Zeitschrift für Kristallographie, Bd. 146, S. 35–41 (1977)

The crystal structure of bicchulite, $Ca_2[Al_2SiO_6](OH)_2$

By **Kurt Sahl** and **Niranjan Deb Chatterjee**

Institut für Mineralogie, Ruhr-Universität, Bochum

(Received 29 January 1977)

Auszug

Die Kristallstruktur von synthetischem Bicchulit wurde mit Röntgen-Einkristallmethoden bestimmt ($R = 0{,}07$ für alle 65 beobachteten Reflexe). Bicchulit hat eine Gerüststruktur vom Sodalith-Typ. Al und Si sind statistisch auf die Tetraederplätze verteilt und nur von Sauerstoffatomen koordiniert. Calcium ist von drei Sauerstoffatomen und drei OH-Gruppen oktaedrisch umgeben. Jeweils vier solche Oktaeder sind über gemeinsame OH–OH-Kanten zu einer Vierergruppe verknüpft. Diese Vierergruppen sind in die Hohlräume des Gerüsts eingelagert.

Abstract

The crystal structure of synthetic bicchulite was determined with single-crystal x-ray methods ($R = 0.07$ for all 65 observed reflections). Bicchulite has a sodalite-type framework structure with Al and Si distributed statistically in the tetrahedral sites, coordinated solely by oxygen atoms. Calcium is coordinated octahedrally by three oxygen atoms and three OH groups. Four such octahedra are linked to a group by OH–OH edges. These octahedra groups occupy the cavities within the framework.

Introduction

Single crystals of synthetic bicchulite, $Ca_2[Al_2SiO_6](OH)_2$ were grown under hydrothermal conditions by GUPTA and CHATTERJEE (1977). The crystals were more or less equidimensional but very small (at most 0.05 mm in diameter). GUPTA and CHATTERJEE (1977) determined the lattice constants of bicchulite from powder patterns (Guinier and powder diffractometer method, Cu radiation). They indexed the powder patterns on the basis of a body-centered cubic cell, as suggested by HENMI *et al.* (1973), and refined the lattice constant to $a = 8.825$ Å. The chemical composition of the synthetic compound was determined by electron microprobe analysis and by water determination as $Ca_2Al_2SiO_7 \cdot H_2O$ (GUPTA and CHATTERJEE, 1977). The natural analog of the synthetic bicchulite has been recently described from two localities (HENMI *et al.*, 1973). Although its occurrence and properties have been given, no attempt has been made so far to solve its crystal structure. The purpose of the present paper is to report on the crystal structure of the synthetic bicchulite.

Experimental

Precession photographs (filtered Cu and Mo radiation) of several single crystals showed diffraction symmetry $m3m$. All interferences with $h+k+l=2n+1$ were missing, even on photographs with very long exposure (160 hours). Reflections were sharp, no diffuse streaks or spots were observed in reciprocal space. Since possible reflections were limited only by the condition $h+k+l=2n$, space group determination led to $Im3m$ and to the corresponding non-centrosymmetric space groups $I\bar{4}3m$ and $I432$.

X-ray data collection

For the crystal-structure analysis, the largest available single crystal (diameter 0.05 mm) was chosen. Data was collected on a Hilger and Watts four-circle diffractometer (Mo radiation, graphite monochromator). To orient the crystal, angular positions of 12 high-angle reflections were refined by the least-squares method; the lattice constant determined by GUPTA and CHATTERJEE (1977) was confirmed. With the experimental density of 2.75 g/cm^3 (HENMI *et al.*, 1973) the cell content is calculated as $Z=4$ formula units $Ca_2Al_2SiO_7 \cdot H_2O$. The diffracted intensity was measured with the θ-2θ step-scan technique up to $\theta = 35°$. Due to the high symmetry and small volume of the crystal, only 65 symmetry-independent reflections with a significant intensity could be determined. During the measurement, two reflections were monitored at frequent intervals to ascertain the stability of the experimental set-up. Data reduction and correction for Lorentz and polarization factors was achieved in the usual manner.

