Borates

A High-Pressure Praseodymium Fluoride Borate Linking Multiple Structural Features of Apatite-Type Compounds

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Abstract: Pr$_5$(BO$_4$)$_3$-(BO$_3$)$_7$F,Cl,OH))$_{1,173}$O$_{2,286}$ (x ≈ 1.6), a boron-containing fluoride-oxoapatite-like compound, was obtained by the application of high-pressure/high-temperature synthesis. It exhibits a superstructure of the apatite type with a tripped c lattice parameter (space group P6$_3$/m) and shows complex anion disorder along the 6_3 screw axis and occupation of distorted octahedra, as well as almost trigonal planar sites, by oxygen and fluorine atoms. Furthermore, a distinct BO_3/ (BO_4+F) group disorder is found; 46% of the sites being occupied by BO_4 groups and 54% by BO_3 groups, with a fluoride ion located near the missing oxygen atom. The rare earth cations in the 4f sites exhibit a specific distorted tricapped trigonal prismatic coordination with a mean metapism twist angle of 21.3°. The crystal structure of Pr$_5$(BO$_4$)$_3$-(BO$_3$)$_7$F,Cl,OH))$_{1,173}$O$_{2,286}$ (x ≈ 1.6) shows much “flexibility” resulting in split and off-site positions of all other rare earth cations. The title compound therefore combines many structural features of apatite-like compounds, for example biologically highly-important carbonated apatites, shedding more light onto the complex structural chemistry of apatites.

Introduction

Due to their enormous biological significance as main mineral components of human and animal hard tissues such as bones and teeth, apatite Ca$_5$(PO$_4$)$_3$(F,Cl,OH) and compounds with similar structures have been objects of extensive studies. Calcium phosphate biomaterials have been especially investigated as potential implant materials, or as scaffolds for growth factors in bone regeneration processes.[1] Recently, Barheine et al. have reported that disordered borate-containing apatite is responsible for the adhesion properties of organic molecules like proteins, and shows enhanced biodegradability in contrast to crystalline hydroxyapatite.[2] Besides their biomedical features, the catalytic and piezoelectric properties of numerous apatites are well known.[3] Apatite-type compounds containing rare earth elements show interesting optical behaviour, and are potentially applicable as fluorescent lamp phosphors and laser-material hosts.[4] Recently, rare earth containing apatite-type oxide ion conductors like La$_x$Y$_2$Ge$_3$O$_9$ have come into focus as potential electrolytes for solid oxide fuel cells (SOFC).[5]

The apatite prototype Ca$_5$(PO$_4$)$_3$F was first reported by Navay et al.[6] in 1930 and was confirmed to adopt P6$_3$/m symmetry.[7] To date, a large variety of compounds with the apatite structure (M$_1$(M$_2$)(M$_3$)(AO$_4$))X are known.[8] The metal cations M can be alkaline earth metals, rare earth elements, Cd or Cr, whereas for the anion X the substituents F, Cl, Br, OH, O, or S are found.[9] The tetrahedrally coordinated atom A can either be a transition metal (V, Mn, Cr) or a group 14 or 15 element (Si, Ge, P, or As).[10] Many apatite compounds adopt structures in lower-symmetric trinetic space groups like P6$_3$/p, P6$_3$/m and P3$_1$, as well as monoclinic ones, for example, P2$_1$/m and P2$_1$.

The scope of the apatite family is broadened by the inclusion of less common M$_1$(AO$_4$)$_1$X and M$_1$(AO$_4$)$_3$X compounds, where the AO$_4$ tetrahedra are replaced by groups with square pyramidal or trigonal planar coordinations. One perfect example is natural hydroxyapatite, building up two thirds of human bone material, where the phosphate groups PO$_4$ are partially replaced by carbonate groups CO$_3$. Finnemane Pb$_3$(AsO$_4$)$_4$Cl$_2$[11] a reduced form of mimetite Pb$_3$(AsO$_4$)$_4$Cl$_2$[12] adopts an apatite structure with P6$_3$/m symmetry and a complete replacement of the AO$_4$ tetrahedra by AsO$_4$ groups, with the arsenic atoms lying above the triangular oxygen plane. Up to now, only a few boron-containing apatites have been described. In most of these structures, boron is present in trigonal planar BO$_3$ groups that partially substitute the tetrahedral AO$_4$ groups.[13] In Ca$_5$(BO$_4$)$_3$F, tetrahedral PO$_4$ groups are fully substituted by planar BO$_3$ groups, leading to a monoclinic structure related to fluoroapatite.[14] Ito et al. reported about the incorporation of boron as BO$_3$ groups in oxaapatite.[15] As
far as we know, La$_{23}(Sb_{1.96}B_{0.04})_2O_7$ is the only compound in whose structure the position $A$ is partially occupied by four-fold-coordinated boron atoms.$^{[14]}

