

CRYSTAL-STRUCTURE DETERMINATION OF TWINNED KETTNERITE

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ABSTRACT

The crystal structure of kettnerite, $\text{CaBi}(\text{CO}_3)\text{OF}$, a 3.7976(5), b 3.7976(5), c 13.569(4) Å, V 195.71(8) Å³, space group $Pmmm$, $Z = 2$, has been refined to an R index of 0.016 on the basis of 265 unique, observed reflections. Although the cell and the distribution of diffraction intensities obey tetragonal symmetry, kettnerite is optically biaxial, and attempts to solve the structure with tetragonal symmetry led to stereochemical nonsense. Introduction of a twin plane *via* reflection on {110} for orthorhombic symmetry simulates tetragonal diffraction-intensity distribution for the merohedral twin, and gives a structure with sensible stereochemistry. Both large cations, Ca and Bi, have [8]-coordination, and Bi^{3+} shows stereoactive lone-pair behavior. The kettnerite structure is layered with a Ca-F layer, a Bi-O layer, and a CO_3 layer with the plane of the (CO_3) group orthogonal to the plane of the layer. Oxy-carbonate minerals are rare relative to hydroxy- and hydrated-carbonate minerals. The only cations that can satisfy the bond-valence requirements for a non-carbonate oxygen atom are those for which there is an electronic driving mechanism to produce a marked asymmetrical distribution of bond valences, such as for the uranyl group, $(\text{UO}_2)^{2+}$, and for large cations with stereoactive lone-pairs of electrons, e.g., Bi^{3+} , Pb^{2+} . In this regard, all oxy-carbonate minerals contain such cations.

Keywords: kettnerite, crystal structure, merohedral twin, stereoactive lone-pair of electrons.

SOMMAIRE

Nous avons affiné la structure cristalline de la kettnerite, $\text{CaBi}(\text{CO}_3)\text{OF}$, a 3.7976(5), b 3.7976(5), c 13.569(4) Å, V 195.71(8) Å³, groupe spatial $Pmmm$, $Z = 2$, jusqu'à un résidu R de 0.016 en utilisant 265 réflexions observées. Quoique la maille et la distribution des intensités de raies diffractées répondent à une symétrie tétragonale, la kettnerite est biaxe dans ses propriétés optiques, et les essais d'une ébauchée de la structure dans cette symétrie n'ont donné que des résultats sans aucun sens stéréochimique. L'introduction d'un plan de macle selon une réflexion sur {110} en symétrie orthorhombique mène à une simulation d'une distribution tétragonale des intensités pour une macle méroédrique, et à une structure stéréochimiquement correcte. Les deux cations de taille importante, Ca et Bi, possèdent une coordination [8], et le Bi^{3+} fait preuve d'un comportement stéréoactif typique de la présence d'une paire isolée d'électrons. La structure, en couches, comporte un niveau Ca-F, un niveau Bi-O, et un niveau de carbonates dont le plan des groupes CO_3 est perpendiculaire aux couches. Les minéraux oxy-carbonatés sont rares en comparaison des minéraux carbonatés hydroxylés ou hydratés. Les seuls cations à pouvoir satisfaire aux exigences en valences de liaison d'un atome d'oxygène non lié à un groupe carbonate sont ceux pour lesquels il existe un mécanisme électronique favorisant une distribution fortement asymétrique des valences de liaison, par exemple le groupe uranyle, $(\text{UO}_2)^{2+}$, et les cations de taille importante contenant une paire isolée d'électrons stéréoactifs, par exemple, Bi^{3+} et Pb^{2+} . Ainsi, tous les minéraux oxy-carbonatés contiennent de tels cations.

(Traduit par la Rédaction)

Mots-clés: kettnerite, structure cristalline, macle méroédrique, paire isolée d'électrons stéréoactifs.

INTRODUCTION

Kettnerite from Krupke, northwestern Bohemia, Czech Republic, was first reported as tetragonal, $P4/nmm$, by Žák & Syneček (1956). Syneček & Žák (1960)

later reported the crystal structure of this material to be orthorhombic, $Cmma$, a 5.36(2), b 5.36(2), c 13.59(3) Å and $Z = 4$. Although this structure correctly located the Ca, Bi, F and non-carbonate O sites, the carbonate group was described as a tetragonal pyramid, which

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obviously is incorrect. The orthorhombic symmetry is in accord with the biaxial optics, but the structure presented by Syneček & Žák (1960) shows no significant deviation from tetragonal symmetry. The present study was done in order to resolve this problem.

