

Refinement of the structure of Ikaite, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$

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Received: August 25, 1982; in revised form January 10, 1983

Crystal structure / $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$

Abstract. Ikaite, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$, is monoclinic, $C2/c$, with $a = 8.792(2)$, $b = 8.310(2)$, $c = 11.021(2)\text{Å}$, $\beta = 110.53(5)^\circ$, $Z = 4$. With 2205 independent reflections taken at -25°C of a naturally grown crystal specimen the structure was refined to a weighted $R_w = 0.028$. The CO_3 group is planar with C–O distances 1.279(2) and 1.290(1) ($2 \times$) Å . The hydrogen bond network is determined. The optical behaviour is explained by structural characteristics.

Introduction

Synthetic hydrates of CaCO_3 were first described by Daniell (1819). Pelouze (1831) was the first to synthesize the hexahydrate. Conditions of formation and stability have been studied by Krauss and Schriever (1930), Brooks et al. (1951), and Marland (1975). — Several claims of natural occurrences, partially questionable though, are listed by Krauss and Schriever (1930). Pauly (1963) discovered euhedral crystals in the waters of the Ika Fjord in Greenland, and named the mineral “Ikaite” after this locality (Fleischer, 1964). — Crystallographic properties of $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ were described by Bütschli (1908), Vetter (1911) and Johnston et al. (1916). A crystal structure analysis at -122° using a synthetic crystal specimen was performed by Dickens and Brown (1970): refinement from photographically collected data, with isotropic temperature factors and without hydrogen atoms, led to $R = 0.10$. It seemed desirable, therefore, to refine the structure to a higher degree of accuracy. Contrary to the investigation of Dickens and Brown, a natural crystal specimen was used in the present study.

Experimental and results

A sediment core retrieved from a water depth of 1950 meters and sub-zero temperatures in a shelf basin of the Bransfield Strait (Antarctica) (Suess et al., 1982) contained $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ single crystals. Since decomposition occurs rapidly at room temperature the crystals were kept below 0°C in a freezer during transport. A specimen of approximately isometric shape and a mean diameter of 0.2 mm was chosen for intensity data collection on a Philips PW 1100 diffractometer with $\text{MoK}\alpha$ radiation and was cooled in a stream of evaporated liquid nitrogen to -25°C . The lattice parameters, as listed in the abstract, were obtained by a least-squares fit to diffractometrically determined Bragg angles of a single crystal. Intensities of 2404 reflections were collected in the range $2^\circ < \vartheta < 40^\circ$. Corrections for absorption were made assuming spherical shape ($\mu = 8.2\text{ cm}^{-1}$). The specimen partially decomposed to calcite during the measurement. At the end of the measurement, the reference reflections yielded only about 60% of the counting rates at the beginning of the measuring process. This effect was taken into account in the refinement procedure: since the data were collected successively with increasing Miller index l , a separate scale factor was assigned to each "layer" with constant l . Calculations were performed using the SHELX-76 system (Sheldrick, 1976).

Atomic parameters of Dickens and Brown (1970) were chosen as starting values for the refinement process. Hydrogen atoms were detected by difference Fourier synthesis. Refinement, using 2205 independent reflections [$I > \sigma(I)$], with anisotropic temperature parameters for the non-hydrogen atoms led to a weighted $R_w = 0.028$ (unweighted $R = 0.034$). Extinction was considered: $g = 1.1 \cdot 10^{-6}$. F_o/F_c lists can be obtained from the authors. Final atomic parameters are summarized in Table 1. Bond lengths within the Ca coordination polyhedron and the geometry of the CO_3 group are listed in Table 2.

