Crystal structure of rubidium vanadium(III) *catena*-[monohydrogen-monoborate-bis(monophosphate)], $RbV[BP_2O_8(OH)]$

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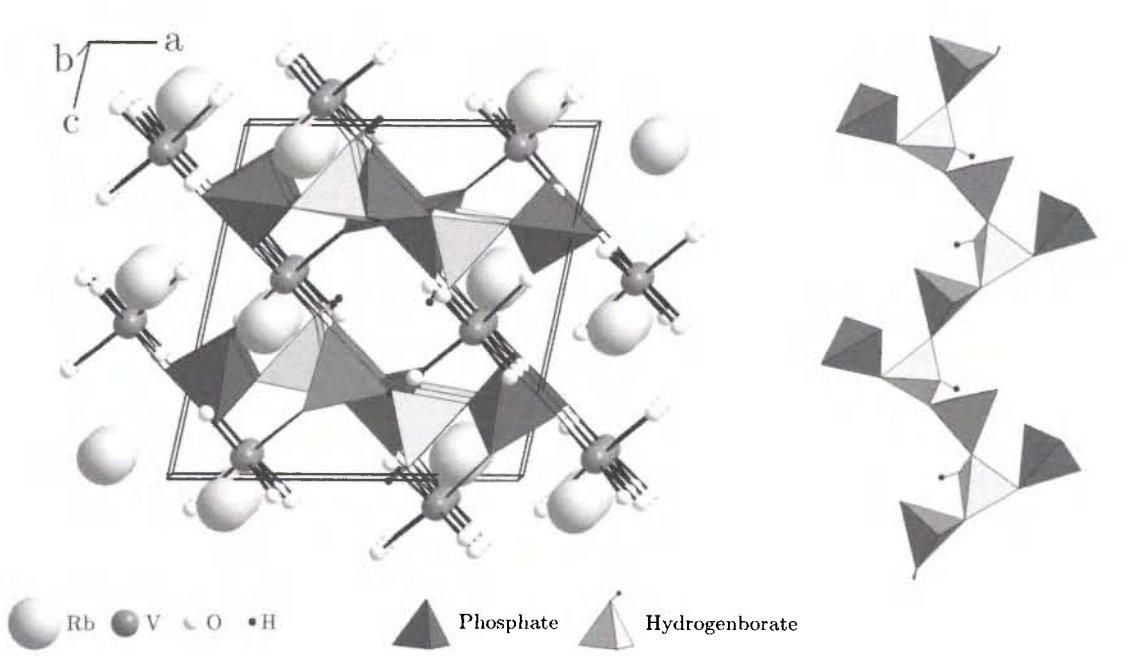

Abstract

BHO_9P_2RbV, monoclinic, $P12_1/c1$ (No. 14), $a = 9.3789(5)$ Å, $b = 8.3296(4)$ Å, $c = 9.6701(3)$ Å, $\beta = 102.0781(8)°$, $V = 738.7$ Å^3, $Z = 4$, $R_{gt}(F) = 0.100$, $wR_{ref}(F^2) = 0.111$, $T = 293$ K.

Source of material

$RbV[BP_2O_8(OH)]$ was prepared under mild hydrothermal conditions from mixtures of a 50 wt.% aqueous solution of RbOH, VCl_3, H_3BO_3 and H_3PO_4 (85%) in the molar ratio 1:1:1:2 (conc. solution, pH 0-1, 7.5 g – 16 g total weight). The syntheses were carried in teflon autoclaves (T = 438 K, three days) under autogenous pressure. The chemical composition was confirmed by ICP-AES and EDX analyses, the water content was determined by thermogravimetric measurements. FT-IR spectroscopic investigations show the presence of OH groups and prove the absence of hydrogen bonds.

