

Refinement of the crystal structure of bicchulite, $\text{Ca}_2[\text{Al}_2\text{SiO}_6](\text{OH})_2$

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Abstract. The crystal structure of synthetic bicchulite was refined from X-ray single-crystal data ($R = 0.012$ for all 121 symmetry-independent observed reflections). Bicchulite has a sodalite-type framework structure with Al and Si distributed statistically on the tetrahedral sites. The calcium ions and empty $(\text{OH})_4$ -tetrahedra occupy the cavities of the framework. The bonding of the hydrogen atoms is discussed.

Introduction

The crystal structure of bicchulite, $\text{Ca}_2[\text{Al}_2\text{SiO}_6](\text{OH})_2$ has recently been determined by Sahl and Chatterjee (1977) from X-ray data measured on a Hilger and Watts four-circle diffractometer (Mo radiation). They used a synthetic single crystal with a diameter of about 0.05 mm, the largest crystal of good quality which was available. Due to the high symmetry and small volume of the crystal, only 65 symmetry-independent reflections with a significant intensity could be measured in the range up to $\theta = 35^\circ$.

The structure was determined and refined to $R = 0.07$. This result, however, was not entirely satisfactory: the distances O–O in the $(\text{Al,Si})\text{O}_4$ -tetrahedra varied between 2.75 and 2.95 Å, the angles O–(Al,Si)–O from 106° to 118° . It was not possible to determine the positions of the hydrogen atoms, which are of importance in view of the rather unusual configuration of the (OH) -groups: they form empty $(\text{OH})_4$ -tetrahedra around the origin and the center of the cell.

In the course of a demonstration of the SYNTEX R $\bar{3}$ Structure Determination System, it was possible to collect a new set of data, using the same crystal, and to complete the refinement of the structure.

X-ray data collection and reduction

Bicchulite crystallizes in space group $I\bar{4}3m$ (No. 217) with $a = 8.825 \pm 0.001 \text{ \AA}$ and a cell content of $Z = 4$ formula units $\text{Ca}_2[\text{Al}_2\text{SiO}_6](\text{OH})_2$ (Gupta and Chatterjee, 1978; Sahl and Chatterjee, 1977). The orientation matrix of the crystal was calculated by least-squares refinement of the angular positions of ten high-angle reflections. The diffracted intensity was measured with a scintillation counter by ω -scan technique up to $\theta = 30^\circ$ (Mo radiation, graphite monochromator). A reference reflection was monitored after each group of 100 reflections. In this manner, 613 reflections with positive indexes h , k , and l were measured which yielded 127 symmetry-independent reflections. Of these, six were considered to be unobserved (less than 1.96σ).

Structure refinement

The positional and isotropic thermal parameters of all atoms except hydrogen as given by Sahl and Chatterjee (1977) were refined by full-matrix least-squares using the facilities of the SYNTEX system. Two cycles of isotropic refinement reduced the R value to 0.027 for all reflections and to 0.023 excluding the unobserved reflections.

The refinement was completed on a Telefunken 440 computer at the Computer Center, Ruhr-Universität, Bochum. In a further least-squares cycle, the thermal parameters were converted to anisotropic. This reduced the R value to 0.020 for all observed reflections (with unit weights). At this stage, a three-dimensional difference Fourier synthesis was calculated. It showed electron densities of at most 0.30 e/\AA^3 at the known positions of the heavier atoms, one further peak of 0.35 e/\AA^3 on the body diagonal of the cell at $x = 0.318$ and spurious background densities of at most 0.2 e/\AA^3 in the rest of the cell.

The peak at $x = 0.318$ was taken as hydrogen location. In a least-squares refinement started with an isotropic temperature factor $B_{\text{H}} = 0.0$ for the hydrogen atoms, the hydrogen position shifted to $x = 0.328$ and B_{H} became negative ($B_{\text{H}} = -0.3$ with an estimated standard deviation of ± 1.3). Therefore, in the last refinement cycles, B_{H} was constrained to zero.

Giving unit weight to all reflections, the R value was reduced to 0.017 for all observed reflections (with weights equal to $1/\sigma^2$, $R_w = 0.012$). Including the six unobserved reflections, a value of $R = 0.026$ was obtained with unit weights. The final atomic parameters are listed in Table 1. The anisotropy of the thermal motion of the atoms is barely pronounced.

A list of observed and calculated structure amplitudes is available on request.

