The crystal structure of shattuckite

AKIRA KAWAHARA

Department of Earth Sciences, Faculty of Science,
Okayama University, Okayama 700

ABSTRACT

The crystal structure of shattuckite ($\text{Cu}_5(\text{OH})_2(\text{SiO}_3)_4$), space group $Pcab$, $a=9.88$, $b=19.82$, $c=5.40\text{\AA}$, $Z=4$, has been investigated by three dimensional intensity data. The newly determined structure is the same as the structure studied by Evans and Mrose (1966) and Le Bihan (1967) in the projection parallel to the c -axis, but the z -parameters of silicon, copper and oxygen atoms are different. The configuration of the nearest neighbours of copper atoms are also different. The copper atoms stay at the centers of the rectangles of oxygen atoms, showing the usual coordination of Cu^{2+} in copper bearing minerals in general.

Introduction

Shattuckite ($\text{Cu}_5(\text{OH})_2(\text{SiO}_3)_4$) is found in the oxidation zones of the copper deposits. The description was first made of the specimen from Shattuck mine, Bisbee, Arizona by Schaller (1915). The cell dimensions, space group and chemical compositions were discussed by Newberg (1964) and Mrose and Vlisidis (1966). The approximate crystal structure and the exact chemical composition were given by Evans and Mrose (1966) and ascertained by Le Bihan (1967) on the basis of two dimensional projection on (001). The chemical composition confirmed by these researchers is $\text{Cu}_5(\text{OH})_2(\text{SiO}_3)_4$. The structure determined based on only one projection seems to need closer examination, because the coordination polyhedra of Cu atoms are different from those generally obtained in other copper bearing minerals.

In this study, the structure of shattuckite has been studied by

three dimensional intensity data. The copper atoms determined by this investigation are all situated at the centers of the rectangles of oxygen atoms.

Some of the specimens used in this investigation were given by the Ecole des Mines in Paris by the courtesy of Drs. M. Fonteilles and P. Sainfeld.

Because of the extremely small size of the specimens, the X-ray counter method could not be adopted. It is desirable to synthesize larger specimens fitting well to counter methods.

Experimental

According to the previous studies, the single crystals of shattuckite were extremely small, and only zero layer Weissenberg photographs were obtained but not the higher layers. Three specimens from Reneville (Congo), Ajo (Arizona) and Kakanda (Katanga) were first examined in detail by X-ray powder methods in this study. Very small single crystals ($0.05 \times 0.01 \times 0.15$ mm) were obtained from the specimen from Ajo. In order to obtain larger specimens, hydrothermal syntheses were made from mixture of CuSO_4 , silica gel and Na_2CO_3 at about 350°C and 1000 atoms (Kawamura *et al.*, 1976). The slightly larger specimens than those from natural specimens were obtained. The needle-like cobalt-blue single crystals were cautiously chosen under the polarizing microscope. The oscillation as well as the Weissenberg photographs were taken about the *a*- and *c*-axes ($\lambda = 1.5418\text{\AA}$). The lattice dimensions were derived by the Weissenberg method with metal silicon powder ($a_0 = 5.4306\text{\AA}$) as standard material and refined by the least-squares calculations (Christ, 1956). The following data are obtained:

Orthorhombic, $D_{2h}^{15} - Pcab$

$a = 9.88(2)\text{\AA}$

$b = 19.82(4)\text{\AA}$

$$c=5.40 (1) \text{ \AA}$$

$$Z=4$$

$$\mu=167 \text{ cm}^{-1} (\lambda=1.5418\text{\AA})$$

The intensity was measured visually by the multifold methods, and Lorentz and Polarization corrections were made in the usual way. No absorption corrections were made due to the very small size of the specimens. The natural and synthetic specimens show exactly the same intensity values. Among the 425 observed reflections, 174 of F_o values were observed to be zero.

From the three dimensional intensity data, Patterson syntheses were made and the positions of copper atoms were found in the map. The positions of silicon atoms were found according to the $(F_o - F_c)$ Fourier maps with the phases given by Cu atoms. Finally, the positions of oxygen atoms were found by the $(F_o - F_c)$ Fourier maps with phases given by Cu and Si atoms. Then the parameters of all atoms determined by Patterson and difference Fourier methods were refined with a diagonal least-squares program and the residual R was reduced to 12.8% excluding zero reflections. The atomic parameters obtained

Table 1. Positional parameters, temperature factors ($\text{\AA}^2$)
with the standard deviations of atomic parameters
shown in parentheses.

	x	y	z	B
Cu(1)	0.0000	0.0000	0.0000	2.90(12)
Cu(2)	0.1689 (6)	0.0252 (3)	0.5430(10)	3.12 (9)
Cu(3)	0.2513 (8)	0.2803 (3)	0.4753(11)	3.58 (8)
Si(1)	0.1003(10)	0.1551 (5)	0.2340(30)	1.30(14)
Si(2)	0.5461(10)	0.1341 (5)	0.2252(30)	1.49(14)
O(1)	0.5072(30)	0.1741(13)	0.9630(70)	3.40(47)
O(2)	0.1544(20)	0.0773(10)	0.2381(50)	0.80(31)
O(3)	0.4981(25)	0.0535(13)	0.2185(65)	3.40(46)
O(4)	0.2093(20)	0.2135(10)	0.2160(60)	1.48(35)
O(5)	0.7065(25)	0.1517(13)	0.2311(75)	2.53(44)
O(6)	0.0154(30)	0.1675(13)	0.9810(60)	3.15(41)
OH	0.3255(30)	0.4714(12)	0.1546(61)	3.14(48)

are shown in Table 1. The interatomic distances and angles for nearest neighbours are also given in Table 2.