EXPERIMENTAL

For the intensity-data measurements, a thin {001} cleavage plate ($0.25 \times 0.17 \times 0.013$ mm) of kettnerite was used. Intensity data were collected on a Siemens P4 four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated MoK α radiation. The setting angles of 15 reflections were used to determine the orientation matrix and refine the cell dimensions. One asymmetric unit of intensity data (assuming orthorhombic symmetry, $+h+k+l$) was collected up to $2\theta = 60^\circ$ using a 0:20 scan-mode with scan speeds inversely proportional to intensity, varying from 1.5 to 29.3°/minute. Reduction of the intensity data, structure determination and initial refinement of the structure were done using the SHELXTL (Sheldrick 1990) package of computer programs. The final structure-refinement, based on F^2 and including the twin component, was done with by SHELXL-93 (Sheldrick 1993). For the plate-absorption correction, 13 intense diffraction-maxima in the range 8 to $57^\circ 2\theta$ were chosen for Ψ diffraction-vector scans at 4° intervals of Ψ (North *et al.* 1968). With reflections omitted within a 10° glancing angle of the plate, the converging R refinement for the Ψ -scan data set (1150 reflections) decreased from 23.4% before correction to 1.8% after the absorption correction. Information relevant to the data collection is given in Table 1.

STRUCTURE SOLUTION AND REFINEMENT

From precession photographs and four-circle diffractometer data, kettnerite seems tetragonal, yet the distinct biaxial optic character ($2V \approx 20^\circ$) of the crystals indicates lower symmetry. The systematic extinctions uniquely indicate $P4/nmm$ symmetry in Laue class $4/mmm$. Assuming tetragonal symmetry and assigning phases to a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 0.636. This anomalously low value, even below the value (0.736) statistically characteristic of noncentrosymmetric space-groups, is one

TABLE 1. KETTNERITE: DATA COLLECTION AND STRUCTURE-REFINEMENT INFORMATION

Space Group: $P4/nmm$ (#59) Radiation: MoK α		Unit-cell contents $2 \times \text{CaBi}(\text{CO}_3)\text{OF}$ μ 46.3 mm $^{-1}$
Unconstrained cell		Constrained cell
a 3.7965(6) Å	α 90.04(2)°	a 3.7976(5) Å
b 3.7982(5) Å	β 89.97(2)°	c 13.569(4) Å
c 13.567(3) Å	γ 89.97(1)°	V 195.71(8) Å 3
Reflections collected	384	R_1 0.016
Reflections used	265	WR_2 0.042
ψ -scan reflections	1150	Goof 1.196
$R = \Sigma(F_o - F_c) / \Sigma F_o $		$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$
$w = 1 / [\sigma^2(F_o^2) + (a \times P)^2 + (b \times P)]$; a and b refine, $P = \{[\max(0, F_o^2)] + 2F_c^2\} / 3$		

Origin at $\bar{1}$.

possible indication of twinning (Herbst-Irmer & Sheldrick 1998). In merohedrally twinned crystals, the additional contribution to the intensity from each individual tends to even out the distribution of intensities such that there are no extreme values, *i.e.*, the E values are more uniformly closer to 1. The E -map coordinates for the $P4/nmm$ model were assigned the appropriate scattering curves, and a model with one Bi, one Ca and two O atoms refined to $R = 0.071$. With the additional sites added from the Fourier map, the structure refined to $R = 0.016$ with anisotropic displacement parameters and an isotropic extinction correction.

Although this seems to be an excellent refinement of the structure, the model makes no stereochemical sense, as the carbonate group is a tetragonal pyramid. Hönle & von Schnering (1988) briefly discussed whether or not it is possible to distinguish between twinning by merohedry and statistical disorder. Although they reached the conclusion that it is not possible in all cases to make this distinction, for kettnerite, the biaxial optics are a clear indication of symmetry lower than tetragonal. To address this problem, we proceeded as follows. Of the seven available subgroups for $P4/n 2_1/m 2/m$, five are tetragonal and two are orthorhombic; the latter afford the most likely solution to the structure. In a case where a twin operator belongs to a crystal system of higher symmetry, it is referred to as twinning by pseudomerohedry (Herbst-Irmer & Sheldrick 1998). Of the two orthorhombic subgroups, $P2/n 2_1/m 1$ ($Pmnn$) and $P2/n 1 2/m$ ($Cmma$), the former is the best choice. The intermediate m -plane of the tetragonal cell, which is the same m -plane as in the reoriented cell for $Cmma$,

