American Mineralogist, Volume 82, pages 1014–1018, 1997

Acentric structure ($P3$) of bechererite, $Zn_7Cu(OH)_{13}[SiO(OH)_3SO_4]$

CHRISTINA HOFFMANN,[1] THOMAS ARMBRUSTER,[1] AND GERALD GIESTER[2]

[1]Laboratorium für chemische und mineralogische Kristallographie, Universität Bern,
Freiestrasse 3, CH-3012 Bern, Switzerland
[2]Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien, Althanstrasse 14, A-1090 Vienna, Austria

ABSTRACT

The crystal structure of bechererite from the Tonopah-Belmont mine, Arizona, was reinvestigated using a single-crystal X-ray diffractometer (Mo$K\alpha$ radiation) equipped with a CCD area detector. The structure was refined in space group $P3$ (a = 8.319(2), c = 7.377(1) Å) with 1247 unique reflections up to $(\sin\theta)/\lambda = 0.65$ leading to $R1$ = 2.7%, w$R2$ = 6.4%. In agreement with the previously reported centric structure ($P\bar{3}$), bechererite is composed of (001) brucite-like sheets formed by edge-sharing $(Zn,Cu)O_6$ octahedra and $\frac{1}{7}$ ordered octahedral vacancies. The layers are connected parallel to c by ditetrahedral $(Zn,Cu)_2(OH)_7$ units. Due to the attractive force of a weak hydrogen bond, the bridging O atom of the ditetrahedral unit is displaced from the threefold axis. A characteristic feature of the structure is isolated tetrahedra, which connect only with one apex to the octahedral sheet. The acentric structure ($P3$) reveals ordering between $SiO(OH)_3$ and SO_4 tetrahedra yielding characteristic distortions of the neighboring $(Zn,Cu)O_6$ octahedra caused by bond-valence requirements of the shared O atoms. The $[SiO(OH)_3]^{1-}$ tetrahedron is only 70(1)% occupied and is partly substituted by tetrahedral $[O_4H_7]^{1-}$ clusters. The existence of H_2O molecules in the $[O_4H_7]^{1-}$ cluster is supported by FTIR spectroscopy.

INTRODUCTION

Bechererite was recently described (Giester and Rieck 1996) as a new secondary mineral from the dumps of the Tonopah-Belmont mine (Arizona). The trigonal crystals with greenish hue have a characteristic acentric habit with the pointed top confined by {241} and $\{6\bar{2}1\}$ forms whereas the bottom is flat (001). In the original description of the structure (Giester and Rieck 1996) the small crystal size with average radii of 0.02 (perpendicular to c) × 0.125 mm (parallel to c) enabled only limited collection of single-crystal X-ray data. Thus the structure was solved and refined in space group $P\bar{3}$ with only 281 unique reflections. Although Giester and Rieck (1996) were aware of the high probability of lower symmetry as indicated by crystal morphology, the available data did not allow a successful refinement in the acentric space group $P3$ owing to correlation problems and insufficient data. Their structure solution, however, indicated that the structural topology can be described with the centro-symmetric space group $P\bar{3}$.

Our interest in bechererite was attracted because of the random S^{6+}-Si^{4+} distribution in the isolated tetrahedra attached to the brucite-like sheet found in the $P\bar{3}$ structure. Both the S^{6+}/Si^{4+} ratio close to one and the difference in charge suggest ordering on separate sites. For this reason we decided to recollect the single-crystal X-ray data with a state of the art CCD-type area detector, which allows more accurate reflection intensities to be measured for small crystals.

EXPERIMENTAL METHODS

A pyramidal crystal of bechererite, 0.140 mm long and 0.037 mm wide at the base, was mounted on a three-circle Siemens SMART system equipped with a CCD area detector for data collection (full sphere of the reciprocal space) up to $(\sin\theta)/\lambda = 0.65$ using graphite-monochromated Mo$K\alpha$ X-radiation. Cell dimensions were not significantly different from those reported by Giester and Rieck (1996). Details of the data collection are summarized in Table 1. Data reduction including Lorentz and polarization corrections were performed with the program SAINT (Siemens 1996). An empirical absorption correction based on Ψ-scans was applied, which reduced the internal R value from 7.1 to 3.6%. The structure was solved in space group $P\bar{3}$ and subsequently transformed to $P3$. Refinements were carried out on the basis of F^2 using scattering curves for neutral atoms with the program SHELXL-93 (Sheldrick 1993). Restraints for floating origin parallel to c were automatically generated by the program. First refinement cycles on 1247 unique reflections disclosed Si-S ordering on the isolated tetrahedral sites. The SiO_4 tetrahedron appeared to be only partially occupied and the population was refined. Furthermore, O3 at 0,0,½ displayed strongly anisotropic displacement parameters within (001), thus this atom was slightly displaced from the threefold axis and refined as a disordered position with an isotropic displacement parameter. Finally, four H positions were extracted from difference-Fourier maps and also refined with fixed iso-

