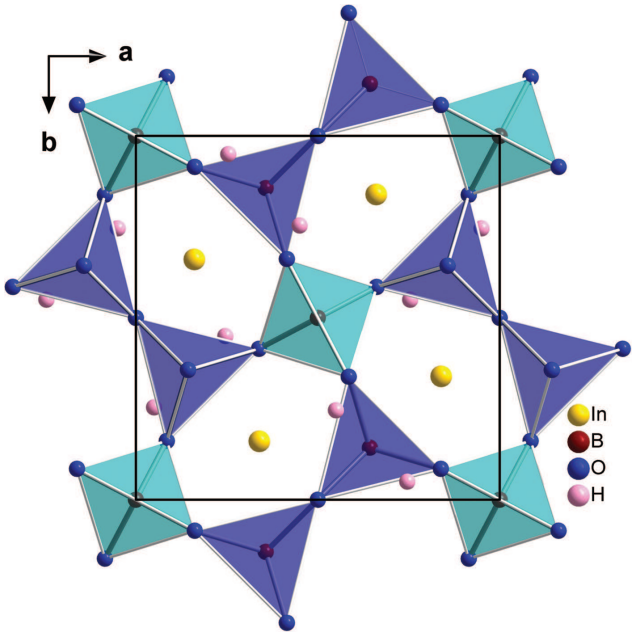
Daniela Vitzthum and Hubert Huppertz*

The crystal structure of $In_{1.2}B_3O_{5.6}(OH)_{1.4}$



https://doi.org/10.1515/ncrs-2018-0083
Received February 26, 2018; accepted March 27, 2018; available online April 12, 2018

Abstract

$In_{1.4}B_3O_{5.6}(OH)_{1.4}$, tetragonal, $P\bar{4}2_1m$ (no. 113), $a = 6.6969(9)$ Å, $c = 4.4865(9)$ Å, $V = 201.21(7)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0117$, $wR_{ref}(F^2) = 0.0297$, $T = 293(2)$ K.

CCDC no.: 434219

Source of material

In_2O_3 (99.9%, ChemPUR, Karlsruhe, Germany) and H_3BO_3 (99.5%, Carl Roth, Karlsruhe, Germany) were weighed in to an In:B ratio of approximately 1:2, then ground and enwrapped in molybdenum foil. Subsequently, the sample was prepared for a typical high-pressure multi-anvil experiment [5–7]. As soon as the maximum pressure of about 12.2 GPa was attained, the heating process started. 1500 °C was reached in 8 min, held for 6 min, then the heating was slowly downregulated to 1100 °C in 40 min. After the following decompression, the sample was freed from its surroundings revealing colorless crystals.

Table 1: Crystal collection and handling.

Crystal:	Prism, colorless
Size:	0.138 × 0.110 × 0.040 mm^3
Wavelength:	Mo K_α radiation ($\lambda = 0.71073$ Å)
μ:	6.962 cm^{-1}
Diffractometer, scan mode:	Bruker D8 Quest Kappa, Φ and ω-scans
$2\theta_{max}$, completeness:	37.9°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12876, 595, 0.0372
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 595
$N(param)_{refined}$:	39
Programs:	SHELX [1, 2], WinGX [3], Diamond [4]

Experimental details

For the refinement, the acentric, achiral, tetragonal space group $P\bar{4}2_1m$ was chosen (Flack-Parsons parameter = 0.056(7) based on 235 quotients [2]). The hydrogen atom H1 was positioned *via* DFIX option of the SHELX system. A refinement with a higher occupancy factor for H1 up to 0.5 and a corresponding reduction of the In ratio to 0.5 leading to the sum formula $InB_2O_5(OH)_2$ is possible but results in higher R values, GOOF and residual electron density.

Comment

By means of high-pressure synthesis, it was possible to obtain another borate compound that adopts the melilite structure. Melilite denominates a group of sorosilicates with the sum formula $(Ca,Na)_2(Mg,Al)_1(Si,Al)_2O_7$ [8] although a variety of different minerals and synthetic compounds with the general constitution $X_2ZT_2A_7$ (X = large cations, T and Z = smaller, tetrahedrally coordinated cations, A = anions) are counted among the melilite-family. As in the recently published first ternary melilite-type borate $Sc_{1.67}B_3O_7$ [9], in $In_{1.2}B_3O_{5.6}(OH)_{1.4}$ the Z and T positions are both occupied by boron atoms, which thus center Q^3 as well as Q^4 tetrahedra. In the *ab* plane, two Q^4 and three Q^3 tetrahedra are corner-linked to five-membered rings resulting in a flat borate layer. Between these parallel layers in the center of the five-membered rings, the square antiprismatically coordinated indium atoms are located. Due to charge neutrality reasons, the atom sites of

***Corresponding author: Hubert Huppertz,** Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 80-82, A-6020 Innsbruck, Austria, Europe, e-mail: hubert.huppertz@uibk.ac.at
Daniela Vitzthum: Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 80-82, A-6020 Innsbruck, Austria, Europe

Table 2: Wyckoff positions, site occupancy factors (S.O.F.), fractional atomic coordinates, and isotropic U_{iso} or equivalent isotropic U_{eq} displacement parameters (Å^2) for $In_{1.2}B_3O_{5.6}(OH)_{1.4}$.

Atom	Wyckoff	S.O.F.	*x*	*y*	*z*	U_{eq} (U_{iso} for H1)
In1	4*e*	0.6	0.66070(2)	0.16070(2)	−0.01085(4)	0.00787(7)
B1	2*b*	1	0	0	1/2	0.0053(3)
B2	4*e*	1	0.8570(2)	0.3570(2)	0.5398(4)	0.0056(2)
O1	4*e*	1	0.8566(2)	0.3566(2)	0.2226(3)	0.0056(2)
O2	2*c*	1	0	1/2	0.6732(4)	0.0077(3)
O3	8*f*	1	0.9150(2)	0.1619(2)	0.6857(2)	0.0063(2)
H1	8*f*	0.35	0.89(2)	0.12(2)	−0.13(3)	0.05(4)

the formally 3+ charged indium atoms cannot be fully occupied. Empty antiprisms give space to the hydrogen atoms in $In_{1.2}B_3O_{5.6}(OH)_{1.4}$, which were determined with a site occupancy factor of 0.35.

Acknowledgements: We thank Dr. Gunter Heymann and Dr. Klaus Wurst for the recording of and the support with the single-crystal data.

References

1. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
2. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
3. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
4. Brandenburg, K.: DIAMOND Ver. 3.2k. Crystal Impact GbR, Bonn, Germany (2012).
5. Huppertz, H.: Multianvil high-pressure/high-temperature synthesis in solid state chemistry. Z. Kristallogr. – CM **219** (2004) 330–338.
6. Walker, D.; Carpenter, M. A.; Hitch, C. M.: Some simplifications to multianvil devices for high pressure experiments. Am. Mineral. **75** (1990) 1020–1028.
7. Walker, D.: Lubrication, gasketing, and precision in multianvil experiments. Am. Mineral. **76** (1991) 1092–1100.
8. Warren, B. E.: The structure of melilite $(Ca, Na)_2(Mg, Al)_1(Si, Al)_2O_7$. Z. Kristallogr. – CM **74** (1930) 131–138.
9. Schmitt, M. K.; Ploner, K.; Hejny, C.; Huppertz, H.: High-pressure synthesis of the first ternary melilite-type compound $Sc_{1.67}B_3O_7$. Z. Anorg. Allg. Chem. **643** (2017) 1844–11848.