Furthermore, some apatite superstructures have been reported in literature, mainly based on a doubling of one lattice parameter. A good overview of the crystal chemistry of apatites including a list containing apatite superstructures is given in ref.[8]. Lodo-oxoapatite was reported by Henning et al.$^{[15]}$ as the first modulated apatite exhibiting superstructure ordering along [001], based on partial ordering of oxygen and iodine ions resulting in a tripling of the c lattice parameter in space group $P6_3/m$. The final structure description, however, still displays disorder as related to the stacking sequence of anions within the iodine-oxygen columns, with the anions being split over two positions each.

$Pr_4(BO_3)_{12}(BO_3)(FH)_{2.5}O_{13.48}$ ($x \approx 1.6$) represents a high-pressure rare earth fluoride-oxoapatite-like compound exhibiting a superstructure featuring a unit cell tripped along [001], in combination with anion disorder along the $6$ screw axis and $BO_4$ ($BO_4$ + F) group disorder. This compound therefore combines the two topics described above in a way that has not been reported so far, and could be a good basis for further understanding of the crystal chemistry in natural hydroxyapatites.

**Experimental Section**

**Synthesis:** $Pr_4(BO_3)_{12}(BO_3)(FH)_{2.5}O_{13.48}$ ($x \approx 1.6$) was obtained from a 1:1:2 mixture of $Pr_3O_4$, $PrF_3$, and $BO_3$, by applying high-pressure/high-temperature conditions of 11.5 GPa and 1573 K, utilizing a Walker-type multianvil apparatus. The starting mixture was ground under argon atmosphere and filled into boron nitride crucibles, which were then positioned inside MgO octahedra and compressed by eight tungsten carbide cubes. $Pr_4(BO_3)_{12}(BO_3)(FH)_{2.5}O_{13.48}$ ($x \approx 1.6$) was obtained in form of greenish crystals that are stable in air at ambient conditions. Further experimental details on the synthesis are provided in the Supporting Information.

**Powder X-ray diffraction (PXRD):** A PXRD pattern of a flat polycrystalline sample of $Pr_4(BO_3)_{12}(BO_3)(FH)_{2.5}O_{13.48}$ ($x \approx 1.6$) was collected in transmission geometry using a Stoe Stadi P powder diffractometer (Stoe & Cie GmbH, Darmstadt, Germany) with Mo$_{K\alpha}$ radiation ($Ge(111)$ monochromator, $\lambda = 0.7093$ pm) operated at 50 kV and 40 mA. The powder diffraction pattern of $Pr_4(BO_3)_{12}(BO_3)(FH)_{2.5}O_{13.48}$ ($x \approx 1.6$) was recorded in the 2$\theta$ range 2.0–45.0’ with a step-size of 0.010’. Lattice parameter refinement was carried out using the INDEX & REFINE tool of the Stoe WinX$^{[20]}$ software suite.$^{[16]}$ The experimental PXRD pattern in comparison with the theoretical powder pattern based on single-crystal diffraction data of $Pr_4(BO_3)_{12}(BO_3)(FH)_{2.5}O_{13.48}$ ($x \approx 1.6$) is shown in Figure S1; refined lattice parameters from powder diffraction data are given in the Supporting Information.