0003–004X/97/0910–1014$05.00

TABLE 1. CCD data collection and structure refinement of bechererite

Diffractometer	Siemens SMART CCD system
X-ray radiation	sealed tube Mo$K\alpha$
X-ray power	50 kV, 40 mA
Temperature	293 K
Detector to sample distance	5.518 cm
Detector 2θ angle	27°
Resolution	0.77 Å
Rotation axis	ω
Rotation width	0.3°
Total no. of frames	2074
Frame size	512 × 512 pixels
Data collection time per frame	60 s
Collection mode	automated full sphere
Reflections measured	3228
Mean I/σ_I	19.0
Max. 2θ	55.0; $-10 \leq h, k \leq 10$, $-9 \leq l \leq 9$
Unique reflections	1247
Reflections $> 2\sigma_I$	1138
Space group, cell dimensions	$P3$, $a = 8.319(2)$, $c = 7.377(1)$ Å
R_{int}	3.58% after empirical abs. correction
R_σ	3.92%
Extinction coefficient	0.0009(6)
Number of l.s. parameters	109
GoF	1.070
$R1$, $F_o > 4\sigma_{F_o}$; 1138 obs.	2.70%
$R1$, all data	3.24%
w$R2$ (on F^2)	6.37%
Flack × parameter	0.06(4)

Note:

$$R_{int} = [\Sigma|F_o^2 - (F_o^2)\mathrm{mean}|]/(\Sigma F_o^2), \qquad R_\sigma = (\Sigma\sigma_{F_o^2})/\Sigma F_o^2,$$

$$R1 = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|), \qquad \mathrm{w}R2 = \sqrt{[\Sigma(F_o^2 - F_c^2)^2]/[\Sigma \mathrm{w}(F_o^2)^2]}$$

$$\mathrm{GoF} = \sqrt{[\Sigma \mathrm{w}(F_o^2 - F_c^2)^2]/(n - p)}.$$

tropic $U = 0.03$ Å^2 and restrained to be 1.00(3) Å apart from the neighboring O, characteristic of an OH group. Highest peaks in the final difference-Fourier maps were +0.64 and -0.47 e/Å^3. Positive peaks are between metal and O positions representing bonding electrons. Strongest correlation between parameters related by a pseudo center of symmetry was < 87%. Using the acentric space group $P3$ the absolute structure could be determined without any indication of twinning by the pseudo center of symmetry dictated by the topology. This is confirmed by the low absolute structure parameter $x = 0.06(4)$ (Flack 1983). Sites related by pseudo-symmetry (center of inversion) are labeled Zn1 and Zn11, O1 and O11, etc. A list of observed and calculated structure factors is given in Table 2[1].

In addition, polarized FTIR spectra of the same single crystal as used for the X-ray experiment were recorded on a Perkin Elmer 1760 FTIR spectrometer equipped with an FTIR microscope.

TABLE 3. Atomic positional parameters and B_{eq} (Å^2) values for bechererite in space group $P3$