Table 1. Bicchulite. Positional parameters, crystallographic sites in space group $I\bar{4}3m$ and thermal parameters^a of atoms (standard deviation in the last digit in parentheses)

Atom	Site	x	y	z	B_{11} $\times 10^4$	B_{22} $\times 10^4$	B_{33} $\times 10^4$	B_{12} $\times 10^4$	B_{13} $\times 10^4$	B_{23} $\times 10^4$
Ca	8c	.1434(1)	.1434(1)	.1434(1)	24.4(5)	B_{11}	B_{11}	- 8(2)	B_{12}	B_{12}
(Si,Al)	12d	$\frac{1}{4}$	$\frac{1}{2}$	0	15(1)	16(1)	B_{22}	0	0	0
O(1)	24g	.1407(1)	.1407(1)	.4220(2)	32(1)	B_{11}	27(2)	3(5)	2(3)	B_{13}
O(2)	8c	.3845(2)	.3845(2)	.3845(2)	30(2)	B_{11}	B_{11}	-15(4)	B_{12}	B_{12}
H	8c	.328(3)	.328(3)	.328(3)	0	-	-	-	-	-

^a The temperature factor is of the form $\exp [-(B_{11}h^2 + B_{22}k^2 \dots)]$.

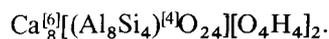
Table 2. Bicchulite. Interatomic distances and angles in the main coordination polyhedra (standard deviation in the last digit in parentheses)

(CaO ₆)-octahedron			(Al _{0.67} Si _{0.33})O ₄ -tetrahedron		
Ca-O(2)	2.311(2) Å	3 ×	(Al,Si)-O(1)	1.716(1) Å	4 ×
Ca-O(1)	2.459(2) Å	3 ×	O(1)-O(1)	2.784(2) Å	4 ×
O(2)-O(2)	2.883(2) Å	3 ×		2.839(2) Å	2 ×
O(1)-O(1)	3.511(2) Å	3 ×	O(1)-(Al,Si)-O(1)	108.4(1)°	4 ×
O(1)-O(2)	3.532(2) Å	6 ×		111.9(1)°	2 ×
	4.754(2) Å	3 ×	(OH) ₄ -tetrahedron		
O(1)-Ca-O(1)	91.1(1)°	3 ×	O(2)-O(2)	2.883(2) Å	6 ×
O(2)-Ca-O(2)	77.1(1)°	3 ×	O(2)-H	0.87(3) Å	1 ×
O(1)-Ca-O(2)	95.5(1)°	6 ×			
	170.6(1)°	3 ×			

Description and discussion of the structure

Bicchulite (Sahl and Chatterjee, 1977) is a tectosilicate with a framework of the sodalite type (Pauling, 1930).

In Table 2, interatomic distances and angles calculated on the basis of the refined parameters are listed. The crystal chemical formula of bicchulite is



In space group $I\bar{4}3m$, the Al and Si atoms have to be distributed statistically on site 12d. The (Si,Al)-positions coordinated tetrahedrally by O(1)-atoms form the three-dimensional framework of the sodalite type in which the tetrahedra are linked by all four corners (Fig. 1 a). Since the Al:Si ratio in bicchulite is 2:1, Loewenstein's rule (1954) cannot be obeyed. It is interesting to note in this respect that in xanthophyllite, a mica in which the Al:Si ratio

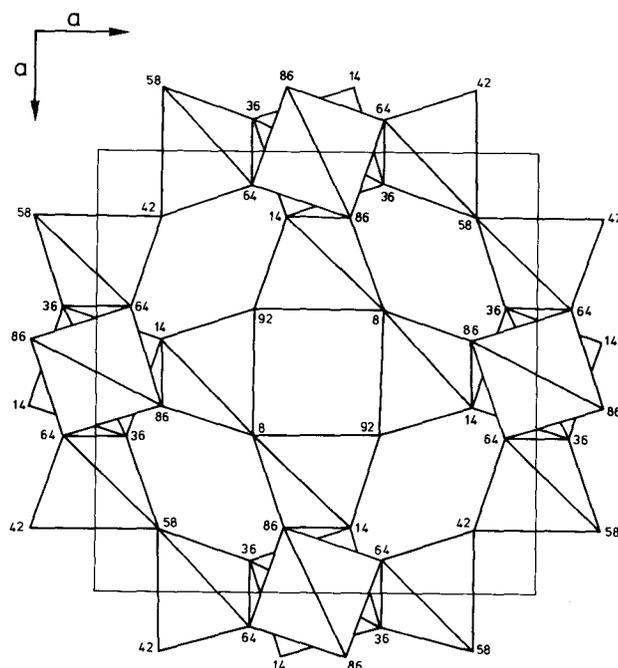


Fig. 1a. Bicchulite. Projection on (001) showing the framework of O(1)-tetrahedra around (Si,Al). Height of atoms in $z/100$

