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Keywords: ilmenites, X-ray absorption, phase composition

P10.05.41*Acta Cryst.* (2008). **A64**, C503**Low temperature structural distortions of brucite**Bryan C Chakoumakos¹, Antonio M. dos Santos¹, Juske Horita¹, Arthur J. Schultz²¹Oak Ridge National Laboratory, Neutron Scattering Science Division, P.O. Box 2008, bldg 7962, Oak Ridge, TN, 37831-6393, USA, ²Argonne National Laboratory, Argonne, IL 60439 USA, E-mail: kou@ornl.gov

Neutron powder diffraction studies of brucite, Mg(OD)₂, indicate subtle structural anomalies at 100K revealed by the temperature dependence of the anisotropic atomic displacement parameters (ADPs). Over the temperature interval 135K to 75K, the anisotropic ADP ellipsoid of the oxygen atom in the single D/H site model changes from prolate to oblate. The anisotropic ADPs of the D/H atom also exhibit anomalous temperature dependence below 135K. In addition, the alpha-angle, defined as the angle between the single-site DO bond and the split-site DO bond, decreases from 300K to 75K then increases at lower temperatures, and below 135K the thermal contraction of the octahedral layer thickness ceases. Additional understanding of this structural behavior is being sought from Raman spectroscopy and heat capacity measurements. The brucite layer is a fundamental building unit of a great variety of geologically important hydrous phyllosilicates, which include micas and clays. Brucite has P3barm1 space group symmetry with 3 atom positions all on 3-fold axes in the asymmetric unit. The Mg atom is at the origin, and the O and D/H atoms have variable z-coordinates. Typically, the D/H position is moved off from the three-fold axis into a fractionally occupied split-position to better accommodate the large ADP found in the single-site model. Oak Ridge National Laboratory is supported by the Division of Materials Sciences, U.S. D.O.E. (contract DE-AC05-00OR22725 with UT-Battelle, LLC).

Keywords: brucite, thermal expansion mechanism, neutron powder diffraction

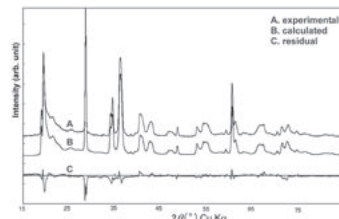
P10.05.42*Acta Cryst.* (2008). **A64**, C503**Simulation of powder XRD patterns from disordered phyllosilicates using information from HRTEM**

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Stacking disorder is a common phenomenon in phyllosilicates but its nature is difficult to be deduced using conventional diffraction techniques. In contrast, recent investigations using high-resolution transmission electron microscopy (HRTEM) have elucidated the structure of stacking disorder in various phyllosilicates, by directly observing individual layers and stacking sequences. Furthermore, simulations of X-ray diffraction (XRD) patterns using the information from the HRTEM results can complement the limited analysis area in TEM and quantify the density of the stacking disorder. In this paper, we describe several successful results to reproduce experimental powder XRD patterns from 2:1 phyllosilicates (pyrophyllite, talc, celadonite, etc.) including

considerable stacking disorder, using the DIFFaX program (Treacy et al., 1991) whose calculation parameters were derived from direct observation of stacking by HRTEM. The attached figure is an example of our results, comparison between the experimental and simulated patterns of disordered talc.



Keywords: stacking faults, high-resolution transmission electron microscopy, simulation X-ray diffraction

P10.05.43*Acta Cryst.* (2008). **A64**, C503**Rietveld and ⁵⁷Fe Mössbauer study of babingtonite from Shimane Peninsula, Japan**Masahide Akasaka¹, Takehiko Kimura¹, Mariko Nagashima²¹Shimane University, Geoscience, akasaka@riko.shimane-u.ac.jp, Matsue, Shimane Prefecture, 690-8504, Japan, ²University of Bern, mariko.nagashima@krist.unibe.ch, CH-3012 Bern Switzerland, E-mail: akasaka@riko.shimane-u.ac.jp