Atom	x/a	y/b	z/c	B_{eq}
Zn1	0.1326(1)	0.4136(1)	0.9997(1)	1.34(2)
Zn11	0.8628(1)	0.5734(1)	0.0007(1)	1.33(2)
Zn2	0	0	0.2469(3)	1.48(2)
Zn21	0	0	0.7571(3)	1.24(2)
S	⅓	⅔	0.5902(7)	1.31(4)
Si	⅔	⅓	0.3926(9)	1.07(8)
O1	⅓	⅔	0.790(2)	1.8(1)
O11	⅔	⅓	0.163(2)	1.8(1)
O2	0.1710(8)	0.6756(8)	0.5230(9)	2.0(1)
O21	0.8536(9)	0.334(1)	0.478(1)	3.5(1)
O3	0.051(2)	0.060(2)	0.501(3)	1.5(2)*
O4	0.9435(8)	0.1867(8)	0.168(1)	1.7(1)
O41	0.0523(8)	0.8045(8)	0.839(1)	1.4(1)
O5	0.3752(7)	0.4826(8)	0.126(1)	1.4(1)
O51	0.6288(8)	0.5284(8)	0.873(1)	1.2(1)
H5	0.347(9)	0.500(9)	0.245(5)	2.37*
H51	0.630(9)	0.587(9)	0.764(6)	2.37*
H4	0.877(8)	0.248(8)	0.212(8)	2.37*
H41	0.05(1)	0.748(9)	0.729(6)	2.37*

Note: The population of Si is 0.70(1), the population of O3 is ⅓. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B_{eq} = \frac{8}{3}\pi^2 \Sigma_i [\Sigma_j(U_{ij}a_i^* a_j^* a_i \cdot a_j)]$.

* B_{eq} with σ in parentheses was refined isotropically, B_{eq} without σ was fixed.

RESULTS

Refined atomic coordinates and anisotropic displacement parameters in space group $P3$ are given in Tables 3 and 4. The structural topology of bechererite can be described by the centrosymmetric space group $P\bar{3}$. However, Si^{4+}-S^{6+} ordering in the isolated tetrahedral sites reduces the symmetry to $P3$ and imposes characteristic distortions to the neighboring octahedral sites. Site population refinements for Si indicate that this tetrahedron is only 70% occupied by Si whereas the coordinating O21 sites are fully occupied. Selected bond lengths and bond valences (Brown and Altermatt 1985) are summarized in Table 5. Because of the strong similarity between Zn and Cu scattering factors and the similar ionic radii (Shannon 1976) of Zn^{2+} (IV: 0.60, VI: 0.74 Å) and Cu^{2+} (IV: 0.57, VI: 0.73 Å), possible ordering of the bivalent cations cannot be resolved. On the basis of bond-valence arguments O3, O21, O4, O41, O5, and O51 must be considered OH groups (Table 5). However, only four protons (H4 bonded to O4, H41 bonded to O41, H5 bonded to O5, and H51 bonded to O51) could be extracted from difference-Fourier maps and subsequently refined.

The H_2O- and OH-sensitive frequency range between 1400 and 5500 cm^{-1} of the FTIR spectrum is characterized by a very strong absorption between 2800 and 3700 cm^{-1}, which was cut by the base line because of the thickness of the applied single crystal. These absorptions are characteristic of OH and H_2O stretching modes and were observed for polarizations parallel and perpendicular to *c*. The second strongest absorption, observed for both polarizations, is at about 1650 cm^{-1} with a shoulder toward lower frequencies. This band is interpreted as an H_2O bending mode and is accompanied by weaker side bands at 1700, 1900, and 1460 cm^{-1}. A very weak but broad

---

[1] For a copy of Table 2, order Document AM-97-644 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington DC 20036, U.S.A. Please remit $5.00 in advance. Deposit items may also be available on the American Mineralogist web site, refer to inside back cover of a current issue for web address.

TABLE 4. Anisotropic displacement parameters for bechererite in space group $P3$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn1	0.0113(4)	0.0125(4)	0.0293(6)	0.0076(3)	−0.0007(5)	−0.0014(5)
Zn11	0.0096(4)	0.0117(4)	0.0293(6)	0.0054(3)	−0.0017(4)	−0.0014(4)
Zn2	0.0181(5)	0.0181(5)	0.020(1)	0.0090(2)	0	0
Zn21	0.0133(4)	0.0133(4)	0.020(1)	0.0066(2)	0	0
S	0.016(1)	0.016(1)	0.018(2)	0.0080(5)	0	0
Si	0.012(2)	0.012(2)	0.017(4)	0.0060(8)	0	0
O1	0.027(3)	0.027(3)	0.013(5)	0.014(2)	0	0
O11	0.020(3)	0.020(3)	0.028(6)	0.010(1)	0	0
O2	0.028(3)	0.039(3)	0.020(3)	0.024(3)	−0.005(2)	−0.004(3)
O21	0.035(3)	0.065(4)	0.035(4)	0.026(3)	−0.002(3)	−0.012(4)
O4	0.013(3)	0.026(4)	0.023(5)	0.008(2)	−0.003(2)	−0.009(3)
O41	0.017(3)	0.015(3)	0.026(5)	0.011(2)	0.004(2)	0.006(2)
O5	0.012(3)	0.018(3)	0.021(4)	0.008(2)	0.002(2)	−0.004(2)
O51	0.014(3)	0.015(3)	0.019(4)	0.010(2)	0.000(2)	0.003(2)