in the tetrahedra is about 3 : 1, the distribution of Al and Si in the linked tetrahedral sites is also statistical (Takéuchi and Sadanaga, 1966).

This distances (Al,Si)–O(1) are equal to 1.716 Å (4 ×), the angles O(1)–(Al,Si)–O(1) equal 108.4° (4 ×) and 111.9° (2 ×), the angles (Al,Si)–O(1)–(Al,Si) equal 130.7(1)° giving a closest approach (Al,Si)–(Al,Si) of 3.12 Å. Jones (1968) has assumed a linear relationship between Si–O and Al–O bonds for statistical distribution on tetrahedral sites. Extrapolating his equation to higher Al content, the distance (Al,Si)–O for an Al : Si ratio of 2 : 1 is calculated to 1.71 Å, in satisfactory correspondence with the observed value.

The calcium atoms and the O(2)H-groups occupy the large cavities of the aluminosilicate framework. The Ca-atoms are coordinated by a distorted octahedron of oxygen atoms: on one side a triangle of O(1)-atoms belonging to different tetrahedra in the framework, on the other side a smaller triangle of O(2)-atoms. Four such octahedra are grouped around the origin and around the center of the cell (Fig. 1 b). The octahedra within each group share O(2)-edges (octahedra from different groups have no common elements). In this manner, empty tetrahedra of O(2)-atoms are formed around the center

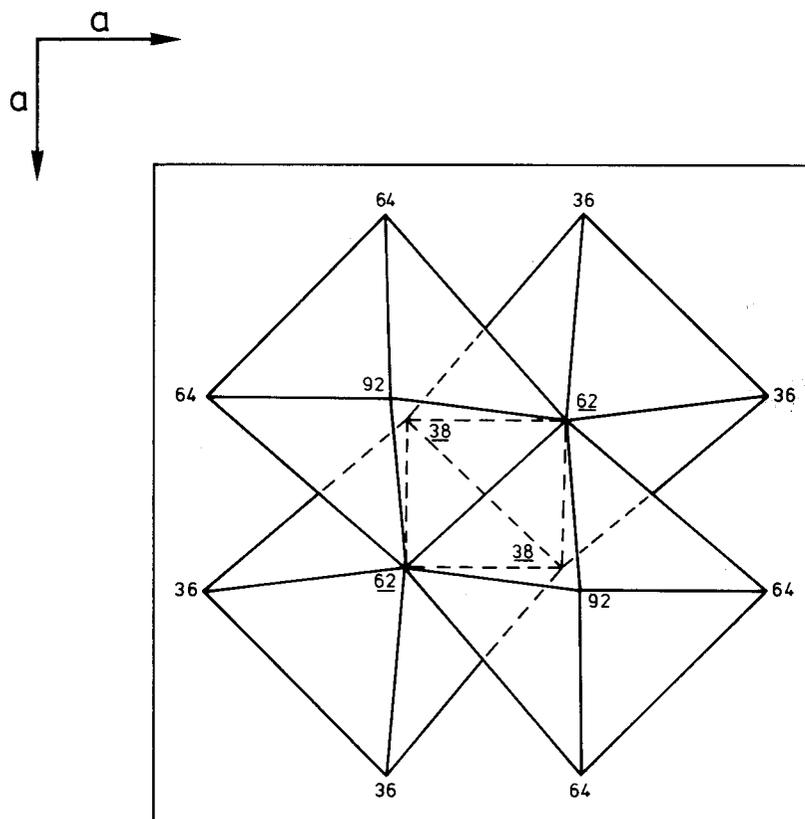


Fig. 1b. Bicchulite. Projection on (001) showing a group of four linked octahedra around calcium atoms. Height of oxygen atoms at corners in $z/100$, height of O(2)-atoms underscored

(Fig. 1b) and origin (Fig. 2) of the cell. Each face of such an empty tetrahedron is shared with one of the four octahedra of its group.