**Single-crystal X-ray diffraction (SCXRD):** Small single crystals of $Pr_4(BO_3)_{12}(BO_3)(FH)_{2.5}O_{13.48}$ ($x \approx 1.6$) were isolated by mechanical fragmentation, and selected under an optical polarization microscope. In line with the known issue with crystal quality of mixed apatites, only one out of dozens of crystals proved to be suitable for detailed single-crystal structure determination. SCXRD data were collected at 173 K with a Bruker D8 Quest diffractometer (Photon 100 detector) equipped with a microfocus source generator (Incoatec GmbH, Geesthacht, Germany) combined with multi-layer optics (monochromatized Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ pm). Semiempirical absorption correction based on equivalent reflections was applied with SADABS-2014/S.$^{[16]}$ Systematic absences and Laue symmetry indicated the hexagonal space groups $P6_3/m$ or $P6_2$. The structure was solved with SHELX5$^{[18]}$ (version 2013/1). Structure refinement (full-matrix least-squares against $F^2$) with SHELXL$^{[20]}$ (version 2014/7) using Stoe X-Step32$^{[21]}$ (Revision 1.05b) was successful in $P6_3/m$; lower symmetries including $P6$ did not result in less disorder or lower residuals. Due to large and highly anisotropic displacement parameters of the boron atoms B1A and B2, as well as the oxygen atoms O4 and O5, these positions were better refined as split positions B1/B1A, B2/B2A, O4/F4, and O5/F5. The ratio of occupation for these split positions was determined by free refinement of the occupancy factors, followed by small manual adaption to yield equal thermal displacement parameters for the boron positions B1/B1A and B2/B2A. The corresponding anion sites O4, O5, F4, and F5 were coupled with the boron occupancies to represent the chemically reasonable (BO$_4$ + F/) Bo polyhedra. At this point, there was still significant electron density in the proximity of the cations Pr1, Pr2, and Pr4. Assuming that the strong anion disorder impacts the positions of the rare earth cations, Pr1 was offset by 21(1) pm from the position on the mirror plane, and Pr2 was also refined as a split position ($d = 22(1)$ pm). Pr4 was also refined as a split position beneath its original position on the $6$ axis. These modifications led to a stable refinement and drastic improvement of the R values. In first approximation, the required F/BO mixing ration was balanced by the disordered positions. In second approximation, the atomic positions on the $6$ axis with high occupancy (F1, F2, and F3) were refined isotropically as fluorine atoms; the remaining positions (O11, O21, O23, and O33) were refined isotropically as oxygen atoms. A comparison of the thermal displacement parameters showed higher values for the fluorine and lower values for the oxygen atoms. Due to the fact that we could not exclude partial occupation by oxygen atoms on the positions of F4 and F5 within the (BO$_4$ + F) groups, refinement of all seven possible positions on the $6$ axis with statistical occupation by F/O would not allow for an exact analysis of distribution. To maintain overall charge neutrality, final refinement cycles were performed using fixed occupancy factors based on the results of their free refinement. The positional parameters of all atoms except those located either on split positions or on the $6$ screw axis were refined with anisotropic displacement parameters. Final difference Fourier synthesis did not reveal any significant residual peaks. Due to the fact that oxygen and fluorine cannot be distinguished unequivocally by means of SCXRD data, the differentiation between O and F on the $6$ screw axis, and also within the (BO$_4$ + F) groups, is a reasonable model based on interatomic distances (see Table S4 in Supporting Information). Occupation of the F4 and F5 positions by oxygen atoms can almost certainly be excluded, due to the fact that the system would therefore relax forming the BO$_3$ group. While not indicated by the single-crystal structure data or infrared (IR) spectroscopy, the presence of OH groups or water molecules in the title compound cannot be excluded. Due to the preparation of the high-pressure assembly at ambient conditions under air, a partial hydrolysis of the starting materials could occur. Furthermore, the presence of H$_2$O and OH groups in oxoapatites and halogen-oxoapatites is quite common.$^{[22]}$ Therefore, we assume the composition of the title compound to be best-represented with the formula $Pr_4(BO_3)_{12}(BO_3)(FH)_{2.5}O_{13.48}$ ($x \approx 1.6$).