Note: Anisotropic displacement parameters are of the form $\exp(-2\pi^2\Sigma_i\Sigma_j U_{ij} h_i h_j a_i^* a_j^*)$.

band was found only in the spectrum polarized parallel to ***c*** at about 5000 cm^{-1}, which is interpreted as a combination band due to H_2O stretching and H_2O bending. A weak additional band occurs at 4400 cm^{-1}, which is assigned to an OH-sensitive combination mode.

DISCUSSION

A crystal chemical comparison of bechererite with related structures is provided by Giester and Rieck (1996). The major differences between the centric structure (space group $P\bar{3}$) solved by Giester and Rieck (1996) and the acentric structure (space group $P3$) refined in this paper are that the upper and lower sides of the brucite-like layer are different (Fig. 1) and that the isolated tetrahedra linked to these sides are composed either of $SiO(OH)_3$ or SO_4. The brucite-like layers are formed by regular Zn11 octahedra, strongly distorted Zn1 octahedra, and ⅐ ordered octahedral vacancies [see Fig. 2 given by Giester and Rieck (1996)]. The regular Zn11 octahedron has Zn-O distances between 2.02 and 2.20 Å, whereas the Zn-O distances in the distorted Zn1 octahedron range from 2.02 to 2.47 Å. The latter coordination is better described as (5 + 1). The long Zn-O distance occurs at fourfold coordinated O1 bonding to three Zn1 and also to tetrahedral S^{6+}. The long Zn-O1 bonds are necessary to provide an appropriate bond valence sum for O1. In contrast, S-O1 bonds are not increased to keep the valence sum of S^{6+} close to 6 v.u. (Table 5). The Zn11 octahedron is more regular because O11 is linked to Si^{4+}, which has a lower bond valence contribution than S^{6+}. The SO_4 tetrahedron exhibits regular S-O distances of 1.47 Å with close to ideal O-S-O angles. The $SiO(OH)_3$ tetrahedron is highly unusual for several reasons. (1) The Si-O bond lengths between 1.68 and 1.69 Å are considerably longer than expected. (2) Only 70% of the tetrahedral sites are occupied by Si, assuming vacancies for the remaining 30%. (3) No vacancies were found for the coordinating O21 sites. The Si vacancies are supported

TABLE 5. Selected bond lengths (Å) and bond valences (v.u.) for bechererite

Atoms			Distance	Valence	Atoms			Distance	Valence
Zn1	O51		2.018(5)	0.428	Zn11	O51		2.023(5)	0.422
Zn1	O5		2.026(5)	0.419	Zn11	O5		2.074(5)	0.368
Zn1	O41		2.076(7)	0.366	Zn11	O51		2.080(6)	0.362
Zn1	O5		2.089(6)	0.353	Zn11	O41		2.139(7)	0.309
Zn1	O4		2.147(7)	0.302	Zn11	O4		2.157(7)	0.294
Zn1	O1		2.471(7)	0.126	Zn11	O11		2.198(7)	0.263
Average			2.138	Σ 1.994	Average			2.112	Σ 2.018
Zn2	O3		1.933(20)	0.539/0.503	Zn21	O3		1.944(20)	0.523
Zn2	O4	× 3	1.924(6)	0.552/0.516	Zn21	O41	× 3	1.976(6)	0.479
Average			1.926	Σ 2.195/2.051	Average			1.968	Σ 1.960
S	O1		1.472(13)	1.508	Si	O11		1.692(15)	0.832
S	O2	× 3	1.475(5)	1.496	Si	O21	× 3	1.676(7)	0.869
Average			1.474	Σ 5.996	Average			1.680	Σ 3.439
O1				Σ 1.886	O11				Σ 1.621
O2				Σ 1.496	O21				Σ 0.869
O3				Σ 1.062					
O4				Σ 1.148	O41				Σ 1.154
O5				Σ 1.140	O51				Σ 1.212
O4	H4		0.98(4)		O21	H4		2.12(6)	
O41	H41		0.93(5)		O2	H41		2.06(4)	
O5	H5		0.94(4)		O2	H5		2.06(4)	
O51	H51		0.94(5)		O21	H51		2.25(5)	

Note: bond valences were calculated according to Brown and Altermatt (1985) without considering H.

