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AN *X*-RAY CRYSTALLOGRAPHIC STUDY OF SCHROECKINGERITE AND ITS DEHYDRATION PRODUCT

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ABSTRACT

X-ray precession patterns of schroeckingerite crystals from Moab, Utah, show that the mineral has triclinic pseudo-hexagonal symmetry. Dimensions of the unit cell containing $2(NaCa_3UO_2(CO_3)_3SO_4F \cdot 10H_2O)$ are $a=9.60\pm0.01$ Å, $b=9.62\pm0.01$ Å, $c=14.46\pm0.01$ Å, $\alpha=91°42'\pm10'$, $\beta=91°48'\pm10'$, and $\gamma=120°05'\pm10'$. The space group is $P\bar{1}$ or $P1$. When the material is dried at 75° C., it loses six of the ten water molecules. The unit cell of the product has $a=b=9.52\pm0.02$ Å, $c=11.10\pm0.02$ Å, $\alpha=95\pm5°$, $\beta=93\pm5°$ and $\gamma=60°00'\pm15'$, and its space group is also $P\bar{1}$ or $P1$ with $Z=2$.

INTRODUCTION

Single crystals of schroeckingerite, $NaCa_3UO_2(CO_3)_3SO_4F \cdot 10H_2O$, were examined by Hurlbut (1954), who reported that the crystals were orthorhombic, with the probable space group *Cmmm* or *Cmm*. From Hurlbut's determination, it was thought these crystals would provide a relatively easy determination of the four uranium positions in the unit cell. However, the present work shows that the structure has lower symmetry.

DESCRIPTION OF THE CRYSTALS

The samples containing the single crystals of schroeckingerite were collected by Professor J. W. Gruner and the author in the summer of 1952 from the Shinarump No. 3 Mine, Seven Mile Canyon, near Moab, Utah. The specimens are from silty stringers in the Shinarump conglomerate. The rock as a whole is very porous and an ideal locality for crystal growth from evaporating aqueous solutions, which probably produced these well-formed schroeckingerite crystals. Most of the crystals grew into small cavities, attached along one edge of the pseudo-hexagonal plate. Abundant gypsum is also present.

Macroscopically, the crystals are transparent, yellow-green, pseudo-hexagonal plates which are very soft and easily bent. Their dimensions vary up to a maximum of one millimeter in diameter and 0.02 mm. thick. There is a decided tendency for one pair of opposite edges to be shorter than the others, suggesting a pseudo-orthorhombic habit rather than pseudo-hexagonal. Microscopically, most of the apparently single crystals are aggregates of several crystals and show complex extinctions in polarized light. These crystals are typified by the photograph given by Hurlbut

(1954). Several single crystals, free of secondary growths, were found which gave sharp extinctions under a polarizing microscope.

OPTICAL PROPERTIES

The optical constants for several crystals were measured, and the averages are listed in Table 1 with Hurlbut's data. The indices and pleochroism are in excellent agreement with his values, and 2V, which was measured on a universal stage with hemispheres of index $n=1.554$, is also in reasonable agreement. The difference of 0.001 between the β index and γ index, which Hurlbut emphasized, was noted in the present study. During the determination of 2V it was observed that the acute bisectrix, which should be normal to the plane of the plate if the crystal is orthorhombic, deviated from the normal by approximately one degree. This departure may be within experimental error and, therefore, is not strong enough evidence to eliminate the possibility of classifying the crystal as orthorhombic. The optical orientation noted is X perpendicular to the plate, Y in the plane of the plate perpendicular to the short edge, and Z parallel to the short edge, which corresponds with Hurlbut's orientation: X $=c_0$, Y $=b_0$, and Z $=a_0$.

