$NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$: A Novel Open-Framework Borophosphate and its Reversible Dehydration to Microporous Sodium Zincoborophosphate $Na[ZnBP_2O_8]\cdot H_2O$ with CZP Topology

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Abstract: Crystals of $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$ were grown under mild hydrothermal conditions at 170 °C. The crystal structure (solved by X-ray single-crystal methods: hexagonal, $P6_122$ (no. 178), $a = 946.2(2)$, $c = 1583.5(1)$ pm, $V = 1227.8(4)\cdot 10^6$ pm^3, $Z = 6$) exhibits a chiral octahedral-tetrahedral framework related to the CZP topology and contains helical ribbons of corner-linked borate and phosphate tetrahedra. Investigation of the thermal behavior up to 180 °C shows a (reversible) dehydration process; this leads to the microporous compound $Na[ZnBP_2O_8]\cdot H_2O$, which has the CZP topology. The crystal structure of $Na[ZnBP_2O_8]\cdot H_2O$ was determined by X-ray powder diffraction by using a combination of simulated annealing, lattice-energy minimization, and Rietveld refinement procedures (hexagonal, $P6_122$ (no. 178), $a = 954.04(2)$, $c = 1477.80(3)$ pm, $V = 1164.88(5)\cdot 10^6$ pm^3, $Z = 6$). The essential structural difference caused by the dehydration concerns the coordination of Zn^{2+} changing from octahedral to tetrahedral arrangement.

Keywords: boron · microporosity · phosphates · reversible dehydration · solid-state structures · zeolite analogues

Introduction

Our recent research on compounds with framework structures[1] is focussed on borophosphates (intermediate phases in systems M_xO_y-B_2O_3-P_2O_5-(H_2O)).[2] Although systematic investigations on borophosphates have started only in the last few years,[3] a broad spectrum of new compounds has already been characterized with various anionic partial structures, such as oligomeric units,[4] chains,[3, 5] ribbons,[6] layers,[7] and three-dimensional frameworks.[8] Systematic treatments of the structural chemistry of borophosphates have also been approached.[2] In relation to microporous and zeolite-analogous systems such as alumosilicates,[9] aluminium/alumophosphates,[10] substituted variants,[11] and gallium/gallo-[12] and zincophosphates,[13] we have succeeded in characterizing new open-framework structures based on boro- and zincoborophosphates. With the syntheses of $A[ZnBP_2O_8]$ ($A = K^+$, NH_4^+, Rb^+, Cs^+) a new class of compounds with tetrahedral frameworks has been realized, whose topologies display a close relationship to alumosilicates (feldspar family and gismondine).[14] A chiral octahedral-tetrahedral framework related to the CZP topology[15] is present in the crystal structures of compounds $M^IM^{II}(H_2O)_2[BP_2O_8]\cdot yH_2O$ (M^I: Li, Na, K; M^{II}: Mn, Fe, Co, Ni, Zn; y: 0.5, 1),[2b, 6a] which contain helical ribbons of corner-linked borate and phosphate tetrahedra. Here, we report on the crystal structure of $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$, which shows a remarkable thermal behavior up to 180 °C. $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$ reversibly releases (and reabsorbs) water, a process which is accompanied by a change of Zn^{II} coordination as the essential structural consequence. The dehydrated compound ($Na[ZnBP_2O_8]\cdot H_2O$) is characterized by a microporous, chiral tetrahedral framework of CZP topology.

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Results and Discussion

$NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$: The crystal structure of $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$ reveals an infinite one-dimensional anionic partial structure. The condensation of BO_4 and PO_4 tetrahedra through common vertices leads to tetrahedral

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ribbons of $^1_\infty\{[BP_2O_8]^{3-}\}$, which are arranged around 6_1 screw axes to form helices (Figure 1). The helical ribbons are built up from four-membered rings of tetrahedra in which BO_4 and PO_4 groups alternate. Each BO_4 tetrahedron is joined to the adjacent four-membered rings of PO_4 tetrahedra along the ribbon in such a way that all vertices of the BO_4 groups participate in bridging functions with PO_4 tetrahedra. The phosphate groups occupy the borders of the ribbons with two terminal oxygen atoms, which act as ligands to complete the coordination sphere around Zn^{2+}.

