

a transition at 493 - 497 K from an ordered, antiferroelectric to a disordered paraelectric phase with a monoclinic structure, spacegroup $A/2a$ [1]. This is accompanied by a pronounced change in the shape and intensity of diffuse scattering and has been modeled with correlated shifts of Ti, Ca and O [1,2]. Previous characterization of this diffuse scattering probed a very limited portion in reciprocal space using synchrotron X-rays [1]. Here, we report preliminary results of a comprehensive neutron single crystal study done at room temperature. A 3D volume in reciprocal space has been measured using the SXD neutron diffractometer at ISIS and several sections have been extracted. Diffuse scattering is characterized by broad bands out to 20\AA^{-1} . We use a Monte Carlo simulation approach to characterise this with the average structure as input in order to provide a starting point for a characterization of the diffuse scattering above the phase transition.

[1] Malcherek T., Paulmann C., Chiara Domeneghetti M., Bismayer U. *J. Appl. Cryst.* 34, 108, 2001. [2] Ghose S., Ito Y., Hatch D.M., *Phys. Chem. Miner.* 17, 591, 1991.

Keywords: neutron diffuse scattering; single crystal diffraction; minerals

FA2-MS01-P18

Synthesis and Crystal Structure of SrFe[BP₂O₈(OH)₂] and CaCo(H₂O)[BP₂O₈(OH)] · H₂O. Prashanth Wilfred Menezes^a, Stefan Hoffmann^a, Yurii Prots^a, Rüdiger Kniep^a. ^aMax-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany.

E-mail: menezes@cpfs.mpg.de

Single crystals of SrFe[BP₂O₈(OH)₂] and CaCo(H₂O)[BP₂O₈(OH)]·H₂O were synthesized under mild hydrothermal conditions and investigated by single crystal X-ray diffraction [1-2]. The crystal structure of SrFe[BP₂O₈(OH)₂] (triclinic, space group $P\bar{1}$ (No. 2), $a = 6.6704(12)\text{ \AA}$, $b = 6.6927(13)\text{ \AA}$, $c = 9.3891(19)\text{ \AA}$, $\alpha = 109.829(5)^\circ$, $\beta = 102.068(6)^\circ$, $\gamma = 103.151(3)^\circ$, $V = 364.74(12)\text{ \AA}^3$, $Z = 2$) contains isolated borophosphate oligomers, [BP₂O₈(OH)₂]⁵⁻ (unbranched tetrahedral triples, Figure 1(a)), which are interconnected by Fe^{III}O₄(OH)₂ coordination octahedra. The resulting framework is characterized by elliptical channels running along [011]. Strontium takes positions inside the channels. SrFe[BP₂O₈(OH)₂] represents the first example in the structural chemistry of borophosphates where the charge of the anionic partial structure is balanced by a divalent and a trivalent cation ($M^{\text{II}}M^{\text{III}}$). The crystal structure of CaCo(H₂O)[BP₂O₈(OH)]·H₂O (triclinic, space group $P\bar{1}$ (No. 2), $a = 6.5793(3)\text{ \AA}$, $b = 7.8320(1)\text{ \AA}$, $c = 8.8172(1)\text{ \AA}$, $\alpha = 68.785(7)^\circ$, $\beta = 82.719(10)^\circ$, $\gamma = 73.985(9)^\circ$, $V = 406.930(19)\text{ \AA}^3$, $Z = 2$) contains layers stacked along [011]. The layers are built from isolated borophosphate oligomers, [B₂P₄O₁₆(OH)₂]⁸⁻ (loop branched tetrahedral hexamers, Figure 1(b)), which are interconnected by dimers of CoO₃O_{2/2}(H₂O) coordination octahedra. Calcium ions and crystal water are located at the borders of the layers, close to intra-layer cavities. CaCo(H₂O)[BP₂O₈(OH)]·H₂O is the

first example in borophosphate crystal chemistry where dimers of metal octahedra together with borophosphate oligomers form a layered arrangement.