TABLE 1. OPTICAL PROPERTIES OF SCHROECKINGERITE FROM UTAH

	This Paper	Hurlbut (1954)
α	1.491	1.490
β	1.537	1.537
γ	1.538	1.538
2V	22.5°	18°
Optic sign	(−)	(−)
Pleochroism		
X	very pale yellow	very pale yellow
Y	yellow-green	yellow-green
Z	yellow-green	yellow-green

UNIT CELL AND SPACE GROUP

Precession patterns about the c-axis and two axes nearly at 90° to the c-axis were obtained from two single crystals using molybdenum $K\alpha(\lambda = 0.7107\text{Å})$ and $\bar{\mu}=30°$. One crystal was oriented with the rotation axis normal to the plane $\bar{1}10$ and essentially parallel to Y, and very clear $hk0$, $hk1$, $hk2$, $hk3$, $hk4$, and $\bar{h}hl$ (Hurlbut's $0kl$) zones were obtained. The other was mounted at a corner of the plate with the rotation axis normal to the plane $\bar{2}10$, and patterns of $hk0$ and $2\bar{h}, h, l$ (Hurlbut's h,

$3\bar{h}, l$) were made. Minor differences in relative intensities were observed when the $hk0$ patterns of the two crystals were compared, but the over-all features were almost identical. Both $hk0$ zones and the $\bar{h}hl$ and $2\bar{h}, h, l$ zones showed the required center of symmetry; the upper level patterns showed no symmetry at all.

If the crystal were orthorhombic, the optical orientation would require one crystallographic axis normal to the plane of the plate and the other two in the plane. Because *mm* symmetry is not observed in the $hk0$ zones, the orthorhombic possibility is ruled out. If the crystal were monoclinic, the optical orientation would require the unique axis to lie either parallel to X, which is normal to the plate, or parallel to Y or Z in the plane of the plate. The latter possibilities (unique axis equal Y or Z) would require the $hk0$ zone to have *mm* symmetry and all upper levels along the *c*-axis to have *m* symmetry; while the former orientation (unique axis equals X) would require *2* symmetry of all these zones and *mm* symmetry of $\bar{h}hl$ and $2\bar{h}, h, l$. Because neither set of conditions is present, the crystal must be triclinic with the space group either $P\bar{1}$ or $P1$. The morphology strongly indicates $P\bar{1}$.

TABLE 2. PSEUDO-ORTHORHOMBIC CELL OF SCHROECKINGERITE

	This Paper	Hurlbut (1954)
a_0	9.59 Å	9.69 Å
b_0	16.69 Å	16.83 Å
c_0	14.46 Å	14.26 Å
α_0	89°15′	90°
β_0	93°50′	90°
γ_0	89°55′	90°
Volume	2,308 Å^3	2,322 Å^3

The cell most nearly corresponding to Hurlbut's orthorhombic cell is given in Table 2, and his values are also listed for comparison. Using four formula units with a formula weight of 888.56, the calculated specific gravity is 2.550, which compares well with the value of 2.544 given by Hurlbut. For triclinic symmetry this cell is twice as large as necessary, and only two formula units are in the unit cell. Because triclinic symmetry does not specify a unique set of axes, a cell was chosen to correspond with the Delaunay (1933) reduced cell. This triclinic cell is related to the pseudo-orthorhombic cell by the reciprocal lattice relations $\vec{a}^* = \vec{a}_0^* - \vec{b}_0^*$, $\vec{b}^* = \vec{a}_0^* + \vec{b}_0^*$, and $\vec{c}^* = \vec{c}_0^*$, where the subscript ($_0$) indicates the orthorhombic parameters. The resulting cell dimensions are as follows:

$$\begin{array}{ll} a = 9.60 \pm 0.01 \text{ Å} & \alpha = 91°42' \pm 10' \\ b = 9.62 \pm 0.01 \text{ Å} & \beta = 91°48' \pm 10' \\ c = 14.46 \pm 0.01 \text{ Å} & \gamma = 120°05' \pm 10' \end{array}$$

$$\text{Volume} = 1154 \text{ Å}^3$$

The cell is very nearly hexagonal, having a γ angle of 120° within the limits of error, and an axial ratio of $a:b:c = 0.9979:1:1.5031$. The matrix transforming Miller indices given by Hurlbut to correspond with this cell is

$$\begin{bmatrix} 1/2 & 1/2 & 0 \\ -1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

CONCLUSIONS

In view of the optical evidence, the very close agreement in orthorhombic cell parameters, and the fact that they are from the same source, the crystals used for this study are believed to be identical with the ones used by Hurlbut. Possibly twinning could explain the orthorhombic symmetry which he reported, although none was noted in this study. The variation in relative intensities noted in the *hk*0 zones of the two crystals, used in this study, may be due to a difference in water content which was shown by Hurlbut to affect the optical constants of a schroeckingerite from Argentina.