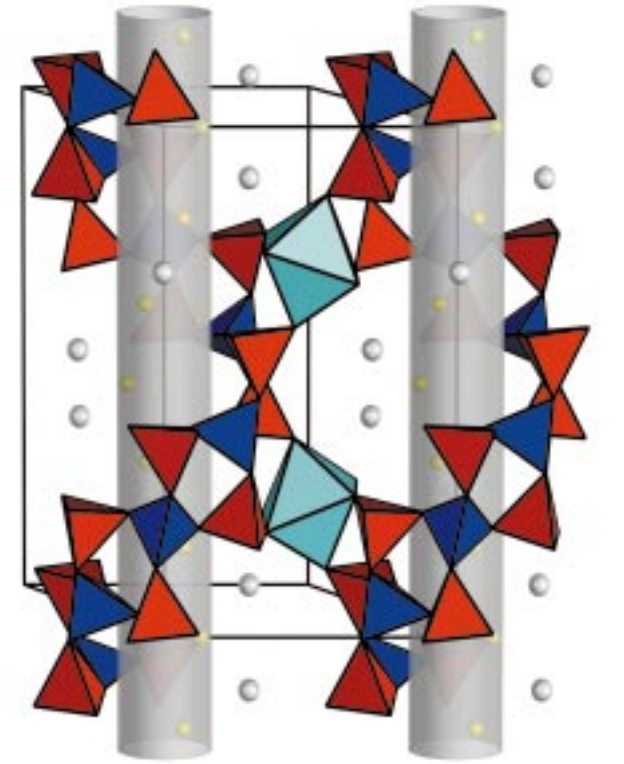

Figure 1. Linkage of borophosphate helices in the crystal structure of the hydrated phase $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$ through $ZnO_4(H_2O)_2$ octahedra (BO_4 tetrahedra: blue, PO_4 tetrahedra: red, Na^+: grey spheres, H_2O in the helical channels: yellow spheres, Zn^{II} octahedral: turquoise). For further details see text.

Abstract in German: *$NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$ wurde unter milden hydrothermalen Bedingungen bei 170 °C dargestellt. Die Kristallstruktur (Einkristalldaten, hexagonal, $P6_122$ (Nr. 178), $a = 946.2(2)$, $c = 1583.5(1)$ pm, $V = 1227.8(4)\cdot 10^6$ pm^3, $Z = 6$) enthält einen makromolekularen Anionenverband aus eckverknüpften Borat- und Phosphat-Tetraedern, die sich um 6_1-Schraubenachsen zu Helices anordnen. Die Verknüpfung der Anionenteilstruktur über gemeinsame Ecken mit Zn^{II}-Oktaedern führt zu einem dreidimensionalen Gerüst, dessen Topologie derjenigen des CZP-Types nahe verwandt ist. Thermische Untersuchungen bis 180 °C belegen einen (reversiblen) Dehydratisierungsprozess, der zur mikroporösen Verbindung $Na[ZnBP_2O_8]\cdot H_2O$ mit CZP-Topologie führt. Die Kristallstruktur von $Na[ZnBP_2O_8]\cdot H_2O$ wurde aus Röntgenpulverdaten über den kombinierten Einsatz von Methoden der Gitterenergie-Minimierung, Simulated Annealing und Rietveld-Verfeinerungen aufgeklärt (hexagonal, $P6_122$ (Nr. 178), $a = 954.04(2)$, $c = 1477.80(3)$ pm, $V = 1164.88(5)\cdot 10^6$ pm^3, $Z = 6$). Die durch den Dehydratisierungsprozess verursachte wesentliche strukturelle Änderung betrifft die Umgebung von Zn^{2+}, dessen Koordinationszahl von sechs (oktaderisch) auf vier (tetraedrisch) verringert wird.*

The free loops of the borophosphate helices are occupied by Na^+, which are fixed by an irregular arrangement of eight [6+2] oxygen atoms from adjacent phosphate groups (O3, O5) and water molecules ($O2_{H_2O}$, $O6_{H_2O}$). A double helix $^1_\infty\{Na[BP_2O_8]^{2-}\}$ is completed; it forms a central channel running along the 6_1 screw axis, which is filled with water molecules ($O6_{H_2O}$) resulting in the formula $^1_\infty\{Na[BP_2O_8]^{2-}\cdot H_2O\}$. The water molecules form hydrogen bonds ($O6_{H_2O}\cdots O6_{H_2O} = 293$ pm) with each other along the helix. The Zn^{2+} ion is coordinated by the oxygen atoms of PO_4 groups (O3, O5) and water molecules ($O2_{H_2O}$); this results in octahedral coordination, $Zn(O_p)_4(O_{H_2O})_2$.

The remarkable organization of the crystal structure of $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$ can be recognized in a view along the *c* axis (Figure 2, left), which shows the arrangement in radial shells: central $O6_{H_2O}$ helix (diameter ~254 pm), B helix (diameter ~502 pm), P helix (diameter ~640 pm), Na helix (diameter ~633 pm), followed by a helix of coordination water $O2_{H_2O}$ (diameter ~809 pm), and finally a Zn helix (diameter ~946 pm).

