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Nanoporous titanium borophosphates with rigid gainesite-type framework structure†

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Nanoporous titanium borophosphates have been synthesized which exhibit a rigid gainesite-type framework of polyhedra. The open-framework character is supported by the reversibility of de- and rehydration processes.

Multicomponent systems MO_x–P_2O_5–(H_2O) (MO_x = metal oxide) have been shown to be a fruitful playground in the search of new open-framework compounds which complement the group of microporous materials.[1] However, the low tendency of PO_4 units to form polyphosphates in aqueous solutions limits the number of new possible compounds, a trend also displayed by the small number of known minerals with P–O–P bridges.[2] By adding boron oxide (B_2O_3) to the systems the ready condensation of borate units—BO_3 and/or BO_4—with phosphate tetrahedra is observed.[3] These so-called borophosphate anions show an amazing structural variety ranging from oligomers, *via* chains and layers to three-dimensional frameworks reminiscent of the rich structural chemistry of silicates.[4] Consequently, templated borophosphates also could be synthesized, *e.g.* $M^{II}(C_2H_{10}N_2)[B_2P_3O_{12}(OH)]$ (M^{II} = Co, Mg, Mn, Fe, Ni, Cu, Zn).[5,6] Inspired by the interesting properties and crystal structures of group 4-silicates (*e.g.* titanium silicates[7]) and phosphates (*e.g.* zirconium phosphates[8]) we recently focused our interest on the synthesis of corresponding borophosphates. Here, we report on a group of isostructural

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Table 1 Lattice parameters[a] with estimated standard deviations of the isotypic phases with chemical compositions[b] $X\{Ti^{IV}_2[B(PO_4)_4]\}\cdot 1 - xH_2O$ (X = Li, Na, K, Rb, Cs, NH_4, H_3O; $0 \le x \le 1$)

X^+	$a/\text{Å}$	$c/\text{Å}$	$V/\text{Å}^3$
NH_4	6.3111(2)	16.365(1)	651.82(5)
K	6.3140(2)	16.3808(6)	653.05(4)
Rb	6.3116(2)	16.4144(7)	653.89(4)
$Na_{0.5}/(H_3O)_{0.5}$	6.3099(2)	16.4372(7)	654.44(4)
$Li_{0.34}/(H_3O)_{0.66}$	6.3184(2)	16.4406(8)	656.34(4)
H_3O	6.3210(2)	16.436(1)	656.70(5)
$Cs_{0.5}/(H_3O)_{0.5}$	6.3148(1)	16.4792(4)	657.14(2)

[a] LaB_6 was used as internal standard (program WINCSD[9]). [b] Derived from chemical analyses and thermogravimetric data.

open-framework titanium borophosphates, showing reversible sorption behavior.

The new class of compounds with the general formula $X\{Ti^{IV}_2[B(PO_4)_4]\}\cdot 1 - xH_2O$ (X = Li, Na, K, Rb, Cs, NH_4, H_3O; $0 \le x \le 1$) (Table 1) was obtained by hydrothermal reactions of Ti/HCl solutions with boric acid and the respective alkali metal phosphate. After treatment at 453 K for three days bluish to white crystalline solids are obtained showing identical X-ray absorption spectra independent of their respective colors (see ESI† Fig. S1). Preliminary EPR and XPS measurements strongly suggest the presence of an unknown but low concentration of Ti^{III} in the bluish samples. The compounds are isotypic as derived from X-ray powder and single crystal diffraction data.