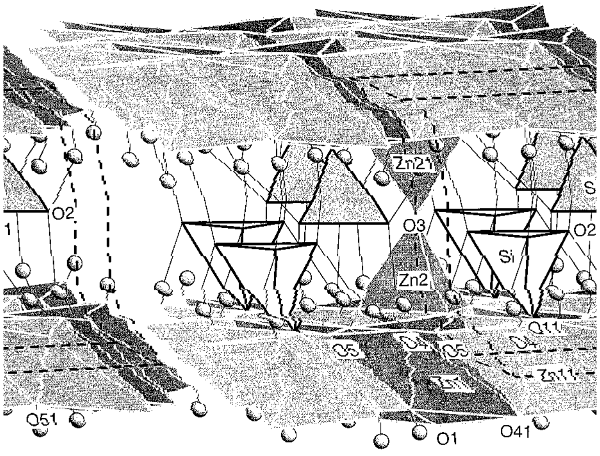

FIGURE 1. Polyhedral model of the bechererite structure in space group *P*3. Spheres represent refined H positions. Solid lines show the hydrogen bonds between the isolated tetrahedra (S, Si) and the neighboring octahedral layers. Dashed lines outline the unit cell.

by the highly variable SiO_2 concentrations found in bechererite analyses (4.4–8.2 wt%) by Giester and Rieck (1996) where SiO_2 even varies strongly within the same single-crystal. One may suppose that in the case of Si vacancies O11 in the brucite-like layer is terminated by H forming an OH group with hydrogen bonds to H_2O molecules close to O21 (Fig. 2). The existence of H_2O molecules is confirmed by FTIR spectroscopy yielding H_2O specific absorptions (H_2O bending mode and a combination band interpreted as H_2O bending and stretching). Thus the observed O21 position is an average of terminal OH groups of the $[SiO(OH)_3]^{1-}$ tetrahedron and H_2O molecules of an $[O_4H_7]^{1-}$ cluster, occurring in the case of Si vacancies (Fig. 2). This could explain the long Si-O distances (Table 5), the large displacement parameter of O21 (Table 4), and the absence of O21 vacancies. The $SiO(OH)_3$ tetrahedron is kept in position by several types of hydrogen bonds. Two bonds, O51-H · · ·O21, from the opposite layer, and O4-H · · ·O21, from the layer connected to the tetrahedron (Fig. 1), could be derived from refined H positions. A corresponding set of hydrogen bonds was found for the SO_4 tetrahedron with O5-H bonding to O2 from the opposite layer and O41-H · · · O2 from the layer connected to the tetrahedron. The strongest link between the layers is formed by ditetrahedral $(Zn,Cu)_2(OH)_7$ units (Fig. 3) where Zn2 has a mean Zn2-O distance of 1.93 Å and Zn21 has a mean Zn21-O distance of 1.97 Å. This size difference could indicate that the smaller tetrahedron, Zn2, is actually occupied by Cu and Zn21 by Zn, which would also lead to the analytically determined Zn/Cu ratio of $^{7}/_{1}$ (Giester and Rieck 1996). In addition, assignment of Cu^{2+} to the Zn2 position leads to more balanced valance sums (Table 5). The OH group at O3 connecting the two neighboring (Zn,Cu) tetrahedra is disordered around the threefold axis (Fig. 3) leading to three randomly occupied O3 sites 0.80 Å apart