Relevant details of the data collection and evaluation are listed in Table S1. Positional parameters, anisotropic and equivalent isotropic displacement parameters, interatomic distances, and interatomic angles (within BO$_4$/BO$_3$ groups only) are provided in Tables S2-S5.
CCDC 1872320 contains the supplementary crystallographic data for Pr₅(BO₃)₃(OH,F)₄O₁₉₂₈ (x ≈ 1.6). These data are provided free of charge by The Cambridge Crystallographic Data Centre / FIZ Karlsruhe deposition service.

Results and Discussion

Crystal structure refinement shows that Pr₅(BO₃)₃(OH,F)₄O₁₉₂₈ (x ≈ 1.6) crystallizes in the hexagonal centrosymmetric space group P6/m with the lattice parameters a = 918.4(2) pm and c = 2163.1(4) pm. A classical representation of the apatitic crystal structure of Pr₅(BO₃)₃(OH,F)₄O₁₉₂₈ (x ≈ 1.6) is given in Figure 1, highlighting the BO₃/BO₄ groups. The rare earth cations surrounding the G₃ screw axis form trigonal planar, tetrahedral, and octahedral sites for the anions in the channels along [001], as well as the metaprisms formed by the rare earth cations Pr₃ and Pr₅.

The superstructure involves tripling of the c lattice parameter with respect to the basic apatite structure type. A representation of the crystal structure with displacement ellipsoids at 90% probability level (Figure 2) illustrates the nature of the superstructure within the unit cell, and depicts the rather strong anisotropic displacement of the rare earth cations as well as the oxygen atoms forming the BO₃ and BO₄ groups.

It is obvious that the superstructure arises from partial ordering of oxygen and fluorine atoms along [001], as well as the partial ordering of the BO₃/(BO₄ + F) group disorder (Figure 3).

In fact, only the (B₂)O₃ groups are found on two faces of the tetrahedron, whereas the (B₁)O₃ group is only located on one side of the tetrahedron. This is depicted in Figure 3, including all relevant interatomic distances. In all cases, only the adjacent planes of BO₃ triangles oblique to [001] are occupied. Carbonate hydroxyapatites are known to show a similar AO₃/BO₃ group disorder, where trigonal planar CO₃ groups partially substitute tetrahedral PO₄ groups, forming one oxygen vacancy per substituting group. However, for these carbonateapatites, including human and animal tooth enamels, no concurring models are reported regarding the locations of vacancies on the oxygen sites of the tetrahedra. Depending on the positions of the vacancies (seen as reduced occupancy factors in the positional parameters of the crystal structure solution), a location of the faces of the tetrahedra, where the CO₃⁻ groups are partially located, is possible. For the calcium-deficient carbonate hydroxyapatite Ca₅[Ca₁,₉(OH)₂][PO₄]₀,₅{(H₂O)₀,₅(OH)₀,₅} [F], Ivanova et al. reported the carbonate ions to occupy those two adjacent faces of a PO₄ tetrahedron, which are parallel to the c-axis.[23] However, polarized IR spectroscopy shows the planes of the CO₃ triangles to be oblique to [001] at an angle of 37 ± 4°.[24] The latter is consistent with the positions of the BO₃ groups in the crystal structure of Pr₅(BO₃)₃(OH,F)₄O₁₉₂₈ (x ≈ 1.6), with part of these groups additionally found on two planes and partly on only one of the four tetrahedral planes.

The oxygen atoms O3 in carbonate hydroxyapatite (equaling O1, O3, respectively O6, O7 in Pr₅(BO₃)₃(OH,F)₄O₁₉₂₈ (x ≈ 1.6)) are split in two positions (at a distance of 37 pm), depending on coordination by phosphorus as PO₄³⁻ or by carbon as CO₃⁻.[23] While this is not the case in Pr₅(BO₃)₃(OH,F)₄O₁₉₂₈ (x ≈ 1.6), we herein find sites near the positions of O4 and O5, which are partly occupied by fluorine atoms (F4 and F5). F4 is shifted 49(1) pm apart from O4, and F5 about 48(1) pm apart from O5, both in the direction off the center of the BO₄ tetrahedra. The resulting positions and interatomic distances lead to the conclusion that the positions of F4 and F5 are occupied wherever the tetrahedral BO₄ group is replaced by a BO₃ group, as is shown in Figure 3. To the best of our knowledge, this has not been reported in an apatitic structure so far.