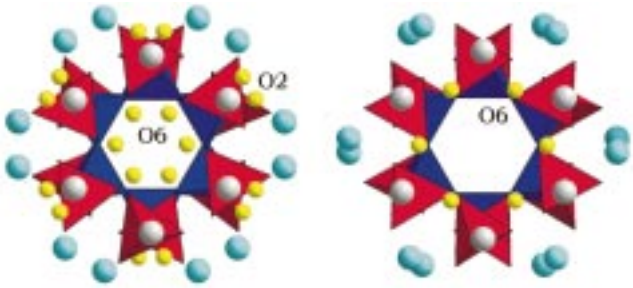

Figure 2. Sections of the crystal structure of the hydrated phase $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$ (left) and the dehydrated phase $Na[ZnBP_2O_8]\cdot H_2O$ (right) as viewed along the hexagonal *c* axis (BO_4 tetrahedra: blue, PO_4 tetrahedra: red, Na^+: grey spheres, H_2O: yellow spheres, Zn^{2+}: turquoise spheres).

The helical tetrahedral ribbons are linked by $ZnO_4(H_2O)_2$ coordination octahedra, giving a chiral octahedral-tetrahedral framework related to the CZP topology (IZA structure designation CZP), which has been previously observed in the crystal structures of $NaZnPO_4\cdot H_2O$[16] and its cobalt-substituted[17] variant (tetrahedral frameworks). In comparison to these crystal structures, boron in the title compound replaces the position of Zn1 in $NaZnPO_4\cdot H_2O$.

$Na[ZnBP_2O_8]\cdot H_2O$: The crystal structure of the dehydrated phase $Na[ZnBP_2O_8]\cdot H_2O$ exhibits mainly differences in Zn^{2+} and Na^+ coordination due to the release of H_2O ligands (coordination water $O2_{H_2O}$ in the crystal structure of $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$). With respect to the hydrated phase the unit cell has a contraction in volume of 5%. This amount of

shrinkage is achieved from the reduction of the *c* lattice parameter by 7%, while the hexagonal basis is slightly enlarged (see Tables 1 and 4 in the Experimental Section).

The octahedral coordination of Zn^{2+} (hydrated phase) changes to tetrahedral environment (dehydrated phase) because of the release of the Zn-coordinating $O2_{H_2O}$ (Figure 3). The coordination number of Na^+ at the same time decreases from [6+2] to [6]. This change in coordination is only affected by minor translations of the remaining oxygen positions. Besides the loss of $O2_{H_2O}$ the major structural change concerns the displacement of the water molecules $O6_{H_2O}$, which are shifted remarkably out of positions inside the channels towards the inner walls; this results in nearly empty channels and the formation of a microporous phase $Na[ZnBP_2O_8]\cdot H_2O$ (Figure 2, right).

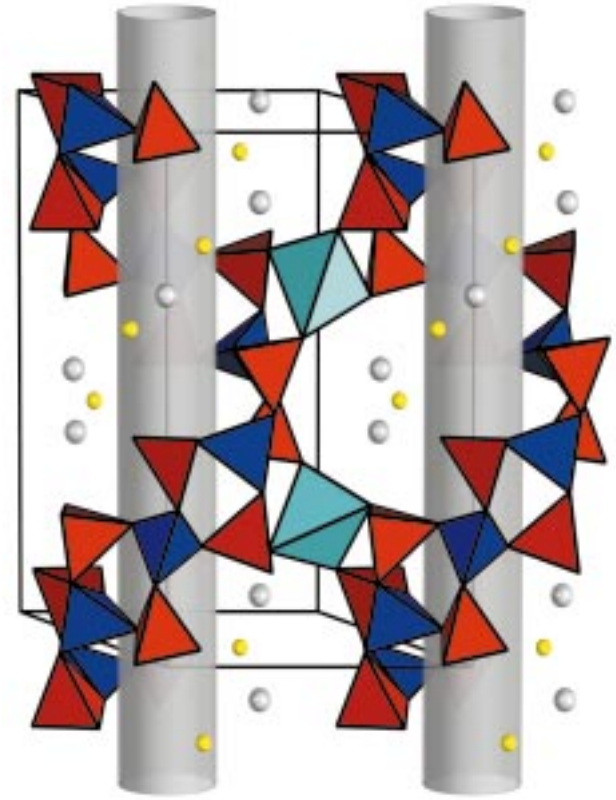

Figure 3. Linkage of borophosphate helices in the crystal structure of the dehydrated phase $Na[ZnBP_2O_8]\cdot H_2O$ through ZnO_4 tetrahedra (BO_4 tetrahedra: blue, PO_4 tetrahedra: red, Na^+: grey spheres, H_2O in the helical channels: yellow spheres, Zn^{II} tetrahedral: turquoise). For further details see text.

