Experimental report

29/06/2020

Proposal: EASY-475 **Council:** 4/2019

Title: An unprecedented hydride borate

Research area: Chemistry

This proposal is a new proposal

Main proposer: Nathalie KUNKEL

Experimental team:

Local contacts: Clemens RITTER

Samples: Sr5(BO3)3D

Instrument	Requested days	Allocated days	From	To
D2B	6	6	14/10/2019	15/10/2019

Abstract:

In search of new mixed-anionic hydrides, which are currently of great interest, we prepared an unprecedented strontium borate hydride compound. While the combination of borate and borohydride has been recently reported, the combination of borate and H- has, to the best of our knowledge, never been reported before.

Our preliminary results, including laboratory X-ray diffraction, solid state MAS NMR, vibrational spectroscopy and calculation suggests the sole presence of hydride next to borate.

However, due to low scattering power of hydride for X-rays, and to gain detailed structural information on position and occupation number, neutron diffraction studies are necessary.

Therefore, we apply for beam time to record a room temperature powder pattern of Sr5(BO3)3D at the high-resolution neutron powder diffractometer D2B. In order to avoid problems with the high neutron absorption cross section of natural boron (10B), we have prepared samples with isotopically pure 11B.

EXPERIMENTAL REPORT FOR PROPOSAL EASY-475

An unprecedented hydride borate

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

Borate hydrides as a new material class – Structure, computational studies and spectroscopic investigations on $Sr_5(BO_3)_3H$ and $Sr_5(^{11}BO_3)_3D$

Thomas Wylezich, Renaud Valois, Markus Suta, Alexander Mutschke, Clemens Ritter, Andries Meijerink, Antti J. Karttunen and Nathalie Kunkel

Chem. A. Eur. J., accepted, 10.1002/chem.202002273

Abstract of the manuscript:

The unprecedented borate hydride $Sr_5(BO_3)_3H$ and deuteride $Sr_5(^{11}BO_3)_3D$ crystallizing in an apatite-related structure are reported. Despite the presence of hydride anions, the compound decomposes only slowly in air. Doped with Eu^{2+}, it shows broad-band orange-red emission under violet excitation due to the $4f^65d$-$4f^7$ transition of Eu^{2+}. A number of characterization methods, including ^1H solid-state MAS NMR and vibrational spectroscopy together with quantum chemical calculations of the ^1H chemical shifts and vibrational spectra as well as X-ray and neutron powder diffraction, elemental analysis and luminescence spectroscopy of an Eu^{2+}-doped sample were applied to study the compound. The observed ^1H chemical shift is in good agreement with previously reported ^1H chemical shifts of ionic metal hydrides as well as with quantum chemical calculations and very different from ^1H chemical shifts usually found for hydroxide ions in similar materials. FT-IR and Raman spectroscopy of different samples containing ^1H, ^2H, ^{nat}B and ^{11}B combined with calculations unambiguously prove the absence of hydroxide ions and the sole incorporation of hydride ions into the borate. The orange-red emission obtained via doping with Eu^{2+} shows that the new compound class might be a promising host material for optical applications.

Experimental Report

Within this work, a fully substituted borate hydride (deuteride) $Sr_5(BO_3)_3H$ ($Sr_5(^{11}BO_3)_3D$) was obtained using a mechanochemical reaction between SrD_2 and carefully dried $Sr_3(BO_3)_2$. The borate deuteride crystallizes orthorhombically in the space group *Pnma* (No. 62), similar to its fluoride analogue, with a = 7.1982(3) Å, b = 14.1461(7) Å, c = 9.8215(4) Å and V = 1000.10(8) $Å^3$. The presence of hydride as well as the absence of hydroxide has been proven by several independent methods, including experimental ^1H MAS NMR spectroscopy and calculated chemical shifts as well as vibrational spectroscopy.

With the help of Dr. Clemens Ritter (Grenoble, ILL) we performed a neutron powder diffraction experiment at the high-resolution diffractometer D2b on the deuteride compound $Sr_5(^{11}BO_3)_3D$. A simultaneous refinement using X-ray and neutron data and the program package FullProf was carried out and the refined plot as well as the list of atomic parameters are listed in Figure 1 and Table 1.

