A Bond Valence Study of Iron Sulfides. <u>Herbert Boller</u>. *Institut für Anorganische Chemie, Johannes-Kepler-Universität Linz, Linz, Austria.*
E-mail: herbert.boller@aon.at

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

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.*
E-mail: gesing@uni-bremen.de

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.
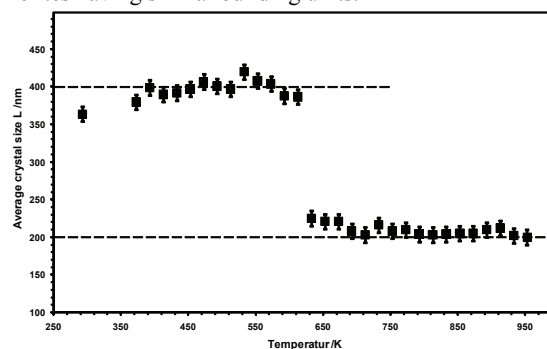

Fig.1 Temperature dependend change of the averagecrystal size of gallosilicate nitrate sodalite

Keywords: microporous solids; crystal structure properties; thermal analysis

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.*
E-mail: Matthias.Gutmann@stfc.ac.uk

$CaTiSiO_5$ 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