hydride for the first time.

So far, we have confirmed the presence of solely hydride by solid state NMR combined with theoretical modelling of the spectra using ab-initio methods, IR spectroscopy and elemental analysis. To support our hypothesis and gain detailed structural information on the position and occupation number, neutron powder diffraction studies are indispensable.

Therefore, we apply for beam time to record a room temperature powder pattern of Sr5(PO4)3D at the high-resolution neutron powder diffractometer D2b.

[1] K. Hayashi, H. Hosono, Green apatites: hydride ions, electrons and their interconversion in the crystallographic channel, Phys. Chem. Chem. Phys. 2016, 18, 8186.

EXPERIMENTAL REPORT FOR PROPOSAL EASY-399

An unprecedented hydride-substituted apatite

The allocation of beamtime allowed to record a neutron powder pattern of a hydride phosphate and resulted in the following publication.

An unprecedented fully H^- - substituted phosphate hydride $Sr_5(PO_4)_3H$ expanding the apatite family

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Eur. J. Inorg. Chem., accepted, 10.1002/ejic.201901151.

Abstract of the manuscript:

The apatite family is a mineral class that also contains the biologically very important hydroxyapatite. Here, we are reporting on the synthesis and characterization of a fully hydride – substituted strontium apatite, which could be obtained via mechanochemical synthesis and subsequent annealing treatment. The full substitution by hydride anions is proven by various methods, such as neutron powder diffraction of a deuterated sample $Sr_5(PO_4)_3D$, as well as ^1H MAS solid state NMR combined with quantum chemical calculations, vibrational spectroscopy and elemental analysis. The present work expands the apatite family from the know halide and hydroxide apatites to the fully hydride-anion – substituted variant and is expected to open up a new field of materials containing coexistent phosphate and hydride anions.

Experimental Report

Using a mechanochemical reaction between SrD_2 and $Sr_3(PO_4)_2$ allowed us to obtain a fully-substituted hydride-phosphate $Sr_5(PO_4)_3D$ crystallizing hexagonally similar to its fluoride and hydroxide analogues in space group $P6_3/m$. The presence of the hydride – anion and absence of hydroxide has been proven by several independent methods. Quantum chemical calculations assuming a hydride phosphate reproduce the experimentally obtained chemical shifts in ^1H MAS NMR spectra as well as the vibrational spectra. Furthermore, elemental analysis also confirms the assumed composition.

Here, we performed a neutron powder diffraction experiment within the help of Dr. Clemens Ritter (Grenoble, ILL) at the high-resolution diffractometer D2B. The compound, $Sr_5(PO_4)_3D$, shows cell parameters a = 9.7169(4) and c = 7.2747(4) Å, which are slightly smaller than its fluoride analogue. The neutron diffraction pattern was simultaneously refined with X-ray data within the program package FullProf and the refined plot as well as atomic parameters can be seen in figure 1 and table 1.

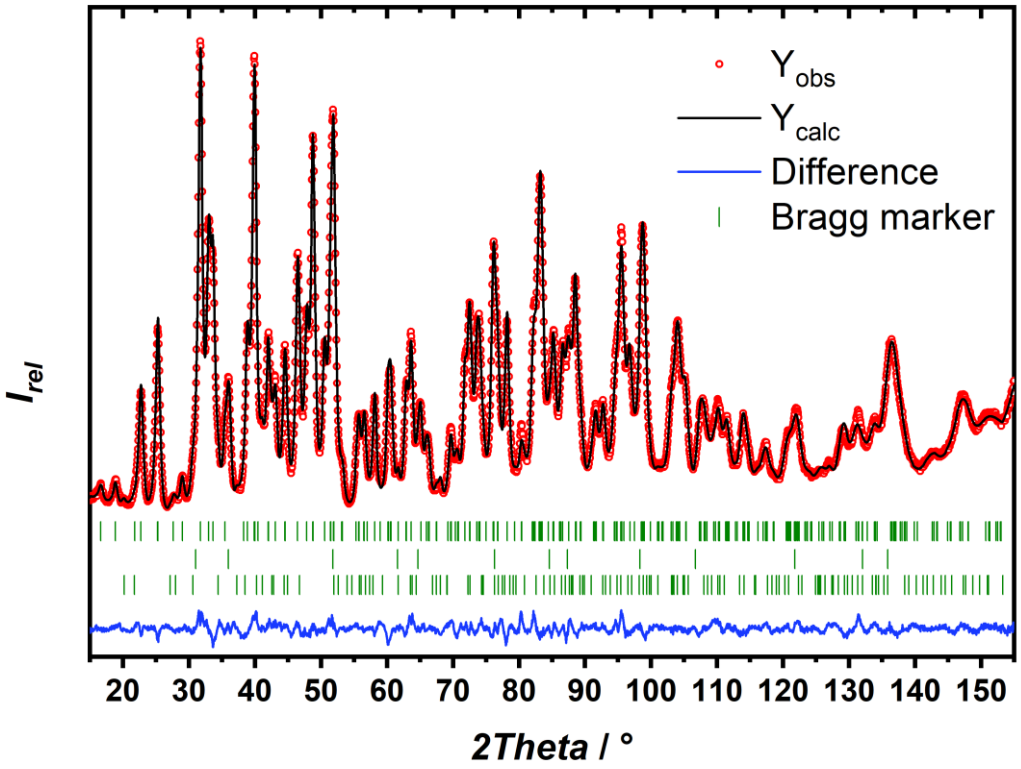

Figure 1: Refinement of the structure $Sr_5(PO_4)_3D$ measured in air-tight vanadium cylinders at the D2B, ILL Grenoble. Bragg markers from top to bottom: $Sr_5(PO_4)_3D$ 85wt%, SrO 6wt%, $Sr_3(PO_4)_2$ 9wt%.

Table 1. Refined lattice parameters and atomic parameters for $Sr_5(PO_4)_3D$ at 300 K obtained from refined neutron powder diffraction.

$Sr_5(PO_4)_3D$		*a* = 9.7169(4) Å, *c* = 7.2747(4) Å, *V* = 594.83(5) Å^3				
Atom	Site	x	y	z	B_{iso}(Å^2)	s.o.f.
Sr1	4*f*	1/3	2/3	0.0023(4)	0.77(4)	1
Sr2	6*h*	0.2389(2)	0.2544(2)	1/4	0.59(3)	1
P1	6*h*	0.3988(3)	0.0289(3)	1/4	0.57(5)	1
O1	6*h*	0.1498(3)	0.4813(3)	1/4	1.00(15)	1
O2	6*h*	0.5808(3)	0.1198(4)	1/4	1.66(6)	1
O3	12*i*	0.3442(2)	0.0829(2)	0.0784(2)	1.15(4)	1
D1	4*e*	0	0	0.2058(23)	7.29(40)	1