However, a similar structural situation can be found in solid-solution fluoride borates like, for example, Eu₂(BO₃)₃(F,OH)₁₉₂₈[25] and Ba₅(BO₃)₃(F,OH)₁₉₀₈[26] with [BO₃]F⁻ ↔ [F₄]⁺ anionic isomorphism. In these compounds, planar BO₃ groups directly neighbored to a fluoride anion in trigonal pyramidal geometry, together with [4F]⁺ groups, are statistically distributed over the crystal structure. The BO₄ groups thereby can appear on each face except at the basal plane of the trigonal pyramid. In the crystal structure of
Pr$_4$(BO$_3$)$_3$·(BO$_4$)$_2$·(F,OH)$_2$·O$_{2.28}$ (x ≈ 1.6), the BO$_3$ groups are only located at one or two planes of the tetrahedra (see above). While no (4F)$^+$ groups are present in the title compound, one could, in coherence with the (BO$_3$)$^-$→(3F)$^-$ anionic isomorphism, describe the disorder of BO$_3$ and (BO$_4$ + F) groups in Pr$_4$(BO$_3$)$_3$·(BO$_4$)$_2$·(F,OH)$_2$·O$_{2.28}$ (x ≈ 1.6) as [(BO$_3$)F]$^-$→(3BO$_4$)$^-$ anionic isomorphic substitution. Having a closer look at the distances between the boron atom of the BO$_3$ groups to the fluoride anions, one can find values of 236(3) and 261(4) pm for Ba$_{12}$Sr$_{10}$(BO$_3$)$_3$·(F,OH)$_2$[26] and Ba$_4$(BO$_3$)$_3$·(F,OH)$_2$·O$_{2.28}$ (x = 0.49)[26,27] respectively. This compares well to the corresponding B–F interatomic distances of 252.3(1) and 253.1(1) pm found in Pr$_4$(BO$_3$)$_3$·(BO$_4$)$_2$·(F,OH)$_2$·O$_{1.6}$ (x ≈ 1.6).

Very recently, Li et al. reported the possible formation of tri-coordinated planar triangle (PO$_4$ + O) groups in a mixed borate-phosphate-fluoride with the composition Ca$_{3.2}$Si$_{2.5}$(PO$_4$)$_2$F$_6$[28] when BO$_4$ is gradually substituted by PO$_4$. At the composition x = 2.0–2.5 and y = 0.5, 0.15, PO$_4$ groups may partially be described as a planar PO$_3$ group in combination with an isolated oxygen atom above the phosphorus atom. At x < 1.2, the crystal structure of Ca$_{3.5}$(BO$_3$)$_3$·(PO$_4$)$_2$F (CBP,F)·yBi$^{3+}$ is reported to correspond to Ca$_{3}$(BO$_3$)$_3$F (space group Cm)[29].

The presence of BO$_3$ as well as BO$_4$ groups in the crystal structure of Pr$_4$(BO$_3$)$_3$·(BO$_4$)$_2$·(F,OH)$_2$·O$_{2.28}$ (x ≈ 1.6) was confirmed by IR spectroscopy measurements of a bulk sample, as is presented in detail in the Supporting Information. The ratio of occupation with BO$_4$ and (BO$_4$ + F) groups in Pr$_4$(BO$_3$)$_3$·(BO$_4$)$_2$·(F,OH)$_2$·O$_{2.28}$ (x ≈ 1.6) was determined by refinement of the occupancy factors of the corresponding boron and oxygen atoms. This yielded 62% BO$_3$ and 38% BO$_4$ for B1 and B1A, and 16% BO$_4$ and 84% BO$_3$ for B2A and B2B, respectively. Summed up, the ratio of BO$_3$:BO$_4$ in Pr$_4$(BO$_3$)$_3$·(BO$_4$)$_2$·(F,OH)$_2$·O$_{2.28}$ (x ≈ 1.6) is 139:161, equating 46% BO$_3$ and 54% BO$_4$ groups. The central atoms of the less frequent groups were termed with the suffix “A”.