Discussion

Since the general outline of the structure has been given already by Dickens and Brown (1970) only some additional and complementary remarks concerning the higher accuracy and the incorporation of the hydrogen atoms will be given. Ca ions as well as CO_3 groups [C and O(1)] lie on twofold axes. The oxygen atoms O(1), O(2), and O(2)' form an almost equilateral triangle (cf. Table 2). The mean C—O distance of 1.286(1) Å practically equals the reported mean value of 1.284(4) Å for the average C—O bond lengths in 34 carbonate groups (Zemann, 1981). Some recent accurate structure analyses of crystals containing carbonate groups in a position allowing aplanarity displayed significant displacement of the carbon atom from the plane of the three oxygen atoms. In the present structure, the CO_3 group should be planar by space group symmetry requirements. But even then deviations from

Table 1. Fractional atomic coordinates and thermal parameters U_{ij} (all $\times 10^4$). The temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	5000	6472(0)	2500	148(1)	101(1)	127(2)	0	51(1)	0
C	5000	3055(2)	2500	109(4)	120(4)	171(6)	0	31(4)	0
O(1)	5000	1515(1)	2500	213(4)	96(3)	325(5)	0	48(4)	0
O(2)	5262(1)	3852(1)	1588(1)	197(3)	160(2)	162(3)	-10(2)	87(2)	-11(2)
O(3)	6146(1)	7222(1)	913(1)	278(3)	196(3)	172(3)	-10(2)	102(3)	-44(2)
O(4)	7872(1)	5581(1)	3829(1)	202(3)	179(3)	172(3)	-8(2)	63(2)	-9(2)
O(5)	6707(1)	8849(1)	3589(1)	177(3)	140(3)	204(3)	10(2)	74(2)	1(2)
H(1)	5795(20)	6897(19)	158(16)	404(43)					
H(2)	6374(23)	8063(23)	905(18)	566(55)					
H(3)	8530(20)	5959(18)	3574(18)	392(43)					
H(4)	8105(19)	5848(17)	4580(16)	330(40)					
H(5)	7628(19)	8838(16)	3567(15)	304(38)					
H(6)	6324(19)	9668(19)	3422(16)	411(44)					

Table 2. Bond lengths (Å) around the Ca ion and bond lengths and angles (°) of the CO_3 group

	Ca—O(2)	2.442(1) (2 ×)	C—O(1)	1.279(2)
	Ca—O(3)	2.387(1) (2 ×)	C—O(2)	1.290(1) (2 ×)
	Ca—O(4)	2.544(1) (2 ×)	O(1)—C—O(2)	120.9(1) (2 ×)
	Ca—O(5)	2.516(1) (2 ×)	O(2)—C—O(2)	118.2(1)
all other	Ca—O	> 4.1	Ca—C	2.839(1)

planarity are possible if two (or more) non-planar groups are statistically distributed. The thermal motion perpendicular to the plane then possibly indicates asymmetry. In the present case, however, the rms displacements of C, O(1) and O(2) are 0.098(2), 0.135(1), and 0.134(1) Å, respectively. The lower value for C and the comparable values for the oxygen atoms are consistent with a librational motion of the CO_3 group, and yield no indication of an aplanarity.

The O—H distances within the water molecules scatter between 0.73 and 0.83 Å, the H—O—H angles between 107.3 and 111.4°. The hydrogen bonding scheme proposed by Dickens and Brown (1970) was verified. The configuration of the hydrogen bonds is listed in Table 3.

The knowledge of the structure allows an estimate of the refractive behaviour of Ikaite. Dickens and Brown (1970) report that n_β is parallel to *b* and that n_γ extinguishes at 17° from *c* in the acute angle β (cf. Fig. 1). Contrary, Johnston et al. (1916) report n_γ to be inclined by 17° in the obtuse angle β . They refer, however, to the setting of Vetter (1911) which differs from the setting used in the more recent papers. Refractive indices were measured by different authors and are listed in Table 4.

