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Crystal structure of calcium nickel(II) (monohydrogenmonophosphate-dihydrogenmonoborate-monophosphate), $CaNi[BP_2O_7(OH)_3]$

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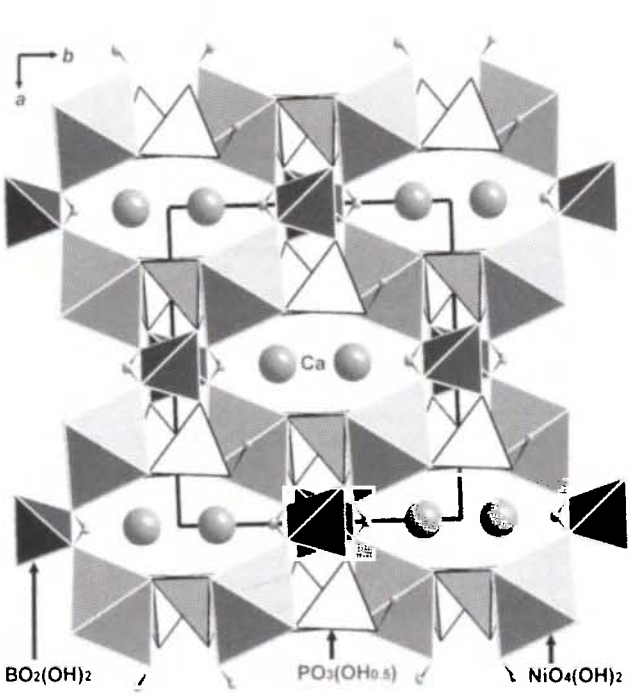

Abstract

$BCaH_3NiO_{10}P_2$, monoclinic, $C12/c1$ (no. 15), a = 10.2515(9) Å, b = 8.3364(5) Å, c = 9.175(1) Å, β = 116.34(4)°, V = 702.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.027, $wR_{ref}(F^2)$ = 0.077, T = 295 K.

Source of material

$CaNi[BP_2O_7(OH)_3]$ was synthesized under mild hydrothermal conditions during the investigation of the system CaO-NiO-B_2O_3-P_2O_5-H_2O. The reaction was carried out with a mixture of 0.2480 g $Ca(OH)_2$ (Aldrich, 95 %), 0.2500 g NiO (Alfa Aesar, 99 %), 0.4606 g B_2O_3 (Alfa Aesar, 99.98 %) and 2.3153 g H_3PO_4 (Merck, 85 %) in the molar ratio Ca:Ni:B:P = 1:1:4:6. The mixture was filled in a 10 ml Teflon-lined autoclave. The degree of filling was about 30 %. The autoclave was placed in the oven with a subsequent heating at 443 K for 8 days. The product was washed with water and dried at 333 K in air. The greenish crystals obtained are up to 0.1 mm in length. The chemical composition was confirmed by chemical analysis.

Discussion

In recent years considerable interest has been devoted to the synthesis and structural characterization of open framework materials with the aim of applications in ion exchangers, molecular sieves and catalysts [1]. Numerous open framework borophosphates have been synthesized with a prominent structural variety [2]. Focusing on hydrated nickel borophosphates only two compounds are known so far: $NaNi(H_2O)_2[BP_2O_8]\cdot H_2O$ [3] and $Ni_{1.5}Mg_{1.5}[B_3P_3O_{12}(OH)_6](H_2O)_6$ [4]. Our investigation on borophosphate systems with nickel and alkaline earth metals (Ca, Sr, Ba) led to two new borophosphates $CaNi[BP_2O_7(OH)_3]$ and $Ca_{0.5}Ni(H_2O)_2[BP_2O_8]\cdot H_2O$ [5].

The crystal structure of the title compound is an isotype of the Na-Fe [6], Na-Al [7], Na-Ga [8], Na-In [9], K-Ga [10], and Na-V [11] analogues. The anionic partial structure (oligomeric borophosphate unit) contains unbranched triple tetrahedral anions $[BP_2O_7(OH)_3]^{4-}$, built up by a dihydrogen borate tetrahedron $[BO_2(OH)_2]$ sharing common corners with two hydrogen phosphate tetrahedra $[PO_3(OH_{0.5})]$. The $NiO_4(OH)_2$ octahedra shares common O-corners with hydrogen phosphate and common $O_{(OH)}$-corners with hydrogen borate groups from the oligomeric unit $[BP_2O_7(OH)_3]^{4-}$. The condensation of oligomers with Ni octahedra results in a three-dimensional framework which contains elliptical channels running along [001]. The cross section of the channels is defined by eight-membered rings formed by four nickel octahedra, two hydrogen phosphate and two dihydrogen borate groups. Ca^{2+} ions are distributed within the channels. The Ni—O bond distances range from 2.02 Å – 2.09 Å, whereas the bond distances Ni—OH are increased to 2.44 Å. The bond distances P—O and B—O in the oligomeric borophosphate groups are similar to those in related borophosphates [6-11].

Table 1. Data collection and handling.

Crystal:	green prism, size 0.12 × 0.11 × 0.05 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	39.92 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7, φ/ω
$2\theta_{max}$:	67.42°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4130, 1176
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1111
$N(param)_{refined}$:	76
Programs:	SHELXS-97 [12], SHELXL-97 [13], DIAMOND [14]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	8f	0.505(5)	0.168(5)	0.094(5)	0.05(1)
H(2)	4d	¼	¼	½	0.4(1)

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca(1)	4*e*	0	0.13280(6)	¼	0.0196(2)	0.0136(2)	0.0204(3)	0	0.0126(2)	0
Ni(1)	4*c*	¼	¼	0	0.0106(2)	0.0067(2)	0.0092(2)	–0.00010(8)	0.0048(1)	0.00022(9)
P(1)	8*f*	0.28381(4)	0.43515(5)	0.32563(5)	0.0086(2)	0.0071(2)	0.0108(2)	–0.0003(1)	0.0044(2)	–0.0009(1)
B(1)	4*e*	0	0.5261(3)	¼	0.0090(9)	0.0070(9)	0.0094(9)	0	0.0035(8)	0
O(1)	8*f*	0.1154(1)	0.4117(2)	0.2573(2)	0.0090(5)	0.0088(5)	0.0157(6)	0.0006(4)	0.0056(4)	–0.0013(4)
O(2)	8*f*	0.1526(2)	0.1867(2)	0.5317(2)	0.0157(6)	0.0161(6)	0.0182(6)	–0.0020(5)	–0.0004(5)	0.0069(5)
O(3)	8*f*	0.1676(1)	0.1049(2)	0.1163(2)	0.0141(5)	0.0088(5)	0.0176(6)	0.0028(4)	0.0099(5)	0.0048(4)
O(4)	8*f*	0.3346(1)	0.3997(2)	0.1977(2)	0.0155(5)	0.0173(6)	0.0202(6)	–0.0061(5)	0.0121(5)	–0.0101(5)
O(5)	8*f*	0.4446(1)	0.1195(2)	0.1021(2)	0.0129(5)	0.0132(6)	0.0156(6)	0.0019(4)	0.0066(5)	0.0062(5)

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