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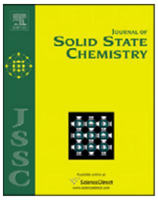

$K_3Ln[OB(OH)_2]_2[HOPO_3]_2$ (Ln=Yb, Lu): Layered rare-earth dihydrogen borate monohydrogen phosphates

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ABSTRACT

Two isotypic layered rare-earth borate phosphates, $K_3Ln[OB(OH)_2]_2[HOPO_3]_2$ (Ln=Yb, Lu), were synthesized hydrothermally and the crystal structures were determined by single-crystal X-ray diffraction ($R\bar{3}$, $Z=3$, Yb: $a=5.6809(2)$ Å, $c=36.594(5)$ Å, $V=1022.8(2)$ Å^3, Lu: $a=5.6668(2)$ Å, $c=36.692(2)$ Å, $V=1020.4(1)$ Å^3). The crystal structure can be described in terms of stacking of Glaserite-type slabs consisting of LnO_6 octahedra interlinked by phosphate tetrahedra and additional layers of $[OB(OH)_2]^-$ separated by K^+ ions. Field and temperature dependent measurements of the magnetic susceptibility of the Yb-compound revealed Curie–Weiss paramagnetic behavior above 120 K ($\mu_{eff}=4.7\ \mu_B$). Magnetic ordering was not observed down to 1.8 K.

1. Introduction

Recent research in the field of borophosphates has revealed that mild hydrothermal route is a promising synthetic approach in the exploration of the systems M_xO_y–B_2O_3–P_2O_5–(H_2O) (M=metal). This strategy has already resulted in numerous compounds with new crystal structures [1]. So far, this route of preparation was restricted to M representing main-group and/or transition elements. In contrast, our efforts are now focused on systems containing rare-earth elements. Up to now, the only reported examples for a rare-earth intermediates are given by the general formula $Ln_7O_6[BO_3][PO_4]_2$, (Ln=rare-earth element), prepared by solid state reaction at high temperatures [2].

Herein, we report on the synthesis and structure as well as physical characterization of two new hydrated rare-earth borate phosphates, which are obtained for the first time under mild hydrothermal synthesis conditions.

2. Experimental details

2.1. Hydrothermal synthesis

$K_3Yb[OB(OH)_2]_2[HOPO_3]_2$: Initially, 0.591 g Yb_2O_3 was dissolved in 1 mL concentrated HCl. Then, 1.8334 g $K_2B_4O_7\cdot 4H_2O$, 3.658 g K_2HPO_4 and 4 mL H_2O (molar ratio of K:Yb:B:P=18:1:8:7) were mixed with the above solution, and the pH value was adjusted to 7 using 0.75 mL concentrated HCl. All starting materials used in the experiments were of analytical grade and were used without further purification. The mixture was transferred to a Teflon vessel with a cover, which was placed in a steel autoclave. The synthesis was conducted at 453 K for 5 days. After that time the autoclave was directly taken out of the hot oven. The product was filtered and washed with distilled water several times and dried at 323 K for 8 h. $K_3Lu[OB(OH)_2]_2[HOPO_3]_2$: 1.7340 g $LuCl_3\cdot 6H_2O$, 1.8336 g $K_2B_4O_7\cdot 4H_2O$ and 3.6372 g K_2HPO_4 were dissolved in 4 mL water and the pH value was adjusted to 6–7 using concentrated HCl. The suspension was transferred into a Teflon autoclave and maintained at 453 K for 3 days. Finally, the autoclave was directly taken out of the oven. Crystals settled at the bottom of the autoclave were washed with distilled water several times and dried at 323 K for 8 h.

2.2. Characterization

The chemical compositions of the products were determined using both inductively coupled plasma-optical emission spectrometry (ICP-OES) on a VARIAN Vista RL instrument and energy-dispersive X-ray spectroscopy (EDXS) carried out on a PHILIPS XL 30. ICP-OES results show that the molar ratio is K:Yb:B:P=2.45:1:1.47:1.78 (calc: 3:1:2:2) for $K_3Yb[OB(OH)_2]_2[HOPO_3]_2$, which suggests the presence of impurities not detected by powder X-ray diffraction (PXRD, Fig. S2). EDXS on three different crystals gave an average

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molar ratio of K:Yb:P=2.83:1:2.31. For $K_3Lu[OB(OH)_2]_2[HOPO_3]_2$ a molar ratio of K:Lu:B:P=2.95:1:1.93:1.97 is determined by ICP-OES, which is close to the ratio derived from single-crystal structure determination.

Thermal investigations (DTA/TG) were carried out in argon atmosphere with heating rates of 5 K/min up to 1273 K (NETZSCH STA 449). The FT-IR spectrum was recorded at room temperature using a Spectrum 100 Optical (PerkinElmer) with universal ATR sampling accessory. The magnetization measurements were performed on a SQUID-magnetometer (Quantum Design, MPMS XL-7) in the temperature range of 1.8–400 K using various external magnetic fields.