Oxidation state and distribution of Fe between two independent octahedral sites, Fe1 and Fe2, in babingtonite from Shimane Prefecture, Japan, were investigated using Rietveld and ⁵⁷Fe Mössbauer method. Babingtonite occurs in cavities of hydrothermally altered gabbro or dolerite, and is associated with prehnite and calcite. It is rhombic in form with edge length of 0.5-1 mm. This mineral has sector zoning, where Fe and Mn contents are different from each other, and compositional zonal structure with Mn and Al-rich core and Fe-rich rim. The chemical formula based on the average composition is (K_{0.004}Na_{0.006}Ca_{2.009})(Mg_{0.113}Mn_{0.094}Fe_{1.696}Ni_{0.02}V_{0.003}Cr_{0.001}Ti_{0.009}Al_{0.058})Si_{5.005}O₁₄(OH). The Fe²⁺:Fe³⁺-ratio based on the assumption that Fe1 and Fe2 sites are occupied by divalent and trivalent cations, respectively, is 45.2:54.8, which was consistent with the result by ⁵⁷Fe Mössbauer analysis: Fe²⁺:Fe³⁺-ratio determined from the area ratio of the doublets of Fe²⁺ (*IS* = 1.160 mm/s, *QS* = 2.482 mm/s) and Fe³⁺ (*IS* = 0.424 mm/s, *QS* = 0.797 mm/s) is 45:55. The site occupancies of cations at the Fe1 and Fe2 sites given by the X-ray Rietveld analysis (*R*_{wp} = 11.84 %, *R*_c = 6.86 %, *S* = 1.73) are (Fe_{0.82}Mg_{0.18})^{Fe1}(Fe_{0.89}Al_{0.11})^{Fe2}. Unit-cell parameters are *a* 7.4656(5), *b* 12.1761(8), *c* 6.6816(4) Å, α 86.156(5)°, β 93.881(3)°, γ 112.257(4)°, *V* 560.27(6) Å³, and average Fe1-O and Fe2-O distances are 2.15 and 2.03 Å, respectively. The crystallographic features are nearly the same as those of babingtonite from other localities.

Keywords: babingtonite, Rietveld analysis, Mossbauer spectral analysis

P10.06.44*Acta Cryst.* (2008). **A64**, C503-504**Single-crystal X-ray diffraction study of chabazite at 123 K**

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Chabazite [idealized formula $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24}\cdot 12\text{H}_2\text{O}$] is one of the most widespread natural zeolites. A consensus on positions of water molecules and exchangeable cations in chabazites had not been obtained, although attempts to determine their positions have been made intensively. However, our previous study (Nakatsuka *et al.*, 2007) successfully determined their positions at room temperature, in a natural chabazite [$\text{Ca}_{1.57}\text{Na}_{0.49}\text{Al}_{3.39}\text{Si}_{8.55}\text{O}_{24}\cdot 12.47\text{H}_2\text{O}$] from Komuro, Oh-hito, Shizuoka Prefecture, Japan, using a single crystal X-ray diffraction method. Consequently, we revealed the presences of five water sites (OW1-OW5) and four exchangeable-cation (Ca1-Ca4) sites. However, locations of hydrogen atoms in chabazites could not be determined. Determining their positions is quite important for gaining insights into the interactions between water molecules and framework and between water molecules. X-ray diffraction study at low temperature is useful for reducing thermal vibrations of atoms and should make the determination of hydrogen positions easy. Here, we perform the single crystal X-ray diffraction study at 123 K using the same sample as that of our previous study (Nakatsuka *et al.*, 2007) and try to determine hydrogen positions. Moreover, we discuss the crystallographic configurations of water molecules and exchangeable cations at low temperature. In the present study, we found five water sites and four exchangeable-cation sites, as well as the case of room temperature (Nakatsuka *et al.*, 2007). Three (OW1, OW3, OW4) of five water sites found at 123 K are the same as those at room temperature, whereas the remaining two water sites (OW2, OW5) are different from those at room temperature. At present, we are examining hydrogen positions on difference Fourier map.

