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A Bond Valence Study of Iron Sulfides. <u>Herbert Boller</u>. *Institut für Anorganische Chemie, Johannes-Kepler-Universität Linz, Linz, Austria.*
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The empirical bond valence method relating a bond length to a corresponding bond valence is a powerful tool for the semi quantitative analysis of interatomic distances in solids. Besides general anomalies information about the valence (oxidation state) of the implied atoms or of the charge distribution in complex anions can be obtained. This has recently been shown for partially ionic thioferrates and thiocuprates [1].In this paper the various iron sulfides, mainly minerals, and Chalcopyrite, $CuFeS_2$, and Cubanite, $CuFe_2S_3$, are studied. Bond valences v_{ij} of a pair of bonded atoms i, j were calculated from the corresponding interatomic distances d_{ij} by the relation $v_{ij}=exp[(R0_{ij}-d_{ij})/b]$. The individual parameters $R0_{ij}$ and b = 0.37 were taken mainly from the work of *O'Keefe and Brese* [2]. The valence (oxidation state) of an atom can in principle be determined from the sum of its bond valences (bond valence sum). In general the bond valence sums of iron and sulfur were found too high indicating shorter Fe-S distances than usual. This is very significant in the case of Mackinawite, the tetrahedrally coordinated iron in Greigite (thiospinell) and the disulfides Pyrite and Marcasite. However, by multiplication of all bond valence sums with a constant so that the bond valence sum of sulfur becomes 2, a realistic estimation of the oxidation state of iron is possible in most cases.

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Keywords: bond lenth/bond strength relationships; iron; sulfide minerals

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Temperature-Dependent Structural and Spectroscopic Studies of Sodium Gallosilicate Sodalites of Nitrite Containing Phases. <u>Thorsten M. Gesing</u>[a], M. Mangir Murshed[b]. *Institut für Mineralogie, Leibniz Universität Hannover, Callinstraße 3, 30167 Hannover, Germany. Present address: [a]FB05 Kristallographie, Universität Bremen, Klagenfurther Straße, 28359 Bremen, Germany. [b]GZG, Abteilung Kristallographie, Georg-August Universität Göttingen, Goldschmidtstraße 1, 37077 Göttingen, Germany.*
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We report temperature-dependent structural and spectroscopic studies of sodium gallosilicate nitrite sodalites $Na_8[GaSiO_4]_6(NO_2)_2$ between 293 K and 973 K at ambient pressure. The crystal structure of the sample was refined from X–ray powder data in the space group $P\bar{4}3n$:

a = 898.92(1) pm, V = 0.72639(2) nm^3, R_{WP} = 0.077, R_p = 0.056, R_I = 0.019 at 293 K for 4000 data points and 14 variable positional parameters. The gallium and silicon atoms on the tetrahedral framework positions are totally ordered. Rietveld calculation determines the twelve fold orientational disorder of NO_2 anion that resides slightly away from the centre of the sodalite cage. Heating X–ray investigations demonstrate a quasi-linear lattice expansion, however, with no phase transition. Distortions of TO_4 tilt, T—O—T angle and T—O distances were observed as function of temperature. The average crystal size of the sodalites can be segregated into two distinct regions within a sharp change of temperature between 613 K and 623 K (Fig. 1). The recorded FTIR and Raman spectra showed typical absorption bands for nitrite containing sodalite phases. The frequency shift of the temperature-dependent FTIR spectral bands of T—O—T symmetric and asymmetric modes were explained in terms of the structural features. This thorough investigation would help understand temperature-dependant structural properties, in particular, of A–, X– and Y–type zolites having similar building units.
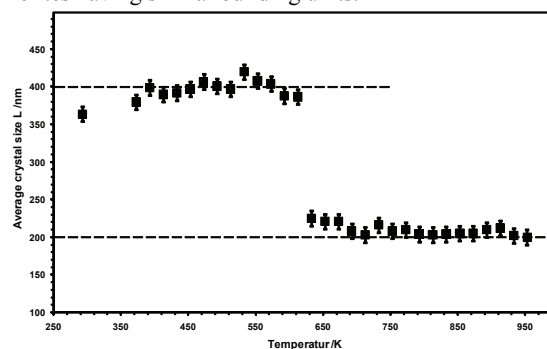

Fig.1 Temperature dependend change of the averagecrystal size of gallosilicate nitrate sodalite