2.3. *Crystal structure determination*

Hexagonal platelets (Fig. S1) of the isotypic compounds $K_3Ln[OB(OH)_2]_2[HOPO_3]_2$ (Ln=Yb, Lu) were selected under a light microscope. Single-crystal X-ray diffraction data were collected on a Rigaku AFC7 (Mercury CCD detector) diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å) at a temperature of 295 K. The isotypic structures were solved by direct methods and refined using the programs SHELXS-97 [3] and SHELXL-97 [3] included in the program suite WinGX [4]. The crystal structure of $K_3Lu[OB(OH)_2]_2[HOPO_3]_2$ was refined as a twin. The lattice parameters were determined by PXRD using LaB_6 as internal standard [5]. The final refinement by full-matrix least-squares methods led to: $K_3Yb[OB(OH)_2]_2[HOPO_3]_2$, M=603.95 g/mol, trigonal, $R\overline{3}$ (No. 148), a=5.6809(2) Å, c=36.594(5) Å, V=1022.8(2) Å^3, Z=3, 2119 measured and 757 independent reflections, $R1$=0.023 and $wR2$=0.054 for all data and $K_3Lu[OB(OH)_2]_2[HOPO_3]_2$, M=605.9 g/mol, trigonal, $R\overline{3}$, (No. 148), a=5.6668(2) Å, c=36.692(2) Å, V=1020.4(1) Å^3, Z=3, 3185 measured and 789 independent reflections, $R1$=0.027 and $wR2$=0.050 for all data. Further details are summarized in Table 1. Atomic positions and displacement parameters for $K_3Yb[OB(OH)_2]_2[HOPO_3]_2$ are given in Table 2. The crystallographic data were deposited at FIZ Karlsruhe under the CSD number 422902 ($K_3Yb[OB(OH)_2]_2[HOPO_3]_2$) and 422903 ($K_3Lu[OB(OH)_2]_2[HOPO_3]_2$).

3. Results and discussion

3.1. *Crystal structure*

Since both crystal structures are isostructural only the Yb-compound shown in Fig. 1 is discussed in detail. Ytterbium exhibits an octahedral coordination with a unique Yb–O distance of 2.202(2) Å (cf. selected bond lengths in Table 3) and two slightly different O–Yb–O angles of 88.2° and 91.8° (site symmetry C_{3i}). Phosphorous is in a distorted tetrahedral coordination of oxygen. Three corners of each tetrahedron are shared with three YbO_6 octahedra, and the corresponding P–O1 distances amount to 1.530(2) Å (3 ×, P site symmetry 3). A longer distance (1.551(4) Å) is observed for the remaining vertex (O2). These two types of polyhedra form a common 2D arrangement characteristic for the mineral Glaserite (Aphthitalite) [6], $K_3Na(SO_4)_2$. This structure type is adopted by a number of rare-earth compounds with the general formula $A_3Ln(XO_4)_2$ (A=Na, K, Ln=rare-earth element, X=P, V, As). The Glaserite-type layers can show different degrees of distortion [7]. The terminal P–O distance in the crystal structure of the Glaserite analog $K_3Lu(PO_4)_2$ [8] amounts to 1.505 Å and is shorter than the distance to the bridging oxygen atoms reflecting a general trend in the crystal chemistry of phosphates [9]. The three short O2 · · · O3 distances

Table 2

Fractional atomic coordinates and equivalent displacement parameters (Å^2) for $K_3Yb[OB(OH)_2]_2[HOPO_3]_2$.

Atom	Wyckoff position	x	y	z	U_{eq}
Yb1	3*a*	0	0	0	0.011(1)
K1	3*b*	1/3	2/3	1/6	0.022(1)
K2	6*c*	1/3	2/3	0.0574 (1)	0.024(1)
P1	6*c*	2/3	1/3	0.0468(1)	0.010(1)
B1	6*c*	0	0	0.1159 (2)	0.018(1)
O1	18*f*	0.3713(4)	0.1840(5)	0.0336 (1)	0.019(1)
O2	6*c*	2/3	1/3	0.0891(1)	0.015(1)
O3	18*f*	0.2093(5)	0.2637(5)	0.1167 (1)	0.023(1)

Table 1

Crystal structure data and refinement parameters for $K_3Ln[OB(OH)_2]_2[HOPO_3]_2$ (Ln=Yb, Lu).

Empirical formula	$B_2\ K_3Yb\ O_{14}\ P_2\ H_6$	$B_2\ K_3\ Lu\ O_{14}\ P_2\ H_6$[a]
Formula weight (g/mol)	603.95	605.9
Temperature (K)	295	295
Crystal size (mm^3)	0.080 × 0.080 × 0.010	0.065 × 0.065 × 0.008
Radiation (Å)	Mo $K\alpha$, 0.71073	Mo $K\alpha$, 0.71073
Crystal system, space group	Trigonal, $R\overline{3}$ (No. 148)	Trigonal, $R\overline{3}$ (No. 148)
Unit cell parameters [b]	a=5.6809(2) Å	a=5.6668(2) Å
	c=36.594(5) Å	c=36.692(2) Å
	V=1022.8(2) Å^3	V=1020.4(1) Å^3
Z	3	3
Calculated density ρ_{calc} (g/cm^3)	2.942	2.958
Absorption coefficient μ (mm^{-1})	8.079	8.479
F(0 0 0)	855	858
θ range for data collection	3.34° to 32.08°	3.33° to 32.23°
Limiting indices	$-8 \le h \le 6, -4 \le k \le 6, -52 \le l \le 53$	$-6 \le h \le 8, -8 \le k \le 6, -52 \le l \le 52$
Reflections collected/unique	2119/757 [R(int)=0.0270]	3185/789 [R(int)=0.0373]
Goodness-of fit on F^2	1.067	1.076
$R1$,$wR2$ [$I > 2\sigma(I)$]	0.0213, 0.0534	0.0238, 0.0497
$R1$,$wR2$ (all data)	0.0227, 0.0536	0.0267, 0.0504
Largest diff. peak and hole	0.838 and −1.412 e/Å^3	0.967 and −2.142 e/Å−3

[a] $K_3Lu[OB(OH)_2]_2[HOPO_3]_2$ refined as twin with 110/0-10/001 matrix and BASF=0.53.

[b] Refined from X-ray powder diffraction pattern with LaB_6 as internal standard using the program WinCSD [5].