The distances from Ca to the O(1) of the framework equals 2.459 \AA ($3 \times$) and are longer than in CaO (2.405 \AA) which crystallizes with NaCl lattice where the oxygen atoms are only bonded to calcium. The distances Ca–O(2) amount to 2.311 \AA ($3 \times$) in bicchulite where three of the O(2)-edges of the octahedron around Ca are shared with neighboring octahedra (Fig. 1b). In $\text{Ca}(\text{OH})_2$ (Busing and Levy, 1957), a layer structure of the CdI_2 -type, each octahedron around Ca shares six edges with neighboring octahedra and the distance Ca–O is 2.368 \AA . Compared with the review of Hahn and Eysel (1970), the distances found here are in the normal range for Ca–O and Ca–OH bonds.

An interesting feature of the structure of bicchulite is the empty tetrahedron of O(2)-atoms in the center of each octahedra-group. Since the

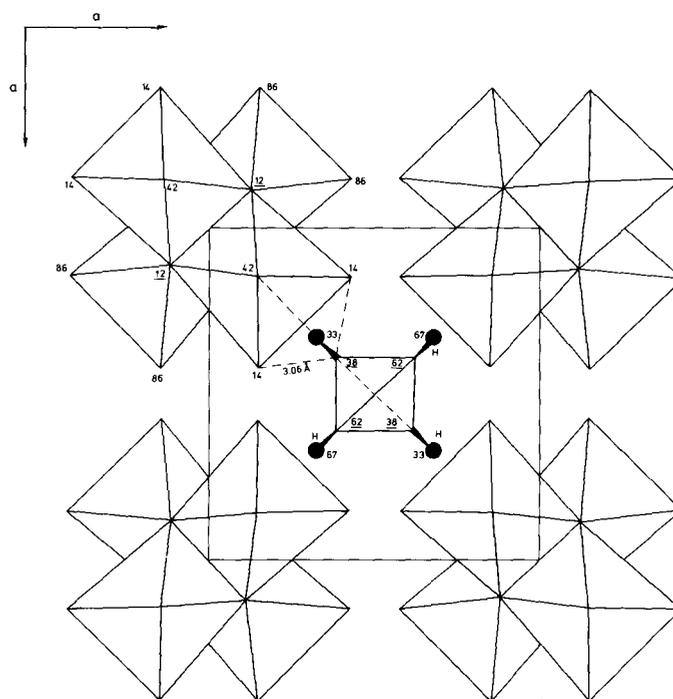


Fig. 2. Bichulite. Projection on (001) showing the tetrahedron of four O(2)-atoms with H-atoms around the center of the cubic cell (as in Fig. 1 b) and the octahedragroup around the origin of the cell (for clarity, the octahedragroup around the center of the cell shown in Figure 1 b was not drawn). Height of atoms in $z/100$, height of O(2)-atoms underscored. The short distances O(2)–O(1) of 3.06 Å are shown in the upper left corner

O(2) are located on the body diagonals of the cubic cell, the tetrahedron is not distorted with distances O(2)–O(2) of 2.883 Å. Each O(2) is bonded to a hydrogen atom with O(2)–H = 0.87 Å. The hydrogen atoms are also positioned on the body diagonals of the cell. They thus form a larger tetrahedron of parallel orientation around the O(2)-tetrahedron (Fig. 2).

The distance O(2)–H = 0.87 Å is rather short in comparison to the average value of 0.98 Å known from neutron diffraction studies (Baur, 1969). Busing and Levy (1957) have refined X-ray and neutron data of $\text{Ca}(\text{OH})_2$. They found O–H = 0.79(4) Å from X-ray data and 0.984 from neutron data because of the shift between electron density and nucleus in the hydrogen atom.

Coordination of the hydrogen atoms

Each hydrogen atom is at a distance of 0.87 Å from one of the O(2)-atoms of an empty O(2)-tetrahedron and at a distance of 3.63(3) Å from the other three

O(2)-atoms of the same tetrahedron, the corresponding angle O(2)–H–O(2) being only 27° . Thus, the empty O(2)-tetrahedron is not stabilized by H-bonds.

The shortest distance H–O(1) in a hydrogen's own octahedragroup amounts to 3.55 Å.