Keywords: microporous solids; crystal structure properties; thermal analysis

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Neutron Diffuse Scattering Study of $CaTiSiO_5$ at Room Temperature. <u>Matthias J. Gutmann</u>[a], Chris K. D. Stock[a], Ian P. Swainson[b]. *[a]Rutheford Appleton Laboratory, ISIS Facility, Chilton Didcot, Oxfordshire OX4 3SH, United Kingdom. [b]Canadian Neutron Beam Centre, National Research Council, Chalk River Laboratories, Ontario, Canada K0J 1J0.*
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$CaTiSiO_5$ is a mineral commonly known as titanite or sphene. At room temperature, it crystallizes in a monoclinic structure, spacegroup P 2_1/a with lattice parameters a=7.0780(18), b=8.7356(21), c=6.5697(15), β=113.700(15)° and forms a highly interconnected network of corner-sharing TiO_6 chains with neighbouring chains linked by SiO_4 tetrahedra and Ca occupying cavities with 7-fold oxygen coordination. Sphene has been reported to undergo

a transition at 493 - 497 K from an ordered, antiferroelectric to a disordered paraelectric hase 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 20Å^{-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.

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Keywords: neutron diffuse scattering; single crystal diffraction; minerals

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Synthesis and Crystal Structure of SrFe[$BP_2O_8(OH)_2$] and CaCo(H_2O)[$BP_2O_8(OH)$] ·H_2O.
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Single crystals of SrFe[$BP_2O_8(OH)_2$] and CaCo(H_2O)[$BP_2O_8(OH)$]·H_2O were synthesized under mild hydrothermal conditions and investigated by single crystal X–ray diffraction [1-2]. The crystal structure of SrFe[$BP_2O_8(OH)_2$] (triclinic, space group $P\bar{1}$ (No. 2), $a = 6.6704(12)$ Å, $b = 6.6927(13)$ Å, $c = 9.3891(19)$ Å, $\alpha = 109.829(5)°$, $\beta = 102.068(6)°$, $\gamma = 103.151(3)°$, $V = 364.74(12)$ Å^3, $Z = 2$) contains isolated borophosphate oligomers, [$BP_2O_8(OH)_2$]$^{5-}$ (unbranched tetrahedral triples, Figure 1(a)), which are interconnected by Fe^{III}O$_4$(OH)$_2$ coordination octahedra. The resulting framework is characterized by elliptical channels running along [011]. Strontium takes positions inside the channels. SrFe[$BP_2O_8(OH)_2$] 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 ($M^{II}M^{III}$). The crystal structure of CaCo(H_2O)[$BP_2O_8(OH)$]·H_2O (triclinic, space group $P\bar{1}$ (No. 2), $a = 6.5793(3)$ Å, $b = 7.8320(1)$ Å, $c = 8.8172(1)$ Å, $\alpha = 68.785(7)°$, $\beta = 82.719(10)°$, $\gamma = 73.985(9)°$, $V = 406.930(19)$ Å^3, $Z = 2$) contains layers stacked along [011]. The layers are built from isolated borophosphate oligomers, [$B_2P_4O_{16}(OH)_2$]$^{8-}$ (loop branched tetrahedral hexamers, Figure 1(b)), which are interconnected by dimers of CoO$_3$O$_{2/2}$(H_2O) coordination octahedra. Calcium ions and crystal water are located at the borders of the layers, close to intra–layer cavities. CaCo(H_2O)[$BP_2O_8(OH)$]·H_2O is the first example in borophosphate crystal chemistry where dimers of metal octahedra together with borophosphate oligomers form a layered arrangement.
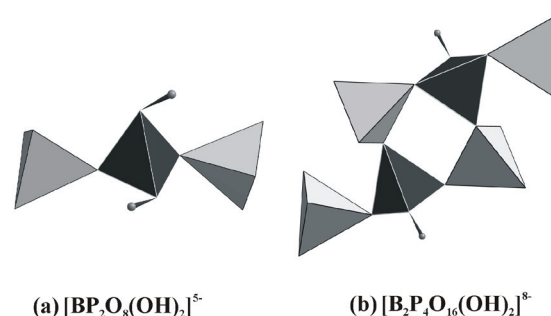

(a) [$BP_2O_8(OH)_2$]$^{5-}$ (b) [$B_2P_4O_{16}(OH)_2$]$^{8-}$

Figure 1. Anionic partial structure of (a) SrFe[$BP_2O_8(OH)_2$] and (b) CaCo(H_2O)[$BP_2O_8(OH)$]·H_2O (grey tetrahedra = BO$_4$; light grey tetrahedra = PO$_4$; 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]. *[a]Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany.*
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A series of transition metal borophosphates with the general formula Mn$_x$Co$_{1-x}$[$BPO_4(OH)_2$] (x = 0, 0.1, 0.2, ..., 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^{II}[$BPO_4(OH)_2$] (M^{II} = Co, Mn) [1] are isotypic 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 $M^{II}O_6$-octahedral chains wound around 3_1 or 3_2 screw axes (running along [001]). The chains are interconnected by borophosphate single chains of alternating BO$_2$(OH)$_2$ and PO$_4$ 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.