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Löwenstein's Rule Extended to an Aluminum Rich Framework. The Structure of Bicchulite, $Ca_8(Al_2SiO_6)_4(OH)_8$, by MASNMR and Neutron Diffraction

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Löwensteins rule of Al−O−Al link avoidance has been extended to aluminum rich frameworks following a study of the material bicchulite, $Ca_8(Al_2SiO_6)_4(OH)_8$, by MASNMR and neutron diffraction which probed the aluminum and silicon distribution. The ^{29}Si NMR spectrum of bicchulite shows that Si−O−Si links are avoided; this also minimizes the number of Al−O−Al connections beween the tetrahedral units. Neutron diffraction shows that the silicon and aluminum are disordered over the long range with the material crystallizing in the space group $I\bar{4}3m$.

The majority of framework structures formed from linked tetrahedral units are aluminosilicates with an upper limit on the Al to Si ratio of 1:1. Aluminosilicates are typically synthesized hydrothermally at moderate temperatures 100−250 °C and invariably obey Löwenstein's rule of aluminum avoidance[1] in that Al−O−Al linkages are prohibited and the Si:Al ratio reaches 1:1 at best. However, some frameworks containing directly linked AlO_4 groups are known. The best characterized materials are the pure aluminate sodalites of the general composition $M_8(AlO_2)_{12}X_2$ where M is a divalent cation, e.g. Ca, Sr, and Cd, and X is a divalent anion, e.g. SO_4, CrO_4, WO_4, O, S, Se, and Te.[2−4] These materials are prepared under dry, high temperature conditions by direct reaction of alumina with metal oxides/salts. The only other well authenticated framework structure containing Al−O−Al linkages is that of $Ca_8(Al_2SiO_6)_4.(OH)_8$ which occurs naturally as the mineral bicchulite.[5,6] This compound can be synthesized using hydrothermal conditions but at rather higher temperatures and pressures than most framework forming reactions. The successful synthesis of these high aluminum frameworks at elevated temperature indicates that obeyance of Löwenstein's rule is kinetic in origin, i.e. that formation of Al−O−Al units is possible under the correct synthetic conditions. In this article we report the structural characterization of bicchulite by high resolution powder neutron diffraction and MASNMR and show that Al−O−Al linkages are avoided as far as possible even in aluminum rich structures.

Bicchulite was prepared hydrothermally following the literature method via gehlenite.[7] $CaCO_3$, Al_2O_3, and SiO_2 in the correct molar ratios were initially fired at 800 °C for two periods of 24 h. and then 1330 °C for 48 h. Powder X-ray diffraction of the product was consistent with formation of $Ca_2Al_2SiO_7$, gehlenite.[7] 2 g of $Ca_2Al_2SiO_7$ was placed in a gold capsule with 0.5 mL of H_2O and sealed; the capsule was heated to 538 °C under 1 kbar hydrothermal pressure for 7 days using a cold-seal hydrothermal bomb and slow cooled to room temperature. The apparatus used is surrounded in a 8 mm steel cabinet and the volume of water under pressure is minimized by using a filler rod to reduce the bomb volume and therefore reduce the potential hazards associated with the experiment. A safety reservoir is also used to balance any pressure changes in the bomb. The powder X-ray diffraction pattern of the product was consistent with the formation of cubic bicchulite.

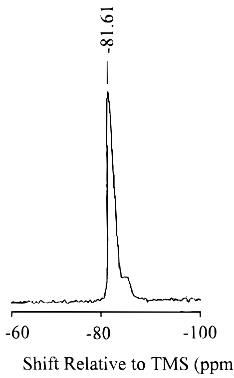

Figure 1. ^{29}Si MASNMR spectrum of $Ca_8(Al_2SiO_6)_4(OH)_8$.