Typically, the crystals exhibit a tetragonal-bipyramidal habit (see ESI† Fig. S2). The crystal structure of the isotypic compounds was determined by single-crystal X-ray diffraction (MoKα radiation) for X = H_3O and K (see ESI† Tables S1–S4). The c/a ratios of the tetragonal unit cells and the space group $I4_1/amd$ indicate a close structural relation to the mineral gainesite, $Na_2Zr_2[Be(PO_4)_4]$.[10] Furthermore, weak superstructure reflections and elongated reflection profiles imply a similar structural disorder (polytypism) as observed for the mineral (SAED and TEM, ESI† Fig. S3). An ordered model of the crystal structure with a monoclinic unit cell is shown in Fig. 1. Boron occupies the position of beryllium in the center of an oxygen tetrahedron. All vertices of the tetrahedron are shared with four neighboring PO_4 units.
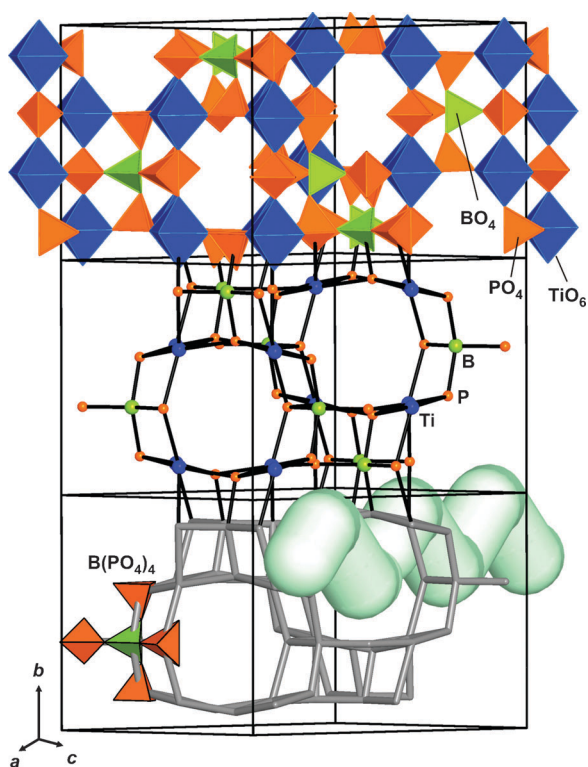
Fig. 1 Polyhedral representation of the gainesite-type framework {Ti$_2$[B(PO$_4$)$_4$]} (upper part, monoclinic unit cell) and the corresponding (4,6)-connected Ti$_2$BP$_4$ net (middle) with corrugated channels running along [101] indicated as light green tube (bottom).

The resulting "propeller"-like [B(PO$_4$)$_4$] unit (Fig. 1) has already been reported for the compounds M$^{II}_6$[B(PO$_4$)$_4$][PO$_4$] (M^{II} = Pb, Sr)[11,12] as well as for the hydrated borophosphate Na$_3$Pb^{II}[B(O$_3$P(OH)],[13] and resembles a cut-out of the tetrahedral framework present in the polymorphs of SiO$_2$ and BPO$_4$.[14] The complex [B(PO$_4$)$_4$] anions are connected to the Ti^{IV}O$_6$ octahedra by sharing common oxygen corners resulting in a three-dimensional framework with exclusively bridging oxygen atoms. The analysis of the three-dimensional framework (ordered model, space group C2/c, see ESI† Table S5) revealed the nanoporous character of this new family of compounds. The (4,6)-connected framework is shown in Fig. 1. A prominent void is found at 0 1/4 1/4 (Wyckoff position 4e) with a volume of 262 Å^3.[15] Interconnection of the voids results in the formation of corrugated channels running along [101].[15] Water molecules, alkali metal ions, and oxonium ions, respectively, occupy positions within the voids/channels of the framework. As can be seen from Table 1, the cell volumes of the isotypic compounds are only marginally affected by the nature of the guest components which underlines the rigidity of the framework.

To prove the "true nanoporous"[1] character of the framework we performed simultaneous thermogravimetric–mass spectrometric measurements (see ESI† Fig. S4). For H$_3$O{Ti$^{IV}_2$[B(PO$_4$)$_4$]}·H$_2$O it was shown that crystal water is released endothermically up to 350 °C (calc. 2 moles of H$_2$O loss: 6.9 wt%/exp.: 7.1 wt%). Similarly to *e.g.* Y-zeolite,[16] the formation of Brönsted acidic oxygen bridges can be assumed corresponding to the chemical formula H{Ti$^{IV}_2$[B(PO$_4$)$_4$]}. Exposure of the dehydrated phase to moisturized argon at 30 °C leads to a mass gain accompanied by an exothermic effect. After about 4.5 hours a constant weight is reached corresponding to full rehydration. Repeated dehydration/rehydration reactions on the same sample gave almost identical results. To verify the stability of the framework *in situ* high temperature synchrotron powder diffraction was performed. Sharp reflections originating from the framework are clearly present up to 350 °C (a = 6.3380(2) Å, c = 16.3151(7) Å, V = 655.38(4) Å^3, see ESI† Fig. S5).

In conclusion, we have demonstrated a powerful approach to combine phosphate and tetrahedral borate units to assemble new framework structures with reversible sorption properties. Furthermore, the analogy of the zirconium beryllium mineral (gainesite) and the new titanium borophosphates implies the existence of a huge family of related compounds.

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