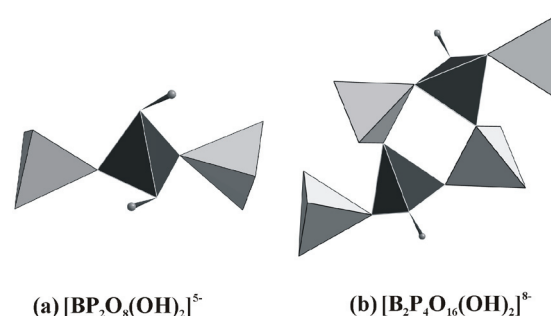


Figure 1. Anionic partial structure of (a) SrFe[BP₂O₈(OH)₂] and (b) CaCo(H₂O)[BP₂O₈(OH)]·H₂O (grey tetrahedra = BO₄; light grey tetrahedra = PO₄; grey spheres = protons).

[1] Menezes P.W., Hoffmann S., Prots Yu., Schnelle W., Kniep R., Z. *Anorg. Allg. Chem.*, 2009 (in press). [2] Menezes P.W., Hoffmann S., Prots Yu., Kniep R., Z. *Anorg. Allg. Chem.*, 2009 (in press).

Keywords: borophosphates; hydrothermal growth; single crystals

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Solid Solution Series in Transition Metal Borophosphates. Falk Gruchow^a, Stefan Hoffmann^a, Rüdiger Kniep^a. ^aMax-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany.

E-Mail: gruchow@cpfs.mpg.de

A series of transition metal borophosphates with the general formula $Mn_xCo_{1-x}[BPO_4(OH)_2]$ ($x = 0, 0.1, 0.2, \dots, 1$) was prepared under mild hydrothermal conditions. The reaction products were obtained in high yields as single phase materials according to powder X-ray diffraction data. The compounds $M^{\text{II}}[BPO_4(OH)_2]$ ($M^{\text{II}} = \text{Co}, \text{Mn}$) [1] are isotopic and crystallize in the chiral space groups $P3_121$ (No. 152) or $P3_221$ (No. 154), respectively. Their crystal structures are characterized by edge-sharing helical $M^{\text{II}}O_6$ -octahedral chains wound around 3_1 or 3_2 screw axes (running along [001]). The chains are interconnected by borophosphate single chains of alternating BO₂(OH)₂ and PO₄ tetrahedra running perpendicular to [001], resulting in a three-dimensional framework structure. As a first example in the interesting group of chiral borophosphates a complete miscibility of Co- and Mn-based phases has been proven experimentally. A linear correlation between the nominal manganese content x and the lattice parameters (or the cell volume V) was found. Further studies regarding morphological aspects, magnetic properties and possible ordering effects of the metal cations are in progress.

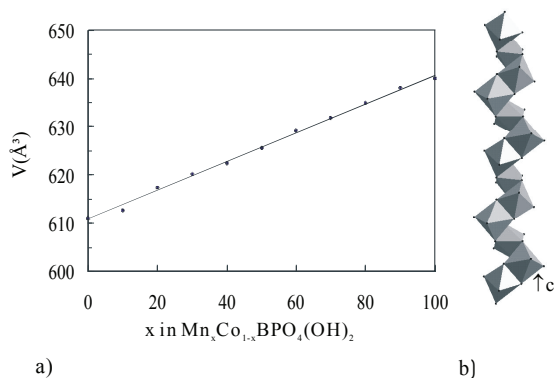


Figure 1. a) Unit cell volume V versus nominal manganese content x in the system $Mn_xCo_{1-x}[BPO_4(OH)_2]$ b) Edge-sharing $M^{II}O_6$ -octahedra wound around a 3_1 screw axis

[1] Huang Y.-X.; Ewald B.; Schnelle W.; Prots Yu.; Kniep R., *Inorg Chem.* **2006**, 45, 7578

Keywords: borophosphates; hydrothermal growth; solid solutions

FA2-MS01-P20

$Sr_{10}(PO_4)_{5.5}(BO_4)_{0.5}(BO_2)$: A Strontium Borate-Phosphate Closely Related to the Apatite Crystal Structure. Shuang Chen^{ab}, Stefan Hoffmann^a, Wilder Carrillo-Cabrera^a, Lev G. Akselrud^c, Yurii Prots^a, Jing-Tai Zhao^b, Rüdiger Kniep^a. ^aMax-Planck-Institut für Chemische Physik fester Stoffe. ^bShanghai Institute of Ceramics, Chinese Academy of Sciences. ^cDepartment of Inorganic Chemistry, Lviv State University. E-mail: shuang.chen@cpfs.mpg.de