The interatomic distances and angles in the BO$_3$ and BO$_4$ groups show values typical for slightly distorted tetrahedral and trigonal planar coordinations, respectively (Figure 3). The mean values of the interatomic distances, however, are slightly larger than expected, with 149.1 pm for (B1)O$_{24}$ 150 pm for (B2A)O$_{23}$ (literature value: 147.6 pm[30]), 139.5 pm for (B1A)O$_{23}$ and 140.1 pm for (B2)O$_{23}$ (literature value: 137.0 pm[31]). Partial substitution of oxygen in the BO$_3$/BO$_4$ groups by fluorine is therefore very unlikely, as this would result in even smaller mean interatomic distances than the literature values given above (mean literature value d(BO$_3$–O/F) in tetrahedral BF$_4$ groups = 139 pm[32] in BO$_3$F$_2$ = 142.8 pm,[33] and in BO$_3$F = 145.0 pm)[33b,34]. Furthermore, calculations of the bond valence sums within the BO$_3$ and BO$_4$ groups have been performed according to the bond-length/bond-strength concept[35]. These result in formal charges for the central boron atoms lower than +3 (B1 = +2.90, B1A = +2.86, B2 = +2.82, B2A = +2.83) and would decrease further by approximately 0.1 each for every oxygen atom being substituted by fluorine.

All praseodymium cations in the crystal structure of Pr$_4$(BO$_3$)$_3$·(BO$_4$)$_2$·(F,OH)$_2$·O$_{2.28}$ (x ≈ 1.6) are in the trivalent state. While minor amounts of tetravalent praseodymium cations cannot be excluded by any method, there is no experimental evidence for significant amounts of tetravalent cations. The light-green color of the product sample, as well as the relatively high mean interatomic distances (see Table S4) compared to literature values of the crystal radii clearly account for Pr$_{3+}$ cations (sum of crystal radii[36]: r(Pr$^{3+}$, C.N. = 7) + r(O$^{2-}$–F$, C.N. = 4) = 241 pm; r(Pr$^{3+}$, C.N. = 8) + r(O$^{2-}$–F$, C.N. = 4) = 247.6 pm; r(Pr$^{4+}$, C.N. = 7) + r(O$^{2-}$–F$, C.N. = 4) = 226 pm; r(Pr$^{4+}$, C.N. = 8) + r(O$^{2-}$–F$, C.N. = 4) = 231 pm). For mixed valent rare earth oxides, for example Pr$_4$O$_{16}$ and Pr$_4$O$_{24}$, such comparison of mean interatomic distances to sums of crystal radii has been shown to be applicable for distinguishing between trivalent and tetravalent rare earth cations.[37] Moreover, the title compound has been found to preferably form at the edge of the
reaction vessel near the boron nitride crucible, which has a slightly reducing effect on the reaction sample.

The rare earth cations Pr3, Pr4, and Pr5 on the M1 positions show distorted tricapped trigonal prismatic coordination characteristic for the apatite structure, with the addition of the capping atoms of Pr3 and Pr5 being either oxygen (O4/O5) or fluorine (F4/F5), depending on the neighboring group being BO4 or (BO4 + F) (Figure 4). The metaprism twist angles $\varphi$ in Pr$_3$(BO$_4$)$_3$·3(BO$_4$)·(F,OH)$_2$·2O$_{28}$ ($x \approx 1.6$) are $\varphi_{Pr3} = 19.1(1) ^\circ$, $\varphi_{Pr4} = 22.2(1) ^\circ$ and $\varphi_{Pr5} = 22.6(1) ^\circ$. $\varphi_{Pr3}$ therefore equals the value found for chloroapatite of 19.1$ ^\circ$, $\varphi_{Pr4}$ and $\varphi_{Pr5}$ are close to the twist angle of (M1)O$_6$ polyhedra in fluoroapatite of 23.3$ ^\circ$. This is in very good agreement with the observation of White et al. as that the metaprism twist angle $\varphi$ of the (M1)O$_6$ polyhedra in apatite-type compounds varies inversely with average ionic radii and unit cell volume.$ ^{[6]}$ Although no data are available for apatitic compounds with praseodymium as the cation for apatite-types structures. The possible sites of the oxygen and fluorine atoms along the 6$ ^i$ screw axis, together with the resulting coordination spheres are shown in Figure 5. Whereas the positions of the fluorine atoms are almost fully occupied, the oxygen sites are only occupied to a minor fraction (see Table S2 in Supporting Information). Note that mainly every other octahedral and trigonal planar site is occupied (F3 and F1, respectively). In natural fluoroapatite, the fluoride ions occupy the sites 2a ($z = 1/4$), triangular interstices between Ca atoms) along $[001]$ only, whereas the anions of apatites containing larger halides or hydroxides (hydroxyapatite) tend to occupy 2b ($z = 0$, octahedral coordination by Ca atoms) or to statistically occupy 4e sites.