The ^1H and ^{29}Si MASNMR spectra of bicchulite were collected using a Bruker AM300 spectrometer and a Varian VXR 300 spectrometer respectively. Sample spin speeds were 4.5 kHz for ^1H and 4 kHz for ^{29}Si. The proton NMR consisted of a single resonance at 6.62 ppm relative to TMS. The ^{29}Si (Figure 1) showed a strong resonance at −81.6ppm relative to TMS with a weak shoulder (5%) at −84.6 ppm. This weak peak is probably derived from amorphous hydrogrossular impurity in the material. A value for the ^{29}Si chemical shift in naturally occurring bicchulite has been given as −86.8 ppm[8] though no interpretation of this datum was given. The significant chemical shift difference between this value and that obtained in this work may result from compositional variations between synthetic and natural samples which may contain iron and/or partial replacement of aluminum by a mixture of magnesium and silicon. Correlations of Si−O−T bond angles and ^{29}Si chemical shift are of high quality and reliability[9] and may be used to check chemical shift values. For a Si−O−Al bond angle of 131.1°, the expected ^{29}Si chemical shift is −80.5 ppm close to the value found in this work. A ^{29}Si chemical shift of −86.8 ppm is representative of a Si−O−Al bond angle close to 144°, much larger than that determined for bicchulite, both here and in the single crystal work;[5,6] this therefore throws some doubt on the validity of the value reported previously.[9]

Powder neutron diffraction data were collected on the instrument D2B at the ILL using a wavelength of 1.594 Å over a period of 6 h; a step size of 0.05° was used over the angular range 5−160°. Structure refinement was undertaken in the space group $I\bar{4}3m$ using the single crystal structure of bicchulite as the starting model.[6] Scattering lengths were taken as 3.45, 4.15, 5.81, 4.90, and −3.74 fm for Al, Si, O, Ca, and H respectively. No evidence was seen for ordering of the framework species, and a mixed occupancy site with a scattering

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Table 1. Atomic Parameters for $Ca_8(Al_2SiO_6)_4(OH)_8$ (Esd's Given in Parentheses)[a]

atom	*X*	*Y*	*Z*	U_i or U_e × 100	site multiplicity/ occupancy
Al/Si	0.250000	0.500000	0.000000	0.69(21)	12/1.0
O	0.14075(18)	0.14075(18)	0.42287(20)	1.43(7)	24/1.0
Ca	0.14373(28)	0.14373(28)	0.14373(28)	1.60(7)	8/1.0
O(H)	0.38264(28)	0.38264(28)	0.38264(28)	1.39(9)	8/1.0
H	0.3115(13)	0.3115(13)	0.3491(17)	3.2(5)	24/0.3333

[a] $R_{wp} = 3.53\%$, $R_p = 2.74\%$, $\chi^2 = 1.66$. Lattice constants $a = b = c = 8.83175(4)$ Å. $\alpha = \beta = \gamma = 90°$. Cell volume = 688.876(3) Å^3. Space group: $I\bar{4}3m$.

Table 2. Bond Lengths (Å) and Selected Angles (deg) for $Ca_8(Al_2SiO_6)_4(OH)_8$ (Esd's Given in Parentheses)

distances		angles	
Al/Si−O × 4	1.7147(8)	O−Al(Si)−O	108.46(8) × 4
Ca−O × 3	2.466(3)		111.52(16) × 2
Ca−O(H) × 4	2.329(4)	Al(Si)−O−Al(Si)	131.15(12)
O−H × 1	0.936(16)	O−H- - -O	144.6(14)
O(H)−O	2.230(19)		

power equivalent to $^2/_3$:$^1/_3$ Al:Si was assigned to the framework. Refinement was undertaken using the GSAS package[10] and initial cycles involved instrumental parameters and positional parameters for all atoms and proceeded smoothly producing reasonable atomic and thermal parameters for all atoms except hydrogen. In order to produce reasonable O−H distances and hydrogen atom temperature factors it was necessary to disorder the hydrogen away from the (*x*,*x*,*x*) site used previously in the single crystal-structure determination[5,6] on to an (*x*,*x*,*z*) site with one-third occupancy, this also produced a small reduction in R_{wp}. Final refined atomic co-ordinates, cell data and fit factors are summarized in Table 1 and derived bond distances and angles are given in Table 2. Figure 2 shows part of the sodalite cage and the orientation of the hydroxide groups within it.