Experimental Section

Synthesis and analytical characterization: $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$ was prepared under mild hydrothermal conditions in teflon autoclaves (internal volume 20 mL). For this $ZnCl_2$ (1.05 g), $Na_2B_4O_7\cdot 10H_2O$ (1.46 g), and $Na_2HPO_4\cdot 2H_2O$ (4.83 g) (molar ratio 2:1:7) were heated at 80 °C in demineralized water (10 mL) and treated under stirring with 37% HCl (5 mL), until the components were completely dissolved. The clear solution was concentrated to about 12 mL by heating to give a highly viscous gel (pH 1), which then was transferred to a teflon autoclave (degree of filling about 55%) and stored at a temperature of 170 °C for periods up to two weeks. The crystalline reaction products were separated from the mother liquor by vacuum filtration, washed with demineralized water, and dried at 60 °C. Single crystals (hexagonal bipyramids) were grown under these conditions to a size up to 0.6 mm. Analytical characterizations carried out by using energy dispersive X-ray analyses (SEM JEOL JSM 6400, EDX-System Link ISIS 300) and atomic absorption spectrometry (Perkin–Elmer AS 4000) resulted in a molar ratio of sodium:zinc:boron:phosphorous of 1:1:1:2. X-ray powder investigations identified the compound to be a member of the isotypic series $M^{I}M^{II}(H_2O)_2[BP_2O_8]\cdot yH_2O$ (M^{I}: Li, Na, K; M^{II}: Mn, Fe, Co, Ni, Zn; *y*: 0.5, 1).[2b, 6a]

Thermal investigations and identification of dehydrated phases: Difference-thermoanalytical/thermogravimetric studies on $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$ up to temperatures of 800 °C were carried out on a Netzsch 409 TG/DTA analyzer (heating rate 5 K min^{-1}, system open to air, corundum crucibles) and indicated a dehydration process running over two distinct stages. In the first step (105–180 °C), two moles of H_2O per formula unit are released corresponding to a weight loss of 9.98% (calculated weight loss 10.48%). Further weight loss of 3.91% between 185 and 347 °C is consistent with the release of most of the remaining H_2O (maximum one mole, calculated weight loss 5.24%). Powder-diffraction investigations of the reaction product after the DTA/TG experiment (maximum temperature 800 °C) indicated the presence of an amorphous solid.

After the first dehydration step the solid material obtained has a perfect X-ray powder pattern that could be used for a successful structure determination (see next section and Figure 5 later). The dehydrated phase $Na[ZnBP_2O_8]\cdot H_2O$ is already (partially) rehydrated to $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$ during cooling down inside the TA equipment (system open to air) and by keeping the TA crucible at room temperature for a period of only one hour before starting the next heating experiment. Figure 4 displays two successive DTA/TG measurements ($T_{max} = 165$ °C, heating rate 3 K min^{-1}, system open to air); the first heating run (green lines) exhibits a weight loss of 9.98% (calculated 10.48%) and already shows a slight increase of weight during the cooling process. The weight loss during the second heating experiment (dashed blue line) is only 7.93%. This lower value is evidently caused by incomplete rehydration of the sample within the small TA container (only one hour at air at room temperature; small free surface area (diameter of the TA container)). A complete rehydration is obtained by exposing the powdered, dehydrated phase to moist air over a period of 12 hours (see section on "Rehydrated phase").

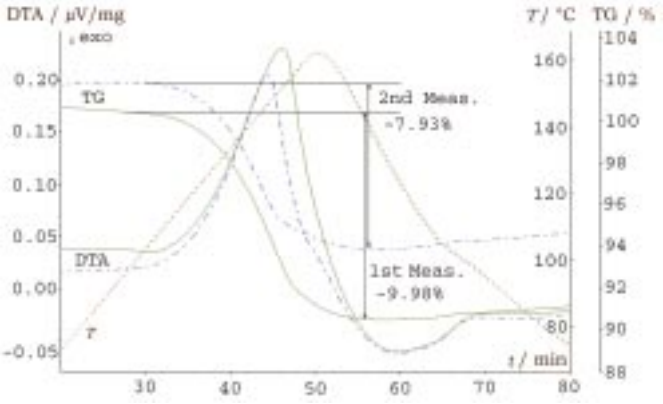

Figure 4. Two successive DTA/TG measurements (Netzsch, heating rate 3 K min^{-1} (red line: temperature), system open to air, $T_{max} = 165$ °C). First cycle (green lines), second cycle (dashed blue lines). For further details see text.

