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$Zn[BPO_4(OH)_2]$: A Zinc Borophosphate with the Rare Moganite-Type Topology

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Abstract: A novel zinc borophosphate $Zn[BPO_4(OH)_2]$ with moganite-type topology (a rare polymorph of silica) has been prepared from a mixture of ZnO, B_2O_3, and P_2O_5 by hydrothermal treatment at 443 K. The crystal structure was determined from single-crystal X-ray data (orthorhombic, *Pbcn* (no. 60), $a=915.07(3)$, $b=897.22(3)$, $c=1059.19(3)$ pm, $V=869.62(5)\times10^6$ pm^3, $Z=8$, $R1=0.028$, $wR2=0.075$). The crystal structure comprises unbranched *vierer*-single borophosphate chains running along [010] and interconnected via $ZnO_2(OH)_2$-tetrahedra by sharing common vertices. The resulting topology of the three-dimensional tetrahedral framework structure is described by the Schläfli symbol $(4^2.6^2.8^2)(4.6^4.8)_2$. Although showing Zn in a tetrahedral coordination, the title compound does not belong to the group of zincoborophosphates but is a special case of a borophosphate containing *vierer* single rings of tetrahedra with the sequence Zn-B-Zn-P.

Keywords: borophosphate · moganite-type topology · solid-state chemistry · tetrahedral framework · zinc

Introduction

Silica, a well-known family of natural minerals, exists in a large number of polymorphous modifications that are built from corner-sharing SiO_4 tetrahedra. These include the stable phases at ambient pressure with increasing temperature: α-quartz, β-quartz, β_2-tridymite, and β-cristobalite; coesite is known as a high-pressure phase with a tetrahedral framework structure.[1,2] Besides these modifications also metastable phases are known, such as β_1-tridymite and α-cristobalite.[1,2] In addition, a rare silica modification, named moganite, was found and identified in ignimbrites of Gran Canaria (Spain) by Flörke et al. in 1974[3] and 1984,[4] respectively. This new modification has a monoclinic crystal structure, space group *I*2/*a*,[5] which can be considered to be built up from alternating layers of (101) slices of right- and left-handed α-quartz corresponding to a periodic Brazil-law twinning on the unit cell scale. The structure is characterized by the presence of 4-, 6-, and 8-rings of SiO_4 tetrahedra; the 4-rings are linked to form chains running along [100] (Figure 1 right) that are not found in quartz. Until very recently moganite was the only known example of this structure type. However, a silica analogue, phosphorus oxynitride (PON), crystallizing in the cristobalite-type structure,[6] was found to transform to a moganite-type phase at high temperature and high pressure.[7] Furthermore, an orthorhombic modification of beryllium hydride[8] has been reported which has a very close topological relation to moganite. Besides these tetrahedral framework structures, a metal-organic framework compound, $[Cu_3(Pytac)_6](H_2O)_{14}$ (Pytac = 2-(4-pyridyl)-thiazole-4-carboxylic acid),[9] and a cadmium cyanide[10] were found to crystallize with moganite topology. In the case of cadmium cyanide,[10] the moganite-type topology was identified by O'Keeffe in a later publication.[11] The crystal structures of moganite along with moganite-type PON and BeH_2 have been refined from X-ray powder and neutron powder diffraction data, respectively.

Borophosphates with a tetrahedral framework structure are of general interest due to their structural relationship to zeolite and silica.[12] Metalloborophosphates, as a branch of borophosphates, have been found with tetrahedral framework structures such as $A[ZnBP_2O_8]$ ($A=K^+$, NH_4^+, Rb^+, Cs^+)[13] with topologies that display a close relationship to alumosilicates (the feldspar family and Gismondine); a chiral zincoborophosphate, $Na[ZnBP_2O_8]\cdot H_2O$,[14] with a close structural relationship to the CZP topology[15] is formed by dehydration of the Na-Zn phase of the isostructural series $M^IM^{II}(H_2O)_2[BP_2O_8]\cdot x\,H_2O$ (M^I = Li, Na, K; M^{II} = Mn, Fe, Co, Ni, Zn; $x=0.5$, 1),[16] which contains helical ribbons of corner-linked borate and phosphate tetrahe-