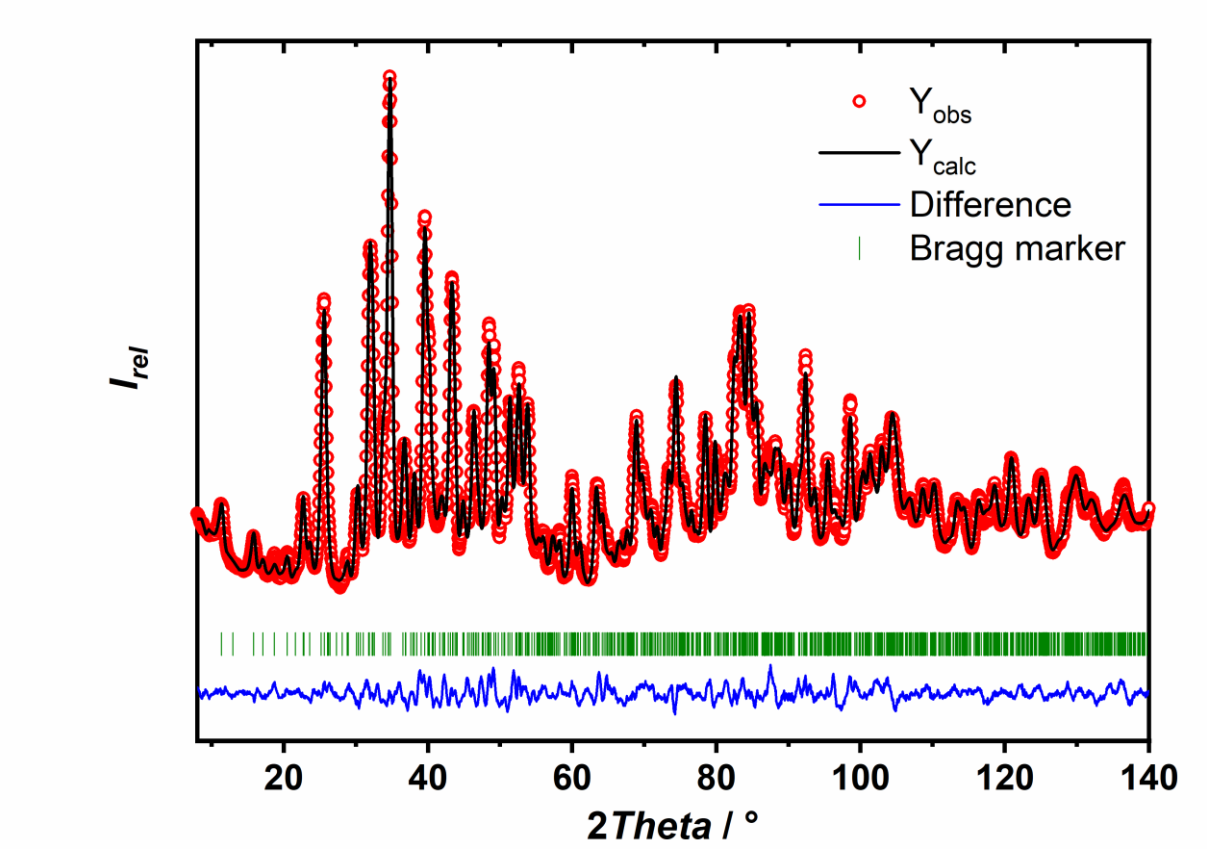

Figure 1: Rietveld refinement of the structural model for the neutron diffraction data of $Sr_5(^{11}BO_3)_3D$ measured at the D2B (ILL). *R*-values not corrected for background: R_p 2.09%, R_{wp} 2.67%, R_{exp} 2.59%, χ^2 1.06. Conventional *R*-values: R_p 7.28%, R_{wp} 8.23%, R_{exp} 8.00%, χ^2 1.06. R_B: 4.09%, $R_{f\text{-}factor}$: 2.37%.

Table S1: Refined lattice parameters and atomic parameters of the structural base model for $Sr_5(^{11}BO_3)_3D$ (*Pnma*) at 300 K obtained from powder neutron diffraction data.

$Sr_5(^{11}BO_3)_3D$		*a* = 7.1982(3) Å, *b* = 14.1461(7) Å, *c* = 9.8215(4) Å, *V* = 1000.10(8) Å^3				
Atom	Site	x	y	z	B_{iso}(Å^2)	s.o.f.
Sr3	8*d*	0.0234(5)	0.1108(2)	0.2531(5)	1.25(7)	1
O5	8*d*	0.0928(6)	0.5870(3)	0.1565(6)	1.40(7)	1
B1	8*d*	0.2072(6)	0.5382(3)	0.0607(5)	2.07(8)	1
Sr2	8*d*	0.2486(5)	0.6195(2)	0.3703(3)	0.84(7)	1
O2	8*d*	0.2734(7)	0.0700(3)	0.4342(5)	0.99(8)	1
O3	8*d*	0.2827(7)	0.0450(2)	0.1038(5)	0.75(6)	1
O4	4*c*	0.1184(12)	¼	0.0445(8)	1.87(15)	1
D	4*c*	0.1151(8)	¼	0.7466(8)	2.65(14)	1
O1	4*c*	0.2781(8)	¼	0.2528(5)	0.26(8)	1
B2	4*c*	0.2737(9)	¼	0.1134(6)	1.06(8)	1
Sr1	4*c*	0.2868(9)	¼	0.5191(4)	0.69(8)	1
O6	4*c*	0.4494(11)	¼	0.0428(7)	1.04(13)	1