Throughout the investigation, the calculations were made on the computer HITAC 8800/8700 at the University of Tokyo and also NEAC 2200/500 at Okayama University.

Table 2. Interatomic distances and angles calculated. The standard deviations are represented in parentheses.

Si(1)-O(1)	1.67(3) Å	O(1)-Si (1)-O(2)	114.3(1.5)°
-O(2)	1.63(2)	O(1)-O(4)	108.2(1.5)
-O(4)	1.58(2)	O(1)-O(6)	105.0(1.7)
-O(6)	1.62(3)	O(2)-O(4)	118.0(1.2)
Si(2)-O(1)	1.67(3)	O(2)-O(6)	106.9(1.5)
-O(3)	1.67(3)	O(4)-O(6)	100.9(1.6)
-O(5)	1.62(3)	O(1)-Si (2)-O(3)	111.9(1.7)
-O(6)	1.65(3)	O(1)-O(5)	98.0(1.7)
Cu(1)-O(2)	2.51(2) × 2	O(1)-O(6)	115.7(1.6)
-O(3)	1.85(3) × 2	O(3)-O(5)	119.0(1.4)
-OH	2.00(3) × 2	O(3)-O(6)	107.4(1.6)
Cu(2)-O(2)	1.95(2)	O(5)-O(6)	104.9(1.8)
-O(2)	2.28(2)	O(2)-Cu(1)-O(3)	86.4(1.0)
-O(3)	1.98(3)	O(2)-OH	97.9(1.0)
-OH	1.95(3)	O(3)-OH	79.1(1.1)
-OH	2.16(3)	O(2)-Cu(2)-O(2)	101.3(0.9)
Cu(3)-O(1)	2.55(3)	O(2)-OH	177.2(1.1)
-O(4)	1.97(3)	O(2)-O(3)	106.7(1.1)
-O(4)	1.89(3)	OH-OH	97.0(1.2)
-O(5)	1.97(3)	O(3)-OH	166.2(1.1)
-O(5)	1.94(3)	O(4)-Cu(3)-O(4)	93.4(1.1)
		O(4)-O(5)	175.8(1.3)
		O(5)-O(5)	92.7(1.3)
		O(5)-O(1)	63.2(1.1)

Description of the structure and discussion

The structure of shattuckite is shown in Fig. 1. The small single, the large single and the large double circles correspond to silicon, oxygen and copper atoms, respectively. Numerals dotted on each

Projection on (001). Large double, large single and small single circles represent copper, oxygen and silicon atoms respectively.

coordination polyhedra about Cu(1) and Cu(2) are clearly shown in Fig. 2. These copper atoms have four nearest neighbours of oxygen atoms in the distance from 1.85 to 2.16Å, staying at the centers of the distorted rectangles of oxygen atoms. Cu(1) and Cu(2) have also two more oxygen atoms at longer distances ranging from 2.28 to 2.51Å (Table 2). These relations are shown by the dotted lines in

Fig. 2. Structure of shattuckite.

Projection on (010). In order to represent the coordination of copper atoms, Cu(1) and Cu(2), only the atoms with $z=0.375\sim 0.625$ are illustrated.

Fig. 2. Cu(3) has one more oxygen atoms, O(1), at $2.55\text{\AA}$, which is distinctly longer than the other four (Table 2).

As for the projection viewed parallel to the c -axis, the structure determined by Le Bihan (1967) and that by the present author can not be distinguished. But according to the present investigation based on the three-dimensional data, the z -parameters of the Si-O chains are different by 0.25 from those by the previous study.

Shattuckite has almost the same cell dimensions and space group as orthopyroxenes, but the arrangement of the Si-O chains and other cations are different according to the special coordination polyhedra of copper atoms, which are in accord with the dsp^2 hybrid orbital model.

REFERENCES

- CHRIST, C.L. (1956) *Amer. Miner.*, **41**, 569.
- EVANS, H.T. & MROSE, M.E. (1966) *Science*, **154**, 506.
- KAWAMURA, K., KAWAHARA, A. & HENMI, K. (1976) *Journ. Miner. Soc. Japan* (in press).
- LE BIHAN, M. Th. (1967) *Bull. Soc. fr. Miner. Crist.*, **90**, 3.
- MROSE, M.E. & VLISIDIS, A. (1966) *Amer. Miner.*, **51**, 266.
- NEWBERG, D.W. (1964) *Amer. Miner.*, **49**, 1234.
- SAKURAI, T. ed. (1971) *Universal Crystallographic Computation Program System*, Crystallographic Society of Japan.
- SCHALLER, W.T. (1915) *Journ. Wash. Acad. Sci.*, **9**, 131.

Received September 20, 1975; revised March 15, 1976.