THE CRYSTAL STRUCTURE OF KETTNERITE, CaBi[OF\(\text{CO}_3\)]

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Macroscopic, microscopic, goniometric, qualitative spectrographic and quantitative chemical data of kettnerite [2] with some new observations are given. The unit cell dimensions determined from the powder and rotating crystal photographs are \(a_0 = b_0 = 5.36 \pm 0.02 \text{Å}, c_0 = 13.59 \pm 0.03 \text{Å}\). There are four molecules in the unit cell. The crystal structure of kettnerite was studied from the ordinary and generalized projections of the Patterson function along the [010] axis. Direct evidence of tetragonal layers (Ca, 2F, Ca) and (Bi, 2O, Bi) parallel to the basal face was found. The spatial arrangement of these layers corresponds to the symmetry of the space group \(P 4/nmm\). These layers alternate in the [001] direction being interleaved by single \(\text{CO}_3\) layers. Both the biaxial character of the mineral and the uncertainty concerning the rotation of the \(\text{CO}_3\) groups indicate a lower, most probably an orthorhombic symmetry. The highest possible symmetry is that of \(Cmnm\). The structure is related to that of the type \(X_1\) found by Sillén et al. for several bismuth oxyhalides and especially to that of bismutite.

INTRODUCTION

Kettnerite from Krupka in the Krušně Hory (NW Bohemia)\(^1\) was described in earlier papers [1], [2]. The association of kettnerite and a minerogenetic study of the deposit are given in [2], [3]. The crystal structure analysis of kettnerite is the basis of this paper.

MACROSCOPIC DESCRIPTION AND MORPHOLOGY

Minute, thin or thick tabular crystals of kettnerite are square-shaped plates. The dimensions of the largest crystals are about 3 mm. They are brown to yellow or yellow-green in colour and more or less transparent. Crystals in druses are irregularly grown together, isolated ones are rare. Coarsely grained aggregates in quartz crystal druse cavities are less frequent.

\(^1\) Documentary specimens of kettnerite are deposited in the collections of the National Museum in Prague (inv. No 43.298) and in the collections of the Mineralogical Dept. of Charles University (inv. Nos 12.391 and 12.392) in Prague.
The hardness, determined by comparison with minerals of the Mohs scale, is 2–3. The powder of the mineral is white with a light brown-violet tone. A cleavage was not observed.

The commonest crystals of kettnerite are thin to thick tabular plates of a basal type (Figs. 1 and 2). The thick ones are plates parallelly grown together with the basal face. They are of a brown to brown-yellow colour. Light yellow-green, thin tabular, square or rectangular crystals with predominating pyramidal forms were rarely found. No goniometric measurements were carried out with these crystals. Goniometric data of the first and commonest type of crystals with their description were given in [2].

From new optical data (see below) a new position of kettnerite crystals appears necessary. The crystals have to be turned by 45°. The form {111} has to be transformed to {201} and {1.010} to {1.1.10}. The φ angles must be changed correspondingly. The ratio \(c/a\) now equals 2.53, in good agreement with \(c/a = 2.54\) (see below).

**MICROSCOPIC DATA**

In addition to the data given in [2] some new observations were made. Both types of kettnerite crystals (see above), brown and light lemon-yellow, give a biaxial interference figure in convergent polarized light. The angle of optical axes is small; sometimes the biaxial character of the crystals is difficult to observe. The thickness of about 6 crystals, used for convergent polarised light observations, was of the order of several tenths of a millimetre.

The observed axial angle 2\(E\) in air measured in Na light, was 11 ± 1°. In [2] by immersion in amorphous sulphur in Na light, \(ω\) (now \(γ\) and \(β\)) was found to be larger than 2°. A negative optical sign of the crystals was also found there. The optical axes plane is perpendicular to the crystal planes (001) and (100) (or (010)). The birefringence is moderate to high.

When not ascribing the biaxial character of kettnerite crystals to an anomaly, a lower than tetragonal symmetry of the crystals (see below) follows from the above data. Similarly E. I. Nefedov [4] found for bismutite crystals 2\(V\) = 45° and assumes an orthorhombic symmetry for this mineral.

**QUALITATIVE SPECTROGRAPHIC ANALYSIS**

Qualitative spectral analyses were given in [2]. In all specimens analyzed a substantial quantity of Bi, Ca and F, a subordinate to insignificant quantity of Pb, Al, Fe, Mg and Si and insignificant to trace quantity of Cu and Mn were found. Only in some specimens was an insignificant to trace quantity of Ag, Ba, Sr, Zn, Be, Mo, Te, Sb, Ti and W found.

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2) For Fig. 1, see Appendix I, p. 290c.