Structure determination and refinement

A three-dimensional Patterson function was calculated which was poorly resolved since many peaks overlapped. Attempts to determine the structure with direct methods, using the program MULTAN (MAIN, WOOLFSON and GERMAIN) always ended in the centrosymmetrical space group $Im3m$ and gave models with unreasonable crystal-chemical features. Thus, trial-and-error was attempted, using the Patterson function to check the developed models. From the distribution of Patterson vectors, the calcium atoms were expected to be in octahedral coordination. Models in space group $Im3m$ or $I432$ inevitably ended up with tetrahedra around (Si, Al) and octahedra around Ca, sharing common faces. Only one arrangement in space group $I\bar{4}3m$ gave atomic coordinations which were satisfactory as far as interatomic distances and linking of polyhedra are concerned. With this model, structure factors were calculated ($R = 0.43$). A Fourier synthesis using the calculated phases showed no significant features besides the assumed positions of the atoms. The atomic parameters were refined by the least-squares method using a local version of the program ORFLS by Busing, Martin and Levy. Several cycles of refinement finally led to a conventional R value of 0.07 for all 65 observed reflections using the positional and isotropic thermal parameters listed in Table 1 (Sahl and Chatterjee, 1977). Because of the small number of observations including many reflections of low intensity, refinement with anisotropic thermal parameters was not pursued. A final Fourier synthesis using the phases calculated with the refined parameters showed no significant additional features (in particular, no information about the position of the hydrogen atoms is to be

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

Atom	Site	x	y	z	B
Ca	$8c$	0.144(1)	0.144(1)	0.144(1)	0.7(1) Å^2
Si and Al	$12d$	0.250	0.500	0.000	0.5(2)
O	$24g$	0.149(2)	0.149(2)	0.424(1)	1.5(3)
OH	$8c$	0.382(3)	0.382(3)	0.382(3)	1.5(5)

Table 2. *Bicchulite. Structure amplitudes of the observed reflections*

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
0	0	2	26.1	11.8	0	4	12	43.2	39.1	1	5	8	43.0	47.1	3	4	5	45.7	44.6
		4	119.9	104.7	0	5	7	35.3	28.0	2	2	2	118.0	118.9			7	43.7	43.5
		6	73.5	89.6	0	7	7	65.1	62.1			4	62.2	54.7			11	48.0	46.7
		8	127.5	116.5			11	58.6	52.6			6	79.4	87.0	3	5	6	30.1	27.0
		10	34.6	43.0	0	8	8	61.5	60.9			8	47.2	43.8	3	7	8	39.6	37.1
		14	52.1	51.8	1	1	2	81.2	83.8			10	52.0	51.5			10	47.5	50.1
0	1	3	116.0	114.0			4	81.8	92.4	2	3	3	35.0	31.4	4	4	6	41.5	50.1
		5	44.3	46.9			6	47.3	44.4			5	42.6	44.4			8	86.5	85.0
		7	30.4	28.1			8	50.2	50.6			7	31.4	36.2	4	5	5	41.7	45.7
		11	39.8	40.7	1	2	3	49.1	47.8	2	4	4	33.4	40.5	4	6	6	41.5	36.1
0	2	2	40.4	42.4			5	40.3	43.8			6	43.9	40.1	4	7	7	76.2	74.4
		4	38.9	46.2	1	3	4	43.1	42.1	2	5	5	35.5	32.9	5	5	8	39.9	32.8
		6	28.6	29.5			6	35.6	31.8	2	6	6	60.2	61.4	6	6	6	48.1	54.8
0	3	3	100.6	106.7			8	45.6	47.4			8	36.1	37.6	6	7	7	39.9	46.1
		7	115.6	119.1	1	4	5	45.8	45.9			10	40.3	41.0					
0	4	4	218.0	211.8			7	59.1	59.5	3	3	4	110.3	112.9					
		10	54.5	59.0	1	5	6	45.0	43.1			6	40.1	48.9					

expected from the available data). A calculation of intensities for the 115 non-significant but not systematically absent reflections in the range up to $\theta = 35°$ gave upper values comparable to the weakest observed reflections. The 65 observed reflections are listed in Table 2.