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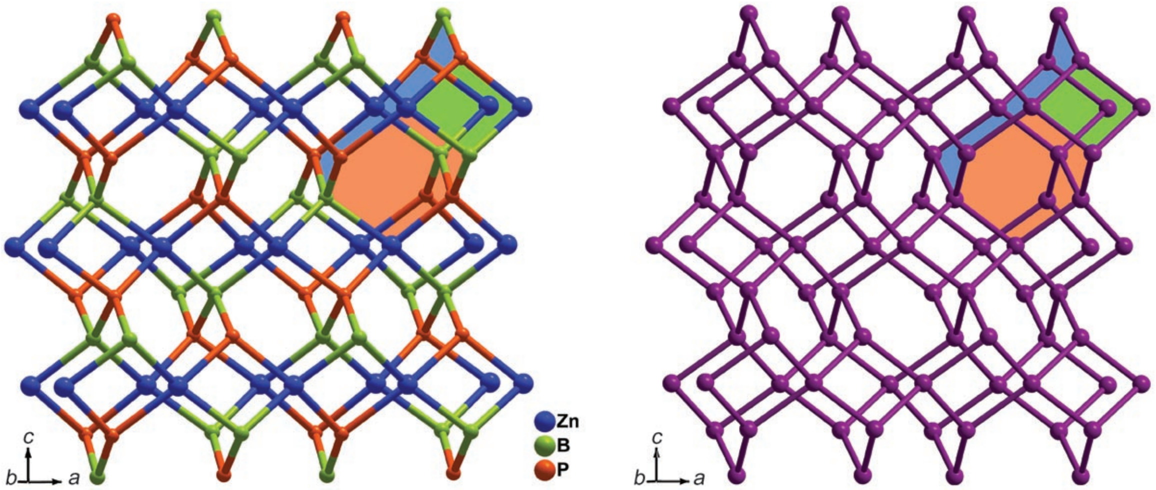

Figure 1. Connectivity of the tetrahedral centers of $Zn[BPO_4(OH)_2]$ (left; Zn: blue, B: green, P: orange) and moganite (a polymorph of SiO_2) (right, violet) viewed approximately along [010]. 4-, 6-, and 8-rings are highlighted in green, orange, and blue, respectively.

dra; two compounds containing the same topology as $Na[ZnBP_2O_8]\cdot H_2O$ have been found by introducing two different organic template ions, $(C_4N_3H_{16})[Zn_3B_3P_6O_{24}]\cdot H_2O$[17] and $(H_4TETA)_{1.5}[Zn_6B_6P_{12}O_{48}]\cdot 1.5\,H_2O$ (TETA = triethylenetetraamine);[18] $A(BeBP_2O_8)\cdot x\,H_2O$ ($A = Na^+, K^+, NH_4^+$),[19] $(NH_4)_{16}[Zn_{16}B_8P_{24}O_{96}]$ and $(NH_4)_{16}[Zn_{13.4}Co_{2.6}B_8P_{24}O_{96}]$[20] are found with ANA topology.[15] Here we report on the novel compound $Zn[BPO_4(OH)_2]$, which has a tetrahedral framework with an analogous topology to moganite (a rare polymorph of silica).[3–5] Its crystal structure was solved and refined from single-crystal X-ray diffraction data. $Zn[BPO_4(OH)_2]$ is isoelectronic ($48e^-$) to silica ($3\times SiO_2$).

Results and Discussion

The single-crystal structure analysis of $Zn[BPO_4(OH)_2]$ (see Table 1 and Table 2) reveals that the new phase consists of a three-dimensional tetrahedral framework with moganite-type(silica) topology (Figure 1). The PO_4 group adopts an almost ideal tetrahedral arrangement: $d_{P-O} = 151.57$–154.66 pm and $\sphericalangle$O-P-O = 106.37–111.28° (average P–O bond length and angle: 153.11 pm and 109.45°). In the borate group, the B–O distances and O-B-O angles are found in a range from 145.8 to 147.5 pm and from 105.04 to 114.21°, respectively. The two crystallographically independent Zn atoms occupy the special positions 4*c* (Wyckoff notation) with a distorted tetrahedral coordination surrounded by two OH groups and two oxygen atoms (Figure 2). Bond lengths and angles in the $ZnO_2(OH)_2$ tetrahedra (d_{Zn1-O}=193.37–194.32 pm and $\sphericalangle$O-Zn1-O = 103.37–111.97°; d_{Zn2-O} = 194.30–196.64 pm and $\sphericalangle$O-Zn2-O = 103.44–112.77°) are of the same order as observed in related compounds containing tetrahedrally coordinated zinc.[7–9] Details concerning the bond lengths and angles are given in Table 3.