Crystal structure determinations

Hydrated phase—single-crystal structure analysis: A suitable single crystal of $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$ was investigated by taking rotation and Weissenberg photographs ($Cu_{K\alpha}$ radiation); these showed the reflection pattern of a primitive hexagonal lattice. The interference conditions—reflections (*000l*) only for $l = 6n$—suggested the possible space groups $P6_1$, $P6_5$, $P6_122$, and $P6_522$. The hexagonal unit-cell parameters were obtained on the basis of 52 centered reflections, by using the least-squares method. The reflection intensities were measured on a Siemens automated

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diffractometer (graphite-monochromator, $Mo_{K\alpha}$ radiation). Details of the data collection and refinement are summarized in Table 1.[18]

The crystal structure of $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$ was solved by direct methods which led to the positions of zinc, phosphorous, sodium, and some of the oxygen atoms. The positions of the remaining oxygen and boron atoms were derived by subsequent least-squares and difference Fourier syntheses.[19] Positional parameters and anisotropic displacement parameters were refined by full-matrix least-squares for all atoms (see Table 2).

Table 1. Crystallographic data of $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$.

crystal system	hexagonal
space group	$P6_122$ (No. 178)
a [pm]	946.2(2)
c [pm]	1583.5(1)
cell volume [10^6 pm^3]	1227.8(4)
Z	6
ρ_{calcd} [g cm^{-3}]	2.736
crystal color, habit	colorless, hexagonal bipyramids
crystal size [mm^3]	$0.30\times0.15\times0.15$
T [°C]	20
$\mu(Mo_{K\alpha})$ [mm^{-1}]	3.499
θ range [°]	$5\le 2\theta\le 60$
index range	$-1\le h\le 12$, $-13\le k\le 14$, $-1\le l\le 22$
scan mode	ω
measured reflections	3217
independent reflections	1196
observed reflections [$F_o>4\sigma(F_o)$]	1020
R_{int}	0.0615
corrections	Lorentzian polarization and absorption (empirical, ψ-scan)
structure solution	direct method SHELXS-86[19]
structure refinement	SHELXL-93[19]
parameters	75
goodness-of-fit on F^2	1.142
Flack parameter	−0.01(3)
R values [$F_o>4\sigma(F_o)$]	$R1=0.0409$, $wR2=0.0828$
R values (for all data)	$R1=0.0544$, $wR2=0.0905$
residual electron density [e $\times 10^{-6}$ pm^{-3}]	0.676/−0.552

Table 2. Atomic coordinates and equivalent displacement factors [$\times 10^4$ pm^2] in the crystal structure of $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$.

	Wyckoff position	x	y	z	U_{eq}
Na	6*b*	0.1931(3)	0.3861(5)	0.2500	0.049(1)
Zn	6*b*	0.54946(4)	0.09891(9)	0.2500	0.0140(2)
B	6*b*	0.8469(4)	0.6938(9)	0.2500	0.014(1)
P	12*c*	0.3893(1)	0.1684(1)	0.41444(8)	0.0113(2)
O1	12*c*	0.2152(4)	0.0206(4)	0.4003(2)	0.0155(7)
O2	12*c*	0.2935(4)	0.4908(4)	0.1124(2)	0.0190(7)
O3	12*c*	0.3853(4)	0.3151(4)	0.3799(2)	0.0166(7)
O4	12*c*	0.4187(4)	0.1834(4)	0.5124(2)	0.0135(6)
O5	12*c*	0.6201(4)	0.1371(4)	0.1234(2)	0.0157(7)
O6	6*a*	0.1340(9)	0.0000	0.0000	0.097(4)

The equivalent isotropic displacement parameter of $O6_{H_2O}$ (located within the channels of the framework) is relatively high (0.0974). Detailed investigations carried out on a single crystal of the isotypic compound $NaNi(H_2O)_2[BP_2O_8]\cdot H_2O$ by using polarization microscopy and X-ray single crystal investigations at low temperature (198 K) revealed no indications for twinning or disorder, because the equivalent isotropic displacement parameter of $O6_{H_2O}$ drops significantly at lower temperature (0.063).[2b] Therefore, the relatively high equivalent isotropic displacement is to be interpreted as thermal motion of the water of crystallization $O6_{H_2O}$. Bond lengths and angles of the BO_4, PO_4, and $ZnO_4(H_2O)_2$ groups in the title compound are consistent with those in related borophosphates[2–8] and zinc phosphates[20] (see Table 3).