Description of the structure

In Table 3, interatomic distances and angles calculated on the basis of the refined model are listed. The crystal chemical formula of bicchulite is $Ca_2^{[6]}[(Al_2Si)^{[4]}O_6](OH)_2$. In space group $I\bar{4}3m$, the Al and Si atoms have to be distributed statistically on site 12*d*. The (Si,Al)-positions are coordinated tetrahedrally by four oxygen atoms with distances (Si,Al)—O of 1.72 Å (4 ×). The tetrahedra are linked to each other by all four corners to form a three-dimensional framework of the sodalite type (Pauling, 1930), Fig. 1*a*. The calcium atoms and the OH groups occupy the large cavities of this framework. The OH groups form empty tetrahedra centered around the lattice points 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, the distances OH—OH in these tetrahedra measuring 2.95 Å (6 ×). The Ca stoms are coordinated by a distorted octahedron of three oxygen atoms and three OH groups: on one side a triangle of oxygen atoms (with Ca—O = 2.47 Å) belonging to different tetrahedra in the framework, on the other side a triangle of OH groups, which is one of the faces of the $(OH)_4$ tetrahedron (with Ca—OH = 2.34 Å). Four such octahedra are grouped around the center of each cavity of the framework, sharing OH—OH edges with each other (octahedra from different groups have no common elements). Thus,

Table 3. *Bicchulite. Interatomic distances and angles in the coordination polyhedra around the cations*

(standard deviation in the last digit in parentheses)

$CaO_3(OH)_3$ octahedron			$(Al_{0.67}Si_{0.33})O_4$ tetrahedron		
Ca—OH	2.34(3) Å	3 ×	(Al, Si)—O	1.72(2) Å	4 ×
Ca—O	2.47(2) Å	3 ×	O—O	2.75(2) Å	4 ×
OH—OH	2.95(4) Å	3 ×		2.95(2) Å	2 ×
OH—O	4.80(3) Å	3 ×	O—(Al, Si)—O	106(1)°	4 ×
	3.59(3) Å	6 ×		118(1)°	2 ×
O—O	3.43(2) Å	3 ×			
OH—Ca—OH	78(1)°	3 ×			
OH—Ca—O	97(1)°	6 ×			
	173(1)°	3 ×			
O—Ca—O	88(1)°	3 ×			

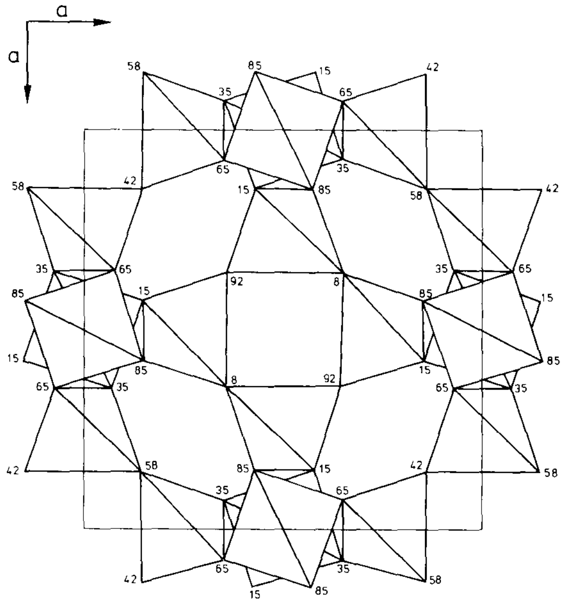

Fig. 1*a*. Bicchulite. Projection on (001) showing the framework of (Si, Al)O_4 tetrahedra. Height of oxygen atoms in $z/100$

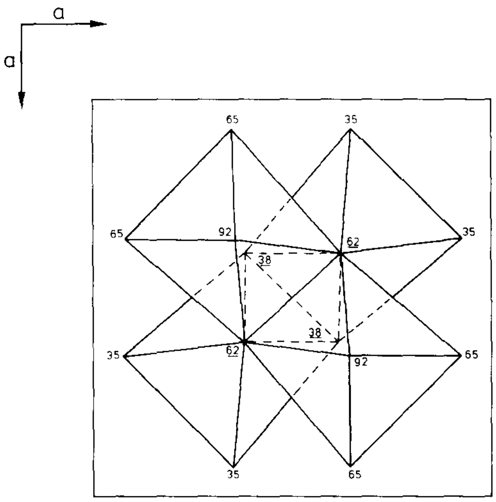

Fig. 1*b*. Bicchulite. Projection on (001) showing a group of four linked octahedra around calcium atoms. Height of atoms at corners in $z/100$ (height of OH groups underscored)

each face of the empty $(OH)_4$ tetrahedron is shared with one octahedron (Fig. 1*b*).