THE DEHYDRATION PRODUCT

Several good crystals of schroeckingerite were dried in an oven at 75° C. for about 4 hours and then placed in a desiccator over anhydrous $CaSO_4$. The crystals were cloudy and appeared to be somewhat porous. The (001) face was pitted, and under the petrographic microscope the crystals lying on this face showed undulatory extinctions. The optical properties of the dehydrated material are given in Table 3. The difference in the α indices may be experimental error because of the difficulty of standing a thin plate on edge in immersion oils and the cloudiness of the crystals. As nearly as could be determined on the imperfect crystals, the optic axis is normal to the plane of the plates. A slight separation of the isogyres, indicating a maximum 2V of 5°, was observed during rotation of the nearly uniaxial interference figure. This separation could be caused by distortions in the crystals and therefore is not definitely established.

TABLE 3. OPTICAL CONSTANTS FOR DEHYDRATED SCHROECKINGERITE

	This Paper	Hurlbut (1954)
α	1.518	1.532
β	1.582	1.582
γ	1.582	1.582
Sign	(−)	(−)
2V	0°–5°	0°
pleochroism		
X	pale yellow	colorless
Y	yellow-green	pale yellow
Z	yellow-green	pale yellow

X-Ray Data

The optical data indicate that only zones parallel or normal to the *hk*0 zone need be examined to reveal the symmetry relationships. Precession patterns using molybdenum $K\alpha$ radiation and $\bar{\mu}=30°$ were obtained of the *hk*0, *hk*1, and 0*kl* zones from one crystal. The *hk*0 pattern was very clear and lattice parameters could be measured with some accuracy. The *hk*1 zone was nearly as sharp, but some streaking of the spots due to warping of the crystal was evident. The *hk*0 zone showed 6-fold symmetry, but the *hk*1 zone showed no symmetry. The 0*kl* pattern showed sharp reflections only along 00*l*, and very diffuse reflections smeared out parallel to 00*l* were noted for values of *k* up to 9. When this 0*kl* pattern is examined closely, the *k*-streaks reveal intensity variations giving the pattern only the required center of symmetry. Using the same reasoning as for schroeckingerite on the relationships between optical data and *x*-ray data, the symmetry for these crystals can be no higher than triclinic. The unit cell is very nearly hexagonal, differing only in the departure of the *c*-axis by a few degrees from normal to the *ab*-plane. Because of the poor 0*kl* pattern it was impossible to determine the departure accurately, and

TABLE 4. CELL CONSTANTS FOR DEHYDRATED SCHROECKINGERITE

	This Paper	Hurlbut (1954)
a	9.52±0.02 Å	9.72 Å
b	9.52±0.02 Å	9.72 Å
c	11.10±0.02 Å	11.03 Å
α	95°±5°	90°
β	93°±5°	90°
γ	60°00′±15′	60°
Volume	870 Å^3	902 Å^3

only estimated angles can be given for α and β. The cell constants are given in Table 4, with Hurlbut's values for comparison.

Using the measured specific gravity of 2.86 and the formula $NaCa_3UO_2(CO_3)_3SO_4F \cdot 4H_2O$ for the dehydrated material as established by Novacek (1939) and verified by Hurlbut, one finds 1.92 formula weights per unit cell. The difference from 2.00 may be due to the formation of open cavities on dehydration as evidenced by the cloudy appearance of the crystals.

CONCLUSIONS

When *x*-ray diffraction patterns of the dehydrated material are compared with the corresponding zones of schroeckingerite, there are actually only small differences in relative intensities, indicating that the main features of the structure are retained on dehydration. The hexagonal symmetry of the *hk*0 photograph of the dehydrate indicates that the projection of the structure along the *c*-axis must have approximately hexagonal or trigonal symmetry even though the whole structure does not possess this symmetry. That the structure is not hexagonal as originally proposed is strongly suggested by the large number of atoms in special positions which would be required to accommodate only two formulas per unit cell of the dehydrated material. Careful measurements of the *hk*0 intensities may show departures from hexagonal symmetry in that zone also.

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