Dehydrated phase—structure determination from X-ray powder data: X-ray powder diffraction measurements were carried out on a Stoe Stadi-P diffractometer with $Cu_{K\alpha1}$ radiation ($\lambda_{K\alpha1}=154.059$ pm, Ge monochromator) and a linear position-sensitive detector (PSD) in Debye-Scherrer geometry by using the capillary technique (diameter 0.1 mm). The preparation of the dehydrated phase $Na[ZnBP_2O_8]\cdot H_2O$ (heat treatment of the hydrated phase at 180 °C for two hours) was carried out in a glove box under argon atmosphere. No correction for absorption has been applied to the data.

Table 3. Selected interatomic distances [pm] and angles [°] in the crystal structure of $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$.

B–O1	146.6(1) 2×	O1-B-O1	102.8(5)
B–O4	147.4(1) 2×	O1-B-O4	112.5(2)2×
		O1-B-O4	113.5(2)2×
		O4-B-O4	102.6(5)
P–O1	155.4(3)	O1-P-O3	105.8(2)
P–O3	151.0(3)	O1-P-O4	107.8(2)
P–O4	157.0(3)	O1-P-O5	111.1(2)
P–O5	150.4(3)	O3-P-O4	111.1(2)
		O3-P-O5	115.4(2)
		O4-P-O5	106.5(2)
Zn–O2	222.0(3)2×	O2-Zn-O2	88.2(2)
Zn–O3	206.6(3)2×	O2-Zn-O3	174.2(1)2×
Zn–O5	208.8(3)2×	O2-Zn-O3	88.1(1)2×
		O2-Zn-O5	81.2(2)2×
		O2-Zn-O5	86.3(2)2×
		O3-Zn-O3	95.8(2)
		O3-Zn-O5	102.2(1)2×
		O3-Zn-O5	89.4(1)2×
		O5-Zn-O5	162.8(2)
Na–O2	238.5(4) 2×		
Na–O5	253.2(6) 2×		
Na–O6	260.0(5) 2×		
Na–O3	303.6(5) 2×		
O6···O6[b]	293		

[a] O2: H_2O-ligands of the Zn-coordination octahedra. O6: H_2O molecules at the inner walls of the $^1_\infty$channels. [b] Hydrogen bond within the $^1_\infty$channels.

The X-ray powder data of the dehydrated phase $Na[ZnBP_2O_8]\cdot H_2O$ could be indexed by using the program ITO.[21] The parameters of the primitive hexagonal lattice with $a=954.04(2)$, $c=1477.80(3)$ pm and $V=1164.88(5)\times 10^6$ pm^3 (values from final Rietveld structure refinement) led to the conclusion that the unit cell contains six formula units (assuming 12×10^6 pm^3 required space per non-hydrogen atom; data are summarized in Table 4). The systematic absences from the X-ray powder pattern (*000l*, $l=6n$) led to the extinction symbol $P6_1$, which corresponds to the possible space groups $P6_1$, $P6_5$, $P6_122$, and $P6_522$. A structure solution procedure was then carried out by using the program TOPAS.[22] First of all, a Pawley[23] fit without a structure model was performed for all possible space groups individually in order to get lattice and peak shape parameters for the energy-minimization/simulated-annealing calculations. The best fitting of the powder pattern was achieved in $P6_122$. With this space group a Rietveld refinement that included additional refineable functions for structure solution was carried out. By using the Lenard-Jones potential equation for the lattice energy minimization in combination with a simulated annealing process (for details of this process see[22] and references therein) a satisfying result was obtained. The energy potentials were set-up assuming mean bond lengths calculated from the single-crystal structure refinement. During the refinement, parameters for the profile, background (values from the Pawley fitting were used), site occupation, and temperature factors were fixed. while zero-point and lattice parameters were refined. As a result a minimum was found (within three hours calculation time on a PII 300 MHz Pentium PC), but still with differences between the observed and calculated intensities. Unusually small bond lengths between cation–cation and anion–anion pairs close to special crystallographic positions could be identified as atoms occupying special positions. After setting-up the right positions a Rietveld refinement was carried out without using energy-minimization/simulated-annealing equations. All positions were checked for occupation and in a final Rietveld refinement all positional and displacement parameters were refined for all atoms independently (Table 5), while hydrogen atoms of the water

Table 4. Crystallographic data of the dehydrated phase $Na[ZnBP_2O_8]\cdot H_2O$ and rehydrated phase $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$.