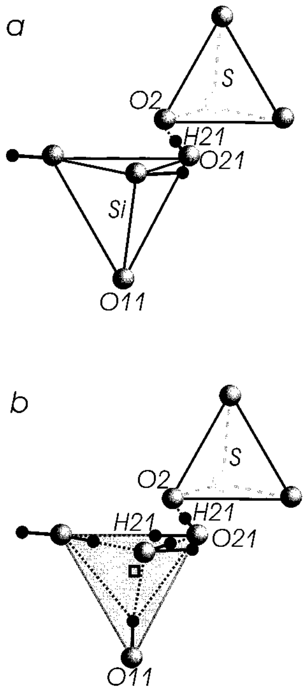

FIGURE 2. Schematic drawing of the isolated tetrahedron linked to O11 interpreted as a partial substitution of an $[O_4H_7]^{1-}$ cluster for $[SiO(OH)_3]^{1-}$. (**a**) The tetrahedron is 70% occupied by Si and the corners at O21 represent OH groups hydrogen bonded to O2 of the adjacent SO_4 tetrahedron. (**b**) The tetrahedron is 30% unoccupied (i.e., vacancy); O11 is terminated by an OH group and the corners at O21 represent H_2O molecules hydrogen bonded to each other and to O2 of the adjacent SO_4 tetrahedron.

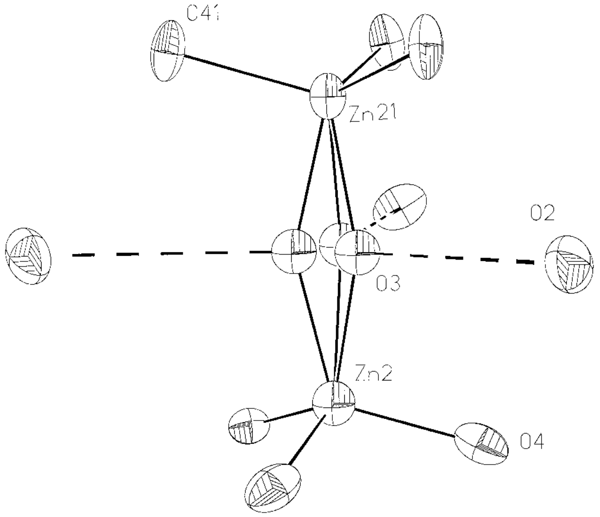

FIGURE 3. Atomic displacement parameters drawn as 80% probability ellipsoids for the ditetrahedral $(Zn,Cu)_2(OH)_7$ units. Weak hydrogen bonds O3-H · · · O2 are responsible for the disorder of O3 (refined with isotropic displacement parameter) causing an energetically more favorable T-O-T angle of 152°.

from each other. The disorder is probably due to a weak hydrogen bond O3-H · · · O2, which also prevents an energetically unfavorable T-O-T angle of 180°. The T-O-T angle becomes 152.2(5)° because of this O3 disorder. The proton at the disordered O3 site could not be located, but it is assumed that the OH group bonds more or less horizontally to the neighboring SO_4 tetrahedron where the O3 · · · O2 distance is 3.18 Å (Fig. 3). Bond valence arguments also indicate that the three OH groups at O21 of the $[SiO(OH)_3]^{1-}$ tetrahedron form hydrogen bonds to the neighboring anhydrous SO_4 tetrahedra with an O21 · · · O2 distance of 2.77 Å (Fig. 2). As pointed out before, the assumed disorder between OH and H_2O at O21, associated with Si vacancies, did not allow us to locate H21.

ACKNOWLEDGMENT

We are indebted to A. Beran (Vienna) for help with the FTIR experiments. An earlier version of this manuscript benefited from the thoughtful reviews of R. Miletich (Bayreuth) and P.L. Zanazzi (Perugia), which are gratefully acknowledged. Nancy Ross (London) is thanked for her effort handling the manuscript as Associate Editor.

REFERENCES CITED

Brown, I.D. and Altermatt, D. (1985) Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. Acta Crystallographica, B41, 244–247.

Flack, H.D. (1983) On enantiomorph-polarity estimation. Acta Crystallographica, A39, 876–881.

Giester, G. and Rieck, B. (1996) Bechererite, $(Zn,Cu)_6Zn_2(OH)_{13}[(S,Si)(O,OH)_4]_2$, a novel mineral species from the Tonopah-Belmont mine, Arizona. American Mineralogist, 81, 244–248.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica, A32, 751–767.

Sheldrick, G.M. (1993) SHELXL-93 program for crystal structure determination. University of Göttingen, Germany.

Siemens (1996) SAINT, Release 4.0. Siemens Energy and Automation Inc. Madison, Wisconsin 53719, U.S.A.

MANUSCRIPT RECEIVED NOVEMBER 19, 1996
MANUSCRIPT ACCEPTED APRIL 22, 1997