Discussion

$RbV[BP_2O_8(OH)]$ (hydrated borophosphate, B:P < 1; [1]) is an isotype of $RbFe[BP_2O_8(OH)]$ [2] and $CsFe[BP_2O_8(OH)]$ [3]. The anionic partial structure contains open-branched vierer-einfach chains $[BP_2O_8(OH)]^{4-}$, which are formed by alternating hydrogenborate and phosphate tetrahedra sharing common corners (figure right). Bond lengths and angles within the anionic chains are consistent with related borophosphates (see [1-3] and refs. therein). V^{3+} is in an octahedral coordination by oxygen sites ($VO_5(OH)$) of three neighbouring tetrahedral chains. By this, an overall three-dimensional linkage of tetrahedra and octahedra ist established. Rb^+ is irregularly coordinated by nine oxygen ligands and one OH group. $RbV[BP_2O_8(OH)]$ is the second known borophosphate besides $CsV_3(H_2O)_2[B_2P_4O_{16}(OH)_4]$ [4] with vanadium in the oxidation state +3.

Table 1. Data collection and handling.

Crystal:	green, needle, size 0.01 × 0.03 × 0.12 mm
Wavelength:	Mo K_α radiation (0.71070 Å)
μ:	83.49 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7-CCD, $0 < \phi < 360°$, $\Delta\phi = 0.5°$, 60 -ω-scan, $\Delta\omega = 0.5°$, $\chi = 90°$
$2\theta_{max}$:	59.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9165, 1672
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1584
$N(param)_{refined}$:	131
Programs:	SHELXS-97 [5], SHELXL-97 [6], DIAMOND [7]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.36(1)	0.58(2)	0.00(1)	0.06(5)

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}
Rb	4*e*	0.1882(1)	0.6016(1)	0.56009(9)	0.0300(5)	0.0231(5)	0.0239(5)	-0.0053(4)	0.0041(4)	-0.0063(4)
V	4*e*	0.2107(1)	0.1502(2)	0.4338(1)	0.0056(6)	0.0077(7)	0.0067(7)	-0.0007(5)	0.0010(5)	0.0004(5)
B	4*e*	0.334(1)	0.559(1)	0.1957(9)	0.012(5)	0.008(5)	0.006(4)	0.001(4)	0.000(3)	-0.001(3)
P(1)	4*e*	0.0740(2)	0.4353(2)	0.2075(2)	0.005(1)	0.007(1)	0.006(1)	-0.0002(8)	-0.0002(7)	0.0014(7)
P(2)	4*e*	0.4220(2)	0.2406(2)	0.2171(2)	0.0050(9)	0.008(1)	0.008(1)	0.0006(8)	0.0001(7)	0.0004(7)
O(1)	4*e*	0.0761(6)	0.0085(6)	0.3073(5)	0.007(3)	0.011(3)	0.012(3)	-0.002(2)	0.002(2)	-0.003(2)
O(2)	4*e*	0.0891(6)	0.3343(6)	0.0805(5)	0.016(3)	0.016(3)	0.008(3)	0.000(2)	0.006(2)	-0.003(2)
O(3)	4*e*	0.1059(6)	0.3426(6)	0.3463(5)	0.012(3)	0.008(3)	0.009(3)	0.000(2)	-0.001(2)	0.001(2)
O(4)	4*e*	0.1874(5)	0.5768(6)	0.2232(5)	0.008(3)	0.009(3)	0.011(3)	-0.001(2)	0.000(2)	-0.001(2)
O(5)	4*e*	0.3168(7)	0.5496(7)	0.0384(6)	0.011(3)	0.010(3)	0.014(3)	-0.004(2)	0.001(2)	-0.002(2)
O(6)	4*e*	0.3480(6)	0.1288(6)	0.3027(5)	0.011(3)	0.008(3)	0.020(3)	0.001(2)	0.009(2)	0.003(2)
O(7)	4*e*	0.3658(6)	0.2223(6)	0.0597(5)	0.015(3)	0.013(3)	0.009(3)	0.003(2)	-0.001(2)	-0.001(2)
O(8)	4*e*	0.4111(6)	0.4171(6)	0.2643(5)	0.014(3)	0.009(3)	0.009(3)	0.001(2)	0.001(2)	0.000(2)
O(9)	4*e*	0.5887(5)	0.2059(6)	0.2510(5)	0.004(3)	0.010(3)	0.014(3)	0.003(2)	0.001(2)	0.003(2)

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