	Dehydrated	Rehydrated
formula	$Na[ZnBP_2O_8]\cdot H_2O$	$NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$
M_r[g mol^{-1}]	307.15	341.16
crystal system	hexagonal	
space group	$P6_122$ (no. 178)	
diffractometer	Stoe STADI P	
monochromator	Ge(111)	
λ [pm]	154.06	
T [°C]	20	
a [pm]	954.04(2)	946.395(8)
c [pm]	1477.80(3)	1581.68(2)
V [10^6 pm^3]	1164.88(5)	1226.86(3)
Z	6	6
θ range	$9° \le 2\theta \le 103.5°$	$9.5° \le 2\theta \le 103°$
no. data points	4701	4676
no. reflections	308	325
positional parameters	19	22
profile parameters	7	7
background parameters	8	6
R_{wp}	0.052	0.074
R_{exp}	0.031	0.033
goodness of fit	1.70	2.24
R_{Bragg}	0.064	0.069

Table 5. Atomic coordinates and isotropic displacement factors [$\times 10^4$ pm^2] in the crystal structure of the dehydrated phase $Na[ZnBP_2O_8]\cdot H_2O$.

	Wyckoff position	x	y	z	U_{eq}
Na	6*b*	0.195(1)	0.390(1)	0.2500	0.190(5)
Zn	6*b*	0.5149(2)	0.0298(2)	0.2500	0.009(2)
B	6*b*	0.834(2)	0.668(2)	0.2500	0.032(9)
P	12*c*	0.3886(6)	0.1581(6)	0.4019(3)	0.011(2)
O1	12*c*	0.214(1)	0.011(1)	0.394(6)	0.011(3)
O3	12*c*	0.367(1)	0.295(1)	0.3673(7)	0.022(5)
O4	12*c*	0.444(1)	0.183(1)	0.5082(6)	0.001(1)
O5	12*c*	0.634(1)	0.160(1)	0.1401(5)	0.024(5)
O6	6*a*	0.238(2)	0.0000	0.0000	0.190(1)

molecules were omitted. Large values for the thermal motion were obtained for Na and $O6_{H_2O}$ (same labelling as in the crystal structure of the hydrated phase); this was also observed in the single-crystal structure of the hydrated phase. Global R values, low R_{Bragg} factor (Table 4), reasonable bond lengths and angles (Table 6),[16, 17, 24] and the difference plot (Figure 5)

Table 6. Selected interatomic distances [pm] and angles [°] in the crystal structure of the dehydrated phase $Na[ZnBP_2O_8]\cdot H_2O$.[a]

B–O11	154.9(3) 2×	O1-B-O1	93.6(3)
B–O4	149.1(3) 2×	O1-B-O4	114.5(4) 2×
		O1-B-O4	115.7(4) 2×
		O4-B-O4	103.3(3)
P–O1	155.2(4)	O1-P-O3	103.6(4)
P–O3	150.5(4)	O1-P-O4	109.1(4)
P–O4	163.8(4)	O1-P-O5	121.6(4)
P–O5	144.2(4)	O3-P-O4	110.3(4)
		O3-P-O5	109.9(4)
		O4-P-O5	102.3(4)
Zn–O3	196.3(3) 2×	O3-Zn-O3	126.6(2)
Zn–O5	201.6(3) 2×	O3-Zn-O5	100.5(1) 2×
		O3-Zn-O5	107.5(1) 2×
		O5-Zn-O5	115.1(2)
Na–O5	265.2(6) 2×		
Na–O6	209.0(5) 2×		
Na–O3	283.0(5) 2×		

[a] O6: H_2O molecules at the inner walls of the ∞^1channels.

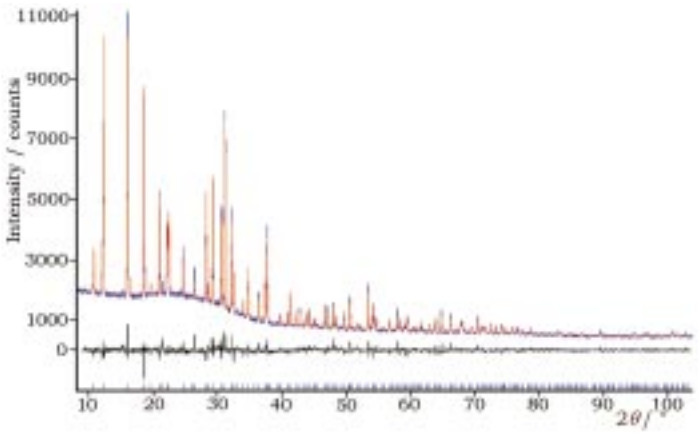

Figure 5. Observed (blue), calculated (red), and difference (black) X-ray powder diffraction profiles for the dehydrated phase $Na[ZnBP_2O_8]\cdot H_2O$, $Cu_{K\alpha 1}$ radiation.

verify a successful structure determination. All other possible space groups were carefully checked and used in the same way as described, but none of them gave a sufficiently good structural model compared with the one found above.