As can be seen from Figure 2, the body diagonal on which a hydrogen atom is located points at a Ca-atom (with H–Ca = 2.82(3) Å) in a neighboring octahedragroup, perpendicular through the middle of an O(1)-face of an octahedron. These three O(1)-atoms have a distance of 2.48(3) Å to the hydrogen atom. The distance from the O(2)-atom belonging to a particular hydrogen to these three O(1)-atoms is 3.061(2) Å and the corresponding angle O(2)–H–O(1) is $125(2)^\circ$ ($3\times$). It is tempting to describe this as a trifurcated O(2)–H...O(1) bond. However, the distance H...O(1) of 2.48 Å seems rather large. If material were available for a neutron diffraction study of bicchulite, the distance O(2)–H might be determined around 1.0 Å instead of 0.87 as found with X-ray data. Correspondingly, the distance H...O(1) would then shorten to around 2.35 Å, a value which compares better to other H-bonds (Baur, 1969). With the scant material available it is not possible to use other experimental methods, such as infrared spectroscopy, to obtain evidence about the presence of H-bonds in bicchulite. Empty $(\text{OH})_4$ tetrahedra in silicates have previously been described in hydrosodalite and in hydrogarnets. In hydrosodalite, $\text{Na}_6[\text{Al}_6\text{Si}_{5.5}(\text{H}_4)_{0.5}\text{O}_{24}] \cdot 0.4 \text{ NaCl} \cdot 0.7 \text{ NaOH}$, Bukin and Makarov (1967) have found with single-crystal neutron diffraction methods that 1/12th of the SiO_4 -tetrahedra are statistically substituted by empty $(\text{OH})_4$ -tetrahedra. They describe hydrogen bonds arcing four of the six edges of the tetrahedra from the outside with O–H = 0.931 Å, H...O = 1.853 Å, and O–O = 2.584 Å, the angle O–H–O being 133.5° . These strong hydrogen bonds contribute to the stability of the $(\text{OH})_4$ -tetrahedra.

The structure of the hydrogarnet $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ was refined by Cohen-Addad et al. (1967) with neutron powder diffraction methods and by Bartl (1969) with X-ray single-crystal methods (Bartl did not determine the hydrogen parameters). The structure contains empty $(\text{OH})_4$ -tetrahedra of tetragonal symmetry which are substituted for the SiO_4 -tetrahedra in grossularite, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$. Cohen-Addad et al. (1967) found distances O–O of 3.16 Å ($4\times$) and 3.26 Å ($2\times$). The hydrogen atoms are located just outside of the four faces of the oxygen tetrahedron with H–O = 0.95 Å, 2.47 Å, and 2.56 Å. From infrared studies, the authors conclude, however, that the structure contains no O–H...O bonds.

The sodalite-type framework

The structure of sodalite, $\text{Na}_8\text{Si}_6\text{Al}_6\text{O}_{24}\text{Cl}_2$ was first determined by Pauling (1930) and refined by Löns and Schulz (1967). To compare sodalite and

bicchulite, Na has to be replaced by Ca and the two Cl-atoms in 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ by the empty $(\text{OH})_4$ -tetrahedra centered around these positions.

Pauling (1930) already remarked that the voluminosity of the tetrahedral framework in sodalite depends on the size of the ions in the cavities: "the framework collapses ... until the oxygen ions come into contact with the sodium ions, which themselves are in contact with the chlorine ions". Taylor and Henderson (1978) have developed a model for the cubic sodalite structure allowing the calculation of the cell dimension from the size of the cavity anion and cation as well as from the T–O–T angle for frameworks of different composition. Their calculation of the lattice constant cannot be applied to bicchulite since the choice of an apparent radius for the cavity anion, the $(\text{OH})_4$ -tetrahedron, would be rather arbitrary. However, for a cell edge of 8.825 Å (as in bicchulite), Taylor and Henderson (1978) calculate a T–O–T angle of about 135° for a framework of composition $(\text{Al}_6\text{Si}_6\text{O}_{24})^{6-}$ and of about 125° for the composition $(\text{Al}_{12}\text{O}_{24})^{12-}$. The framework in bicchulite has the composition $(\text{Al}_8\text{Si}_4\text{O}_{24})^{8-}$ and the angles (Al,Si)–O(1)–(Al,Si) are equal to 130.7° (see above). Thus, the 'collapse' of the framework in bicchulite fits into the general pattern found in sodalite-type structures by Taylor and Henderson (1978).

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