Keywords: zeolite crystal chemistry, microporous materials, low-temperature single-crystal diffractometry

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Structural behaviour and thermal phase transitions of borosilicates with large cations

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The knowledge of borosilicate structures with tetrahedral boron and silicon is very limited in comparison with the number of related aluminosilicate structures. Present work aims at studying the crystal structures and phase transformations as a function of temperature and chemical composition in ternary borosilicate systems with large (K, Rb, Cs, Sr) cations. During the years microporous compounds RBSi_2O_6 (R = K, Rb, Cs) isotopic with cubic leucite (ANA) are studied extensively by us. Structural (cubic $I-43d$ \leftrightarrow cubic $Ia3d$) transitions of K-Rb, K-Cs and Rb-Cs boroleucites are presented as a function of composition and temperature. Compared with natural aluminosilicates (ANA), borosilicates exhibit lower melting points and smaller coefficients of thermal expansion. Recently a new low symmetrical presumably orthorhombic polymorph of KBSi_2O_6 was prepared in hydrothermal conditions. High-temperature X-ray diffraction (HTXRD) showed that this modification undergo a series of reversible displacive transitions first into tetragonal and then to the cubic phase. Above 1000 °C Cs-rich ANA borosilicates decompose, releasing a gas phase and forming stoichiometrically different $\text{CsBSi}_5\text{O}_{12}$ phase. Its structure was refined in CAS framework type. $\text{CsBSi}_5\text{O}_{12}$ also decomposes above 1070 °C via liberating a gas phase. After treatment at 1100 °C its XRD pattern contained the maxima of SiO_2 only. In $\text{SrO-B}_2\text{O}_3\text{-SiO}_2$ system $\text{Sr}_3\text{B}_2\text{SiO}_8$

(unindexed pdf 32-1224) was prepared by solid state reaction; it was indexed in orthorhombic space group $Pcmn$: $a=3.924(1)$, $b=5.416(2)$, $c=12.427(7)$ Å. According to HTXRD $\text{Sr}_3\text{B}_2\text{SiO}_8$ expands anisotropically. This research is supported by Russian Foundation for Basic Researches (08-03-91952) and by grant of Russian President for young scientists (MK-3661.2007.5).

Keywords: zeolite-like borosilicates, high-temperature x-ray diffraction, crystal structure determination

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Zeolite-based (guest-host) systems: Structure, interactions and optical properties

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Zeolites are characterised by a porous framework built from SiO_4 and AlO_4^- tetrahedra whose global negative charge is balanced by exchangeable cations sparse throughout the structure. The use of molecular sieves (zeolites, microporous metallophosphates) possessing large cages and channels of uniform sizes enables the incorporation of guest molecules that may seat in well defined positions. Contrary to usual applications as selective sorbants or catalysts where the (guest-host) system has only a transient character and where adsorbed molecules are highly mobile, in (chromophore-zeolite) systems a permanent and controlled arrangement of molecules is advisable. In all cases detailed understanding of the guest-host interactions (hydrogen bonding, ion pairs) is a primary step to tailor-made functional materials at a molecular level. Despite frequent defects or disorder induced by the sample preparation, diffraction remains the main source for structural information (framework topology, cationic distribution in the cavities, interaction of the guest entity with the framework), supplemented by local spectroscopies (XAFS, UV-Visible) or Monte-Carlo simulations. We will present examples of X-Ray and neutron diffraction studies on (guest@zeolite) systems used as pigments, exhibiting Second Harmonic Generation properties, or whose colour is sensible to water sorption. The influence of sample preparation over optical properties (guest molecules loading rate, structural defects, cationic distribution) will be discussed.

Keywords: zeolites-microporous materials, guest-host structures, structure determination using X-ray and neutron di