**Conclusion**

By the application of high-pressure/high-temperature synthesis, Pr$_3$(BO$_4$)$_3$·3(BO$_4$)·(F,OH)$_2$·2O$_{28}$ ($x \approx 1.6$), a fluoride-oxoborate with apatite-like structure was obtained. The title compound exhibits complex disorder of anions along $[001]$, as well as BO$_4$/ (BO$_4$ + F) group disorder. Partial ordering results in an apatite superstructure with a tripled lattice parameter c. Pr$_3$(BO$_4$)$_3$·3(BO$_4$)·(F,OH)$_2$·2O$_{28}$ ($x \approx 1.6$) thereby combines structural features that have only been reported in different apatitic compounds, for example, the AO$_6$/AO$_5$ group disorder in carbonate hydroxyapatite, the main component of human and...
animal hard tissues, and the superstructure of iodo-oxoapatite \( \text{Ca}_n(\text{PO}_4)_3\text{IO} \). The formation of \( \text{BO}_3 \) tetrahedra instead of trigonal planar \( \text{BO}_3 \) groups is preferred at high-pressure conditions during the synthesis—known as the pressure-coordinate rule. Therefore, the synthesis of apatite structures with exclusively \( \text{BO}_3 \) groups replacing the \( \text{PO}_4 \) groups of the apatite prototypes will be an interesting objective for future research. Owing to their high potential as scaffolds of growth factors and carriers for controlled protein release for bone regeneration and for biodegradable bone implants, further research in high-pressure synthesis of borate-containing hydroxyapatites and their characterization will be of great interest.

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** apatite • borates • high-pressure chemistry • lanthanides • solid-state structures

[1] A. Ito, H. Aoki, M. Akao, N. Miura, R. Otsuka, S. Tsutsumi, *J. Ceram. Soc. Jpn. (Jpn. Ed., 1988-1991) 1998, 96, 305–309.

[2] D. Maizza, M. Tribaudino, A. Delmastro, B. Lebech, *J. Solid State Chem.* 2000, 155, 389–393.

[3] P. Alberius Henning, S. Lidin, V. Petricek, *Acta Crystallogr. Sect. B* 1999, 55, 165–169.

[4] WinXx™ index, v 2.7.2, Stoe & Cie GmbH, Darmstadt, Germany, 2008.

[5] A. G. Sheidrick, *SADABS* v. 2014/5, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS Inc., Madison, Wisconsin, USA, 2014; b) G. M. Sheldrick, *Acta Crystallogr. Acta.* 2008, 64, 112–122.

[6] A. G. Sheidrick, *Acta Crystallogr. Sect. C* 2015, 71, 3–8; b) G. M. Sheldrick, *Acta Crystallogr. Acta.* 2015, 71, 3–8.

[7] K-XStep32, Revision 1.05b, Stoe & Cie GmbH, Darmstadt, Germany, 1999.

[8] A. Knappwost, Naturscienceertern 1995, 46, 555–556; b) V. P. Olevskii, S. P. Ionov, T. V. Belyaevskaya, S. M. Barinov, Inorg. Mater. 2002, 38, 182–184.

[9] T. L. Ivanova, O. V. Frank-Kamenetskaya, A. B. Kol’tsov, V. L. Ukolova, *J. Solid State Chem.* 2001, 160, 340–349.