TABLE 2. KETTNERITE: ATOMIC PARAMETERS (U^2 's $\text{Å}^2 \times 10^4$) AND BOND-VALENCE SUMS

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ca	¼	¼	0.4000(1)	74(4)	74(4)	96(8)	0	0	0	81(4)
Bi	¼	¼	0.09435(2)	118(2)	118(2)	94(2)	0	0	0	110(2)
C	¼	¼	0.2558(7)	135(23)	135(23)	34(35)	0	0	0	101(16)
O1	¼	¼	0	71(14)	71(14)	91(26)	0	0	0	78(11)
O2	¼	¼	0.1576(6)	312(23)	312(23)	78(30)	0	0	0	234(16)
O3	0.546(2)	¼	-0.2991(5)	148(26)	117(25)	198(29)	0	47(26)	0	154(12)
F	¼	¼	½	125(13)	125(13)	114(24)	0	0	0	122(10)

TABLE 3. KETTNERITE: SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Ca-O3	2.466(4) x 4	Bi-O1	2.290(1) x 4
Ca-F	2.334(1) x 4	Bi-O2	2.820(2) x 4
C-O2	1.332(12)	O2-C-O3	117.6(4) x 2
C-O3	1.268(7) x 2	O3-C-O3	124.8(8)

TABLE 4. BOND-VALENCE* (νu) TABLE FOR KETTNERITE

	Bi	Ca	C	Σ
O1	$x4\downarrow 0.52$ $x4\rightarrow$			2.08
O2	$x4\downarrow 0.18$ $x4\rightarrow$		1.17	1.89
O3		$x4\downarrow 0.26$ $x2\rightarrow$	$x2\downarrow 1.39$	1.91
F		$x4\downarrow 0.26$ $x4\rightarrow$		1.04
Σ	2.80	2.08	3.95	

* Calculated from the constants of Brese & O'Keeffe (1991) except for Bi-O which are taken from Brown (1981).

gives rise to the same problem with respect to the carbonate group as did the 4-fold axis. For this reason, the *Cmma* choice of space group Synček & Žák (1960) is inappropriate.

With *Pmnm*, the correct space-group, the model refined to $R = 0.041$ with anisotropic-displacement parameters. Employing a twin law with a mirror plane parallel to (110), the crystal structure refines to $R = 0.016$. When refining twinned crystals, one must be careful to apply appropriate constraints or the refinement becomes unstable (Hönle & von Schnering 1988). The contribution of one twin component refined to 0.52(1), *i.e.*, virtually equal volumes of each component of the twin. This would be the expected result for merohedrally twinned crystals as the scale of twinning would be considerably smaller than the size of crystal used in the structure-data collection. The final residual electron-densities are +0.81 and -0.76 $e^{-}/\text{Å}^3$. Table 2 lists the final positional and anisotropic-displacement parameters, Table 3 gives the selected interatomic distances, and Table 4 contains the bond-valence table. Observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0S2.

DESCRIPTION OF THE CRYSTAL STRUCTURE

Kettnerite has two large-cation sites with similar but distinct polyhedra. The Bi polyhedron, with [8]-coordi-

nation, is a square antiprism compressed along [001] (Fig. 1a). The O1 atoms occur at the center of the cube edges, with short Bi-O1 bond-lengths of 2.29 Å, whereas the O2 atoms occur at the corners of the cube, giving long bond-lengths of 2.82 Å. The compression along [001] is a consequence of the stereoactive lone pair of electrons associated with Bi³⁺ ions. The stereochemically active lone pair of electrons also manifests itself in the bond lengths, with a considerable increase in the Bi-O2 bond length relative to that of Bi-O1. The Ca polyhedron also has [8]-coordination, but the square antiprism is skewed to a truncated tetrasphenoid (Fig. 1b). In this unusual configuration, the bond lengths are nearly equal, with Ca-O3 at 2.466 and Ca-F at 2.334 Å. The distinct nature of these two polyhedra, combined with the stereoactive lone-pair behavior of Bi³⁺, leads to complete order of the Bi and Ca.