The open-framework structure of $Zn[BPO_4(OH)_2]$ is built from unbranched *vierer*-single borophosphate chains of alternating $BO_2(OH)_2$ and PO_4 tetrahedra extending along [010] (Figure 3). The chains are interconnected by $ZnO_2(OH)_2$ tetrahedra to form a three-dimensional tetrahedral framework structure (Figure 4) with 8-ring channels running along [100] and providing free space for the hydrogen positions. The unbranched *vierer*-single borophosphate chains are built from alternating $BO_2(OH)_2$ and PO_4 tetrahedra and have also been found in the crystal structures of $M^{II}[BPO_4(OH)_2]$ (M = Mn, Fe, Co)[21] and $Fe[B_2P_2O_7(OH)_5]$.[22]

Table 1. Crystallographic data and refinement results of $Zn[BPO_4(OH)_2]$.

molecular formula	$Zn[BPO_4(OH)_2]$
formula weight [$g\,mol^{-1}$]	205.17
space group	orthorhombic, *Pbcn* (no. 60)
a [pm]	915.07(3)
b [pm]	897.22(3)
c [pm]	1059.19(3)
V [10^6 pm^3]	869.62(5)
Z	8
ρ_{calcd} [$g\,cm^{-3}$]	3.13
$\mu(Mo_{K\alpha})$ [mm^{-1}]	5.96
crystal size [mm^3]	$0.12\times0.08\times0.03$
T [K]	295(2)
2θ range [°]	6.36–60.0
hkl range	$-12\leq h\leq 12$, $-12\leq k\leq 12$, $-14\leq l\leq 10$
measured reflections	5813
independent reflections	1240
R_{int}/R_σ	0.029/0.025
observed reflections ($F_o > 4\sigma(F_o)$)	1162
number of parameters	92
$R1$ [$F_o > 4\sigma(F_o)$]/$R1$ (all data)	0.028/0.030
$wR2$ [$F_o > 4\sigma(F_o)$]/$wR2$ (all data)	0.075/0.077
goodness-of-fit on F^2	1.09
residual electron density (max/min) [$10^{-6}e\,pm^{-3}$]	0.55/−0.54

To classify the structure of $Zn[BPO_4(OH)_2]$, the tetrahedral centers and their interconnections are used by omitting

Table 2. Atomic coordinates and equivalent displacement parameters (10^4 pm^2) in the crystal structure of Zn[$BPO_4(OH)_2$]; standard deviations in parentheses.

Atom	site	*x*	*y*	*z*	U_{eq}/U_{iso}[a]
Zn1	4*c*	1/2	0.13783(4)	1/4	0.01212(13)
Zn2	4*c*	0	0.12516(3)	1/4	0.01192(13)
B1	8*d*	0.2424(2)	0.5265(2)	0.0786(2)	0.0081(4)
P1	8*d*	0.23618(5)	0.22634(5)	0.42734(5)	0.00874(15)
O1	8*d*	0.35556(15)	0.26124(14)	0.33265(13)	0.0159(3)
O2	8*d*	0.09608(15)	0.50355(16)	0.13239(14)	0.0165(3)
O3	8*d*	0.08602(15)	0.25933(14)	0.37334(13)	0.0154(3)
O4	8*d*	0.35523(15)	0.49243(15)	0.17139(13)	0.0152(3)
O5	8*d*	0.24086(14)	0.18695(16)	0.05198(14)	0.0114(3)
O6	8*d*	0.24588(14)	0.05921(16)	0.46128(14)	0.0132(3)
$H2_{O2}$	8*d*	0.050(4)	0.430(4)	0.116(3)	0.043(9)
$H4_{O4}$	8*d*	0.339(4)	0.423(4)	0.217(3)	0.048(9)

[a] Hydrogen was refined with isotropic displacement parameters.

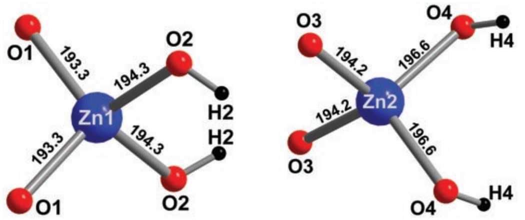

Figure 2. Ball-and-stick presentation of the two crystallographically independent $ZnO_2(OH)_2$ tetrahedra. Bond lengths given in pm.

Table 3. Selected bond lengths [pm] and angles [°] for the crystal structure of Zn[$BPO_4(OH)_2$]; standard deviations in parentheses.