[10] J. C. Elliott, in *Studies in Inorganic Chemistry*, Vol. 18, Elsevier, Amsterdam, The Netherlands, 1994.

[11] E. Antic-Fidancev, G. Corbel, N. Mercier, M. Leblanc, *J. Solid State Chem.* 2000, 153, 270–274.

[12] A. S. Rashchenko, T. B. Bekker, V. V. Bakakin, V. V. Seryotkin, V. S. Shevchenko, A. E. Kokh, S. Y. Stonoga, *Cryost. Chem.* 2012, 12, 2955–2960; b) T. B. Bekker, V. P. Solntsev, A. P. Yeliseyev, S. V. Rashchenko, *Cryost. Chem.* 2016, 16, 4693–4699.

[13] A. T. B. Bekker, S. V. Rashchenko, V. V. Bakakin, V. V. Seryotkin, P. P. Fedorov, A. E. Kokh, S. Y. Stonoga, *CryostEngComm* 2012, 14, 6910–6915; b) S. V. Rashchenko, T. B. Bekker, V. V. Bakakin, V. V. Seryotkin, A. E. Kokh, P. Gille, A. I. Popov, P. P. Fedorov, *J. Appl. Crystallogr.* 2013, 46, 1081–1084.

[14] X. Li, Z. Wang, J. Liu, X. Meng, K. Qiu, Q. Bao, Y. Li, Z. Wang, Z. Yang, P. Li, *Inorg. Chem.* 2018, 57, 13783–13799.

[15] S. Lei, Q. Huang, Y. Zheng, A. Jiang, C. Chen, *Acta Crystallogr. Acta.* 1989, 45, 1861–1863.

[16] A. E. Zobetz, *Z. Kristallog.* 1990, 191, 45–57; b) F. C. Hawthorne, P. C. Burns, J. D. Grice in *Mineralogy, Petrology and Geochemistry. Reviews in Mineralogy* Vol. 33 (Eds.: E. S. Grew, L. M. Anovitz), Mineralogical Society of America, Washington, 1996.

[17] E. Zobetz, *Z. Kristallog.* 1982, 160, 81–92.

[18] A. K. Matsumoto, R. Hagiwara, Z. Mazej, E. Goreshnik, B. Žemva, *J. Phys. Chem. B* 2006, 110, 218–2138; b) Z. Mazej, E. Goreshnik, K. Hironaka, Y. Katayama, R. Hagiwara, *Z. Anorg. Allg. Chem.* 2009, 635, 2309–2315; c) E. Goreshnik, A. Vakulkà, B. Žemva, *Acta Crystallogr. Acta.* 2010, 66, 69.

[19] A. I. T. Pilz, M. Jansen, *Z. Anorg. Allg. Chem.* 2011, 637, 2148–2152; b) T. Pilz, H. Nuss, M. Jansen, *J. Solid State Chem.* 2012, 186, 104–108.

[20] A. G. Cakmak, J. Nuss, M. Jansen, *Z. Anorg. Allg. Chem.* 2009, 635, 631–636; b) Z. Zhang, Y. Wang, B. Zhang, Z. Yang, S. Pan, *Angew. Chem. Int. Ed.* 2018, 57, 6577–6581; *Angew. Chem.* 2018, 130, 6687–6691.

[21] A. A. Byström, K. A. Wilhelmi, *Acta Chem. Scand.* 1951, 5, 1003–1010; b) L. Pauling, *J. Am. Chem. Soc.* 1947, 69, 542–553; c) N. E. Brese, M. O’Keefe, *Acta Crystallogr. Acta.* 1991, 47, 192–197; d) I. D. Brown, D. Altermatt, *Acta Crystallogr. Acta.* 1985, 41, 244–247.

[22] R. D. Shannon, *Acta Crystallogr. Acta.* 1976, 32, 751–767.

[23] A. J. Zhang, R. B. von Dreele, L. Eyring, *J. Solid State Chem.* 1995, 118, 133–140; b) A. J. Zhang, R. B. von Dreele, L. Eyring, *J. Solid State Chem.* 1995, 118, 141–147.

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