As is typical of carbonate structures, kettnerite is layered (Fig. 2), with a Bi-O layer, a Ca-F layer and a segregated "standing-on-end" (Grice *et al.* 1994) carbonate layer. This arrangement resembles that found in the REE fluorocarbonate minerals such as bastnäsit-(Ce) (Ni *et al.* 1993) and the REE bicarbonate thomasclarkite-(Y) (Grice & Gault 1998). This type of

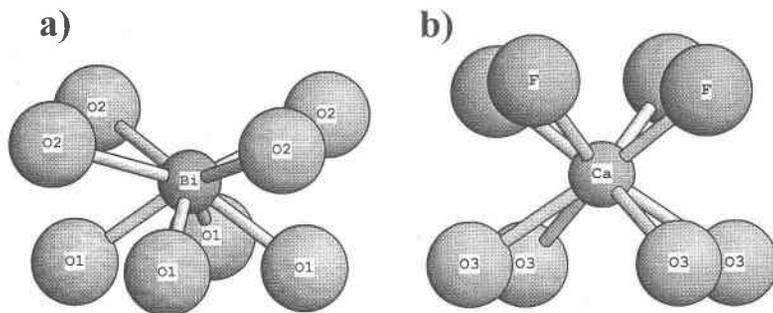


FIG. 1. The large-cation coordinations in kettnerite in oblique projection with [001] vertical: (a) Bi³⁺; (b) Ca²⁺.

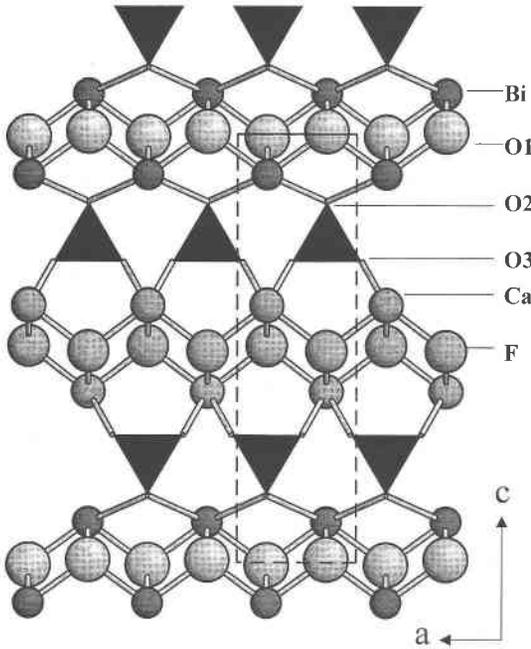


FIG. 2. The structure of kettnerite projected on (010), showing the layering in the structure. The (CO_3) groups are represented by filled triangles. The unit cell is outlined.

layering is characteristic of carbonates with cations of high coordination-number and a high ratio of cations relative to carbonate groups. The 7 Å c -repeat is common in Bi carbonates: kettnerite $c = 13.57 \text{ \AA}$ ($\sim 2 \times 7 \text{ \AA}$); beyerite, $\text{CaBi}_2(\text{CO}_3)_2\text{O}_2$, $c = 21.76 \text{ \AA}$ ($\sim 3 \times 7 \text{ \AA}$); bismutite, $\text{Bi}_2(\text{CO}_3)\text{O}_2$, $c = 13.70 \text{ \AA}$ ($\sim 2 \times 7 \text{ \AA}$). In the original descriptions, all these minerals were characterized as tetragonal, with $a \approx 3.8 \text{ \AA}$, which is the distance between oxygen atoms at the corners of the square antiprism. On the basis of the structure solution of kettnerite, it seems unlikely that either beyerite or bismutite is tetragonal.

POSSIBLE HYDROGENATION-HYDRATION OF KETTNERITE

The topology of the kettnerite structure (Fig. 2) and the distributions of bond valences (Table 4) suggest that kettnerite could possibly become partly, or even completely, hydroxylated or hydrated [as occurs for rutherfordine (Finch *et al.* 1999, Čejka & Urbanec 1988, Urbanec & Čejka 1979)]. For hydroxylation, the structure is separated along (001) through the O2 atoms, and H atoms are attached to the O2' anion attached to the carbonate group (H1 in Fig. 3a) and to the O2'' anion attached to four Bi atoms (H2 in Fig. 3a), accompanied by an $a/2$ shift. In this structure, the C–O2' bond-valence is 1.2 vu , and the Bi–O2'' bond-valence is 0.8 vu (total

contribution for the four Bi atoms). The proposed bond-valence arrangement satisfies the valence-sum rule (Fig. 3a), and should give an infrared spectrum with two distinct OH-stretching bands. For hydration, the structure is separated in the same plane, two H atoms are attached to the O2' anion attached to the carbonate group (H in Fig. 3b), and there is a shift of $a/2$ in this plane. In this structure, a sensible bond-valence arrangement results, with an increase from 1.2 to 1.4 vu for the C–O2' bond valence and a decrease from 0.8 to 0.6 vu for Bi–O2'' (again total contribution for the four Bi atoms). Note that the hydroxylated arrangement produces a bicarbonate, $\text{CaBi}[\text{CO}_2(\text{OH})]\text{OF}(\text{OH})$, and the hydrated arrangement is a carbonate, $\text{CaBi}(\text{CO}_3)\text{OF}(\text{H}_2\text{O})$.