$Ca_8(Al_2SiO_6)_4(OH)_8$ has a sodalite type structure but unusually has four anions per beta cage. The calcium and hydroxide ions form two interpenetrating tetrahedral units within the cages. The coordination geometry of the calcium ion thus consists of three hydroxide oxygens plus three oxide ions of the framework producing a roughly octahedral environment. Weaker interactions exist to a fourth hydroxide ion and three further framework oxygens. The hydroxide ions are not aligned directly along the 3-fold axis of the unit cell, which would produce an extremely unusual symmetrical trifurcated hydrogen bond. Displacement off the 3-fold axis occurs to produce one stronger interaction to just one of the framework oxygens. The O−H- - -O bond angle of 144.6° is typical of such an environment with a weak hydrogen bond length of 0.96 Å as found in hydrates.[11]

Analysis of the powder neutron diffraction data shows that the bicchulite framework consists of a **long range** disordered arrangement of the aluminum and silicon atoms. Any long range ordering of these atoms would be readily distinguished by neutron diffraction due to their significantly different scattering lengths. The average tetrahedral bondlength of 1.7147(8) Å is very close to that expected from a weighted average (1.713 Å) of typical four coordinate Si−O and Al−O distances (Si−O 1.624 Å, Al−O 1.757 Å). However, the ^{29}Si MASNMR data essentially consists of a single resonance demonstrating that the distribution of silicon and aluminum is not wholly random and consistent with the silicon solely in $Si(OAl)_4$ environments. If the silicon nuclei were fully disordered then a number of Si environments $Si(-OSi)_n(-OAl)_{4-n}$ would occur producing the characteristic multiline spectrum (n = 0,1, 2, 3, 4; relative intensities 16:32:24:8:1). This indicates that in this aluminum rich framework that either Si−O−Si or Al−O−Al links are avoided as far as possible. The latter can be derived from the fact that distributing the silicon such that each has an immediate environment of $Si(OAl)_4$ also minimizes the total number of Al−O−Al links in the structure. The weak resonance at −84 ppm in the ^{29}Si MASNMR spectrum is unlikely to derive from a low level of $Si(OAl)_3(OSi)$ environments as the chemical shift separation of these and $Si(OAl)_4$ environments is typically 5−6 ppm and the assignment of this resonance to the impurity hydrogrossular correct. The ^{1}H chemical shift of 6.62 ppm is typical of a moderately weakly hydrogen bonded OH group.[12]

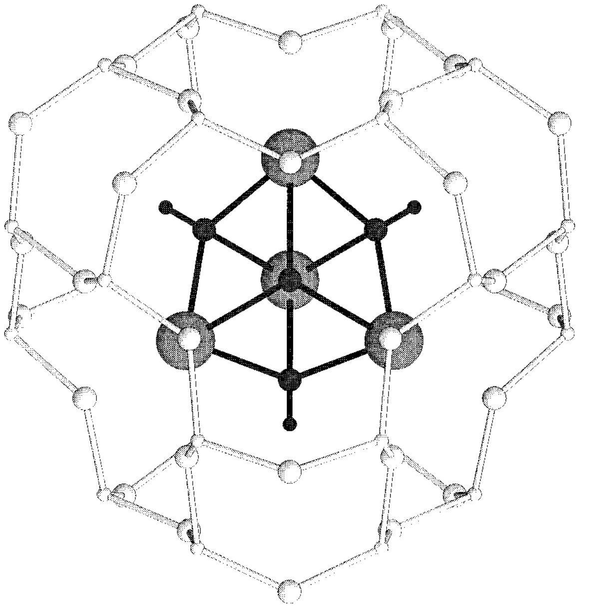

Figure 2. The sodalite cage of $Ca_8(Al_2SiO_6)_4(OH)_8$, viewed down ⟨111⟩, highlighting the occluded species. The four hydroxide oxygens are shown as medium−small, dark spheres bonded to hydrogen (small, dark); only one of the three sites over which the hydrogen atoms on each oxygen are disordered is shown. The calcium ions are shown as large, medium-gray spheres.

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