The structure of sodalite, $Na_8Si_6Al_6O_{24}Cl_2$ was first determined by PAULING (1930) and refined by LÖNS and SCHULZ (1967). Sodalite crystallizes in space group $P\bar{4}3n$ in which an ordered distribution of six Si and six Al atoms on two sixfold sites is possible. In bicchulite however, the relation Si to Al is 1:2 so that an ordered distribution in $P\bar{4}3n$ or in $I\bar{4}3m$ is not possible. This gives a plausible reason for the different symmetry.

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 $(OH)_4$ tetrahedra centered around these positions (instead, in hauynite and in nosealite, the Cl atoms are replaced by SO_4 groups). In the structure of $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$, PONOMAREV *et al.* (1970) describe a lattice of the sodalite type with orthorhombic deformations. Part of the water is coordinated to the aluminum atoms in the framework. Calcium is reported to be coordinated octahedrally by oxygen and by the rest of the water.

Discussion of the structure

In bicchulite, the distances $(Al_{0.67}Si_{0.33})$—O in the framework tetrahedra were determined to be 1.72 Å. The tetrahedra are rather distorted with distances O—O = 2.75 and 2.95 Å and angles O—(Al, Si)—O = 106° and 118°. These interatomic distances and the distortions are comparable to those in the structure of gehlenite, $Ca_2Al_2SiO_7$ (LOUISNATHAN, 1971). The TO_4 groups in the latter (with $T = Al_{0.5}Si_{0.5}$) have distances T—O ranging from 1.68 to 1.72 Å and angles O—T—O between 101° and 117°.

In bicchulite, Ca is coordinated by a deformed octahedron of three oxygen atoms (2.47 Å) and three OH groups (2.34 Å). HAHN and EYSEL (1970) have made a survey of coordination polyhedra around calcium. From this study, the distances found in bicchulite are in the normal range for Ca—O and Ca—OH bonds.

The geometry of the empty $(OH)_4$ tetrahedra in bicchulite cannot be discussed without knowledge about the positions of the hydrogen atoms, which the available experimental data does not yield.

An attempt to discuss the deformations of the coordination polyhedra in bicchulite in the usual manner, considering the linking of the polyhedra, is not convincing. PAULING (1930) remarked in the description of the structure of sodalite that "the framework, while strong, is not rigid, for there are no strong forces tending to hold it tautly expanded. In sodalite the framework collapses... until the oxygen ions come into contact with the sodium ions, which themselves are in contact with the chlorine ions". The deformations in bicchulite can be understood in a similar manner.

The authors thank Mr. A. POSPIECH for technical assistance in the data collection.

Literature

A. GUPTA and N. D. CHATTERJEE (1977), Synthesis, composition, thermal stability and thermodynamic properties of bicchulite, $Ca_2[Al_2SiO_6](OH)_2$. (in preparation).

TH. HAHN and W. EYSEL (1970), Calcium—crystal chemistry. *Handbook of Geochemistry*. Springer-Verlag, Berlin.

CH. HENMI, I. KUSACHI, K. HENMI, P. A. SABINE and B. R. YOUNG (1973), A new mineral bicchulite, the natural analogue of gehlenite hydrate, from Fuka, Okoyama Prefecture, Japan and Carneal, County Antrim, Northern Ireland. Mineralogical Journal **7**, 243—251.

J. LÖNS and H. SCHULZ (1967), Strukturverfeinerung von Sodalith, $Na_8Si_6Al_6O_{24}Cl_2$. Acta Crystallogr. **23**, 434—436.

S. J. LOUISNATHAN (1971), Refinement of the crystal structure of a natural gehlenite, $Ca_2Al(Al,Si)_2O_7$. Canadian Mineralogist **10**, 822—837.

L. PAULING (1930), The structure of sodalite and helvite. Z. Kristallogr. **74**, 213—225.

V. I. PONOMAREV, D. M. KHEIKER and N. V. BELOV (1970), Crystal structure of tetracalcium trihydrotrialuminate, $C_4Al_3H_3$. Akad. Nauk SSSR, Doklady **194**, 1072—1075.

K. SAHL and N. D. CHATTERJEE (1977), Zur Kristallstruktur von synthetischem $Ca_2Al_2SiO_7 \cdot H_2O$ (Bicchulit). Naturwissensch. **64**, 94.