Zn1−O1 (×2)	193.37(13)	O1-Zn1-O1	110.14(8)
Zn1−O2 (×2)	194.32(13)	O1-Zn1-O2 (×2)	111.97(6)
		O1-Zn1-O2 (×2)	109.63(6)
		O2-Zn1-O2	103.37(8)
Zn2−O3 (×2)	194.30(13)	O3-Zn2-O3	103.44(8)
Zn2−O4 (×2)	196.64(13)	O3-Zn2-O4 (×2)	111.31(6)
		O3-Zn2-O4 (×2)	112.77(6)
		O4-Zn2-O4	105.45(8)
B1−O4	145.8(2)	O4-B1-O6	114.21(15)
B1−O6	146.5(3)	O4-B1-O2	110.74(15)
B1−O2	147.0(2)	O6-B1-O2	108.78(14)
B1−O5	147.5(2)	O4-B1-O5	105.04(14)
		O6-B1-O5	110.05(15)
		O2-B1-O5	107.77(14)
P1−O1	151.57(14)	O1-P1-O3	111.28(8)
P1−O3	151.76(14)	O1-P1-O5	111.28(8)
P1−O5	154.46(15)	O3-P1-O5	110.28(7)
P1−O6	154.66(15)	O1-P1-O6	108.25(8)
		O3-P1-O6	109.21(7)
		O5-P1-O6	106.37(8)
O2−H2	0.81(3)		
O4−H4	0.80(4)		

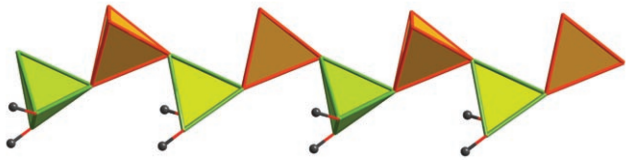

Figure 3. Unbranched *vierer*-single chain built from alternating $BO_2(OH)_2$ and PO_4 tetrahedra linked via common O corners. BO_4 tetrahedra: green, PO_4 tetrahedra: orange. H atoms: gray spheres.

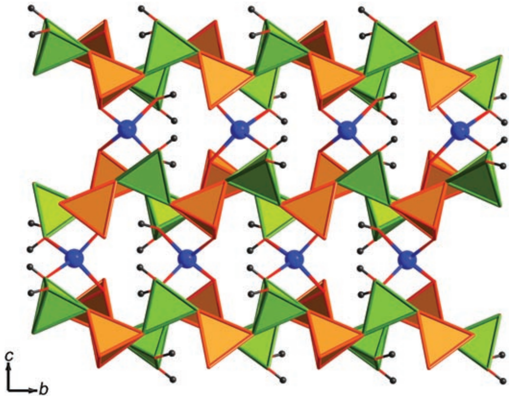

Figure 4. Unbranched *vierer*-single borophosphate chains extending along [010] interconnected by $ZnO_2(OH)_2$ tetrahedra forming a 3D tetrahedral framework structure. BO_4 tetrahedra: green, PO_4 tetrahedra: orange, Zn atoms: blue spheres, H atoms: gray spheres.

the oxygen atoms (Figure 1 left). As defined by O'Keeffe, "3- and 4-connected nets, particularly uninodal ones, are conveniently characterized by a vertex symbol (3,4); in this symbol a number specifies the size of the smallest ring contained in an angle, and a subscript if present indicates that more than one ring of specified size is contained in that angle and gives their number",[11] in a 4-connected net there are six angles at a vertex. The net of the title compound contains two kinds of nodes: B1 and P1 at 8*d* (Wyckoff notation) and Zn1 and Zn2 at 4*c* with the ratio of 2:1. When viewed down the *b* axis (Figure 1 left), one can visualize an undulating layer composed of 4-rings (green) and 6-rings (orange) sharing edges or vertices. The 3D net is generated by alternately connecting B and P nodes to those in adjacent layers above and below where the 8-rings (blue) are formed. The long (Schläfli) notation for B and P nodes is $4.8_6.6.6.6.6$, and $4.4.6_2.6_2.8_4.8_4$ for the Zn nodes, giving the net symbol $(4.4.6_2.6_2.8_4.8_4)(4.8_6.6.6.6.6)_2$ which can be represented by the short symbol $(4^2.6^2.8^2)(4.6^4.8)_2$. The topology of the open framework of the title compound exhibits the moganite (silica) topology (Figure 1 right). Although there is still a dispute about the actual existence of moganite because the crystal structure was solved from a few microcrystalline aggregates only and because the crystal structure can be described by a periodic Brazil-law twinning on the unit cell scale,[3] the title compound with moganite topology could provide convincing proof of the existence of moganite because it not only is isoelectronic to silica but also was even synthesized in form of single crystals and structurally characterized from single-crystal data.