Strontium borate-phosphate $Sr_{10}(PO_4)_{5.5}(BO_4)_{0.5}(BO_2)$ was prepared from $SrCO_3$, $NH_4H_2PO_4$ and H_3BO_3 at high temperature (1150 – 1550 °C) and was found to be free of alkali metal compounds. X-ray structure determination was carried out on a single crystal obtained from the melt (space group $P\bar{3}$ No.147; $a = 9.7973(8)$ Å, $c = 7.3056(8)$ Å, $V = 607.29(10)$ Å³, $Z = 1$). $Sr_{10}(PO_4)_{5.5}(BO_4)_{0.5}(BO_2)$ is a derivative of the apatite crystal structure. Strontium sites are found to be fully occupied while $[PO_4]^{3-}$ tetrahedra are partly replaced by $[BO_4]^{5-}$ groups. The crystal structure contains Sr cations occupying the 6g (Sr1) and 2d (Sr2, Sr3) sites, isolated tetrahedral $[PO_4]^{3-}/[BO_4]^{5-}$ groups, and linear $[BO_2]^-$ groups located in the hexagonally shaped (trigonal antiprismatic) channels formed by Sr1 atoms and running along [001] (Figure 1). The space group of the present compound is reduced to $P\bar{3}$ because the orientation of the $[PO_4]^{3-}/[BO_4]^{5-}$ tetrahedra destroys the mirror plane characteristic for the apatite crystal structure ($P6_3/m$) [1].

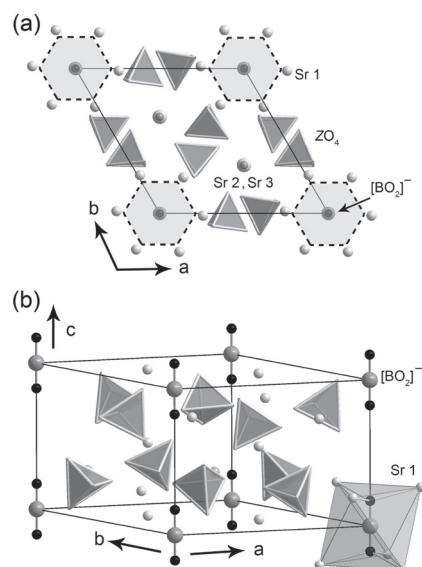


Figure. 1 Crystal structure of $Sr_{10}(PO_4)_{5.5}(BO_4)_{0.5}(BO_2)$: (a) Projection along [001] showing the hexagonally shaped channels formed by Sr1 around the three-fold inversion axis ($Z = P_{0.95}B_{0.05}$). (b) Side view emphasizing the linear $[BO_2]^-$ groups and the corresponding trigonal antiprism formed by Sr1.

[1] Calvo C., Faggiani R., Krishnamurthy N., *Acta Crystallogr.* **1975**, 31 B, 188.

Keywords: apatite; strontium borate-phosphate; crystal structure

FA2-MS01-P21

$NaSc[BP_2O_6(OH)_3] [(HO)PO_3]$: Synthesis and Crystal Structure of the First Alkali Metal Scandium Borophosphate Hydrogenphosphate. Stefan Hoffmann^a, Prashanth Wilfred Menezes^a, Yurii Prots^a, Rüdiger Kniep^a. ^aMax-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany. E-mail: hoffmann@cpfs.mpg.de

Metal phosphates and borophosphates have received much attention because of their fascinating structural architectures and potential applications [1-2]. The combination of complex borophosphate anions together with (hydrogen) phosphate groups is rather rare and may generate a new class of materials with novel properties. The first alkali metal scandium borophosphate hydrogenphosphate, $NaSc[BP_2O_6(OH)_3] [(HO)PO_3]$, was synthesized under mild hydrothermal conditions in the course of our investigations in alkali metal containing scandium borophosphates. The crystal structure was determined from single crystal X-ray data: monoclinic, space group $P2_1/c$ (No. 14), $a = 5.0010(4)$ Å, $b = 12.4271(9)$ Å, $c = 15.8340(14)$ Å, $\beta = 94.201(4)^\circ$, $V = 981.41(11)$ Å³ and $Z = 2$. The anionic partial structure of $NaSc[BP_2O_6(OH)_3] [(HO)PO_3]$ contains isolated