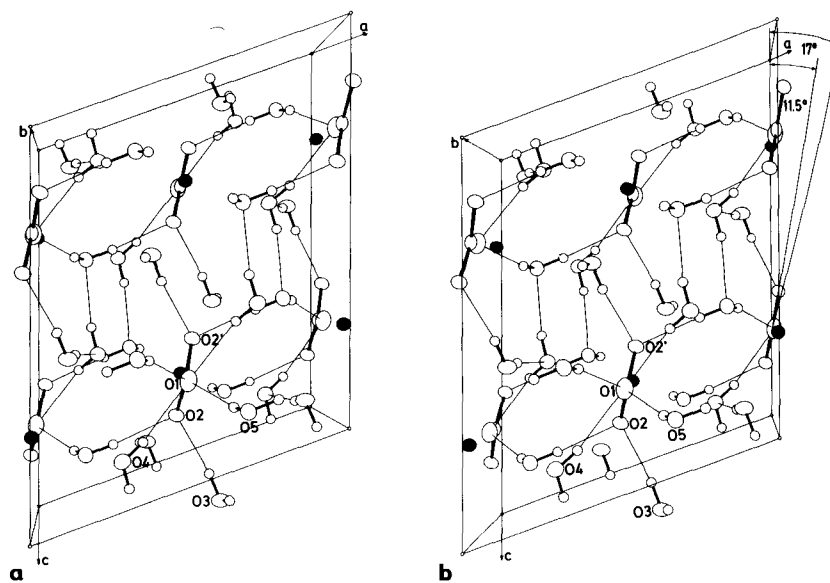
The considerable double refraction and the negative character is caused by the CO_3 groups which are arranged parallel to each other. Their plane

Table 3. Bond lengths (Å) and angles (°) of the hydrogen bonds

	O...O	O-H	H...O	$\angle(\text{O}-\text{H}\dots\text{O})$
O(3)-H(1)...O(2)	2.744(1)	0.825(17)	1.923(16)	173.6(1.9)
O(3)-H(2)...O(4)	2.906(1)	0.728(19)	2.184(19)	172.0(2.1)
O(4)-H(3)...O(1)	2.859(1)	0.791(20)	2.088(21)	164.6(1.6)
O(4)-H(4)...O(5)	2.778(1)	0.811(17)	1.982(19)	167.1(1.6)
O(5)-H(5)...O(2)	2.740(1)	0.818(18)	1.922(18)	176.7(1.5)
O(5)-H(6)...O(1)	2.709(1)	0.753(15)	1.979(15)	163.6(1.6)

Table 4. Refractive indices and extinction angle σ

n_x	n_β	n_y	σ	Authors
1.460	1.535	1.545	—	Johnston et al. (1916)
1.455	1.538	1.545	—	Pauly (1963)
1.482	1.530	1.542	—	Suess et al. (1982)
—	—	—	17°	Dickens and Brown (1970)
1.480	1.545	1.535	15.8°	present theoretical estimation

**Fig. 1.** Stereoscopic view as seen down the b -axis. Hydrogen atoms are drawn with a uniform fixed radius. Hydrogen bonds are denoted by lines. Ca ions are black. The planar CO_3 groups form angles of 11.5° with the c -axis. Extinction is at 17° from the c -axis

forms an angle of 11.5° with the c -axis (Fig. 1) which is in rough agreement with the extinction angle of 17° . The deviation will be caused by the water molecules which contribute to the mutual polarization within the structure. This interaction can be considered using the computer program DIPSUM of Pohl (1978). For that purpose, the C-atom is assumed to be non-polarizable, and the polarizabilities of Ca and oxygen atoms of the carbonate group are assumed to be 0.42 and 1.43 \AA^3 , respectively (Pohl, 1979), and the polarizability of the water molecules is estimated to be 1.47 \AA^3 (by means of the Lorentz-Lorenz formula applied to water (Pohl, 1982)). The calculated values are listed in Table 4. The angle of extinction amounts to 15.8° , which agrees fairly well with the experimentally determined angle of 17° .

Thanks are due to Dr. H. L. Keller for providing the low temperature attachment and to one of the referees who focussed our attention to the optical properties. Calculations were performed at the Rechenzentrum der Universität Kiel.

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