Rehydrated phase—structure determination from X-ray powder data: The rehydrated phase was obtained by exposing the powdered, dehydrated compound to moist air for a period of 12 hours. The powder data of the rehydrated phase $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$ could also be indexed by using the program ITO.[21] The parameters of the primitive hexagonal lattice with $a = 946.395(8)$, $c = 1581.68(2)$ pm and $V = 1226.86(3) \times 10^6$ pm^3 (values from final Rietveld structure refinement) are in good agreement with the single-crystal data. The systematic absences from the X-ray powder pattern (*000l*, $l = 6n$) led to the extinction symbol $P6_1$, which corresponds to the possible space groups $P6_1$, $P6_5$, $P6_122$, and $P6_522$ and fits very well to the single-crystal X-ray structure data. A Rietveld refinement of the structure using the program TOPAS[22] was carried out with the space group $P6_122$, because the structure of the single crystal was solved in this space group. Moreover, the same atomic position data were used as for the starting model. Positional parameters were refined for all atoms independently (Table 7), while hydrogen atoms of the water molecules were omitted.

Table 7. Atomic coordinates and isotropic displacement factors [$\times 10^4$ pm^2] in the crystal structure of the rehydrated phase $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$.

	Wyckoff position	x	y	z	U_{eq}
Na	6*b*	0.1913(3)	0.3826(3)	0.2500	0.029(2)
Zn	6*b*	0.5497(1)	0.0994(1)	0.2500	0.003(1)
B	6*b*	0.8395(8)	0.6790(8)	0.2500	0.002(1)
P	12*c*	0.3917(3)	0.1694(3)	0.4144(1)	0.002(1)
O1	12*c*	0.2105(6)	0.01992(5)	0.3984(3)	0.005(1)
O2	12*c*	0.2896(5)	0.4892(5)	0.1120(3)	0.010(2)
O3	12*c*	0.3866(5)	0.3186(5)	0.3760(3)	0.005(1)
O4	12*c*	0.4284(6)	0.1862(5)	0.5087(2)	0.005(1)
O5	12*c*	0.6157(5)	0.1386(6)	0.1268(3)	0.005(1)
O6	6*a*	0.1513(9)	0.0000	0.0000	0.165(1)

Isotropic displacement parameters were constrained to be equal for the tetrahedrally coordinated B and P and for the oxygen atoms labeled 1, 3, 4, and 5, while the others were refined unconstrained. This led to a very good refinement and the structural parameters were in good agreement with the X-ray single-crystal result. Global R values, low R_{Bragg} factor (Table 4), and the difference plot (Figure 6), which shows only minor deviations, indicate a successful structure refinement. No other phases or impurities in the X-ray data could be found. Remarkably high displacement parameters again were calculated for Na and $O6_{H_2O}$. This has been also observed in the single-crystal investigation and accounts for only weak bonds between the

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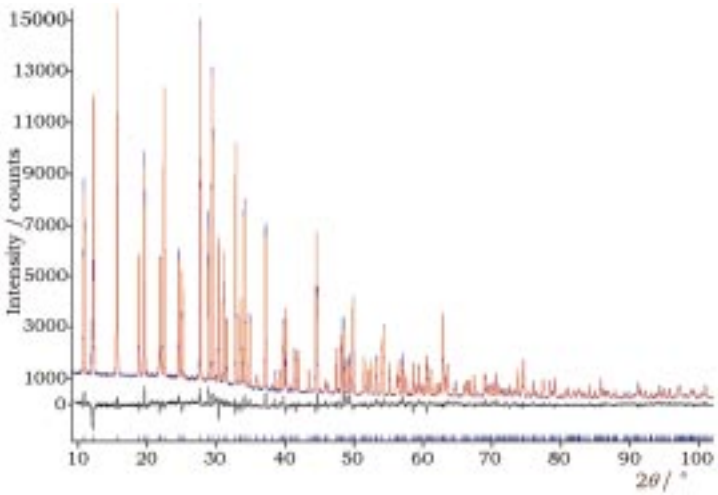

Figure 6. Observed (blue), calculated (red), and difference (black) X-ray powder diffraction profiles for the rehydrated phase $NaZn(H_2O)_2[BP_2O_8]\cdot H_2O$, $Cu_{K\alpha 1}$ radiation.

coordination partners. The other possible space groups were checked in order to give a better structural model for the observed powder pattern, but these attempts failed.

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