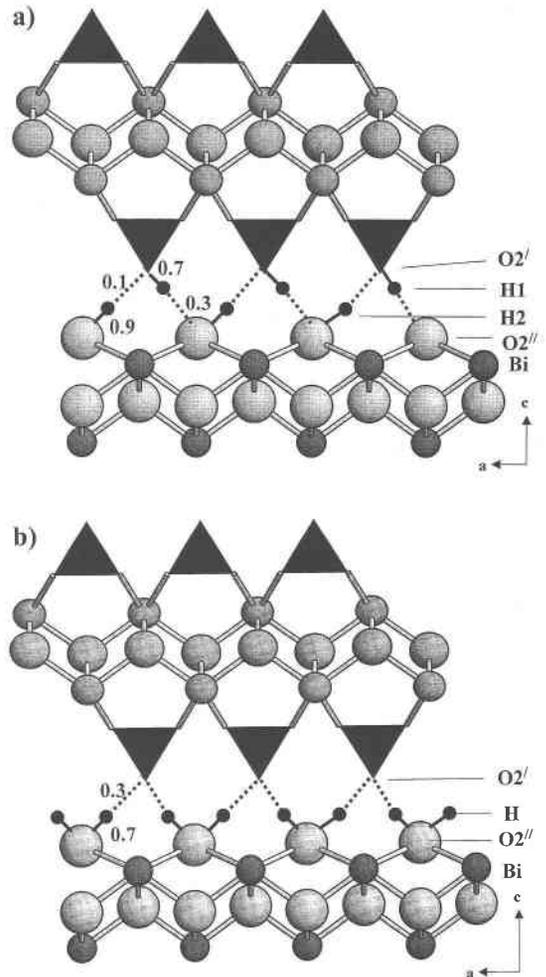


FIG. 3. The hypothetical structures of kettnerite: (a) hydroxylated, and (b) hydrated. The numbers on the figure are the bond valences (vu) associated with each H atom.

OXY-CARBONATE MINERALS

REFERENCES

Carbonate minerals usually contain alkali, alkaline-earth and rare-earth elements as cations. As all of these elements have either a low valence or a large coordination number, they are weak Lewis acids. Weak Lewis acids bond with weak Lewis bases, and thus there are favorable crystal-chemical conditions for the presence of (OH)⁻ and (H₂O) groups in carbonate minerals, which explains why oxy-carbonates are a rarity in minerals. Exceptions to this include the minerals beyerite CaBi₂(CO₃)₂O₂, bismutite Bi₂(CO₃)O₂, kettnerite CaBi(CO₃)OF, mroseite CaTeO(CO₃)O₂, shannonite Pb₂(CO₃)O, widemannite Pb₂(UO₂)(CO₃)₃, and rutherfordine (UO₂)(CO₃). The minerals in this seemingly disparate collection have a point in common: all involve cations with unusual electronic properties. The oxygen anions in the uranium carbonates that are not part of a carbonate group bond very strongly to U⁶⁺, forming the uranyl (U⁶⁺O₂) group. The other minerals all contain cations with stereochemically active lone-pair electrons. This is not by chance; in an oxy-carbonate, the oxygen atom(s) not bonded to C must have its bond-valence requirements satisfied by bonding to the other cation(s) in the structure. It is unusual for anion coordination numbers to exceed [4] in minerals. This being the case, the average bond-valence to an oxygen atom is usually ≥ 0.5 *vu*. This requirement is not normally compatible with the presence of cations with Lewis acidities much lower than 0.50 *vu* (e.g., Ca, Ba). However, the situation is different for cations with stereoactive lone-pair behavior (e.g., Pb²⁺, Bi³⁺). For these cations, the anions are of two types: (1) anions positioned to one side of the cation and having very short bond-lengths; (2) anions generally positioned to the other side of the cation, and having very long bond-lengths. The short bonds typically have bond valences of 0.50 *vu* or larger, and the long bonds have bond valences of 0.20 *vu* or smaller. Thus four of these short bonds can satisfy the bond-valence requirements of the non-carbonate O atoms. This is what happens in kettnerite, and presumably also in beyerite, bismutite, mroseite and shannonite.

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