Although zinc is tetrahedrally coordinated, the title compound cannot be counted as part of an anionic partial structure because the resulting framework is neutral in charge. Thus, the compound does not belong to the zincoborophosphate family but is a special case of tetrahedral borophosphates with B:P = 1:1. Up to now, all known metalloborophosphates contain a common fundamental building unit which is the dominant structural motif for all these compounds: unbranched *vierer*-single rings consisting of two phosphate groups connected via one metallate and one borate tetrahedron (*M*-P-B-P) or via two metallates (*M*-P-*M*-P) or via two borate tetrahedra (B-P-B-P).[12] The title compound, however, contains a *vierer*-single ring motif with the sequence Zn-B-Zn-P. The metalloborophosphates known up to now contain framework anions with the composition *M*:B:P = 1:1:2; the title compound, however, has a composition of *M*:B:P = 1:1:1.

Conclusion

We have synthesized and characterized a novel zinc borophosphate with the rare moganite-type topology (Schläfli symbol as $(4^2.6^2.8^2)(4.6^4.8)_2$). The crystal structure is constructed from unbranched *vierer*-single borophosphate chains interconnected via $ZnO_2(OH)_2$ tetrahedra, which results in a three-dimensional tetrahedral framework. Due to the charge neutrality of the tetrahedral framework the title compound does not belong to the family of zincoborophosphates.

Experimental Section

Preparation and analytical characterizations: The title compound was prepared from a mixture of ZnO (1.628 g, Alfa, p. a.), B_2O_3 (0.624 g, Alfa, 99.5 %), P_2O_5 (2.840 g, Merck, 95 %), and H_2O (7.5 mL) by hydrothermal treatment. The mixture was stirred at 373 K till a homogeneous colorless gel was obtained which then was transferred into a Teflon autoclave (20 mL, ROTH, filling degree 30 %) and treated at 443 K for three days. After that, the Teflon autoclave was directly removed from the oven and cooled down to room temperature. Colorless platelet crystals with an orthorhombic habit (Figure 5) were separated from the mother liquid by vacuum filtration followed by washing and drying at 333 K. The phase purity of $Zn[BPO_4(OH)_2]$ was checked by X-ray powder diffraction (Huber Image Foil Guinier Camera G670, $Cu_{K\alpha_1}$ radiation, Ge monochromator). The lattice parameters were obtained from powder data (LaB_6 as standard).

The chemical composition of the title compound was confirmed by elemental analysis. Zn, B, and P were analyzed by applying ICP-OES (Varian Vista, radial observation), whereas H was determined with a LECO CHNS-932 by applying the hot extraction method: Exptl/Calcd (%): Zn 32.2(5)/31.87, B 5.20(2)/5.27, P 14.63(8)/15.10, H 0.99(1)/0.98.

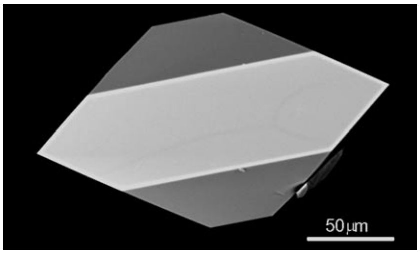

Figure 5. SEM image of an orhorhombic single crystal of $Zn[BPO_4(OH)_2]$.

The thermal stability was investigated under nitrogen atmosphere during heating and cooling (5 K/min) in the range from room temperature to 1273 K (NETZSCH STA 409). The thermogravimetric curve of crystalline samples of $Zn[BPO_4(OH)_2]$ shows a sharp single-step weight loss of 9.19 % occurring from 623 to 1073 K, corresponding to the removal of one H_2O per formula unit (8.78 % calcd).

Crystal structure determination: A suitable colorless platelet single crystal (Figure 5) of dimensions $0.12 \times 0.08 \times 0.03\ mm^3$ was isolated from the reaction gel. The intensity data were collected at 295 K on a Rigaku AFC7 four-circle diffractometer, equipped with a MERCURY-CCD detector ($Mo_{K\alpha}$ radiation, graphite monochromator). For data collection, ϕ as well as ω scans were performed (0.6° per step, 40 s per image). The data were corrected for Lorentz and polarization effects; an absorption correction was made by applying the multiscan mode. The crystal structure was solved in the space group *Pbcn* (no. 60) by direct methods using the program SHELXS-97–2,[23] and refined by full-matrix least-squares procedures using the program SHELXL-97–2.[24] After localization of zinc, phosphorus, and some of the oxygen positions, the missing non-hydrogen atom sites were taken from difference Fourier maps. After anisotropic displacement parameters had been included in the refinement, both hydrogen atoms were located from difference Fourier maps and refined without any restraints. For the final runs the lattice parameters obtained from powder data were used. Details of the data collection and relevant crystallographic data are summarized in Table 1, atomic positions and selected bond lengths and angles are given in Table 2 and Table 3, respectively.

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (+49) 7247–808–666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-418734.

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