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Crystal-structure refinement of cattierite*

J. Lynn Pratt and Peter Bayliss

Department of Geology, University of Calgary, Alberta T2N 1N4, Canada

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Abstract. The crystal structure of cattierite (CoS_2), which has a pyrite-type structure, has been refined to a R value of 0.015 in space group $Pa\bar{3}$. No conclusive evidence was found to show deviations from cubic symmetry.

Introduction

The crystal structure of cattierite, CoS_2, has been reported by Kerr (1945) as isotypic with pyrite in cubic space group $Pa\bar{3}$. Bond lengths for this crystal structure have been derived by Elliott (1960). Because this is a basic structure, it was decided to refine these values, especially since other members of the pyrite group have been reported with non-cubic symmetry *e.g.* cobaltite (Giese and Kerr, 1965), gersdorffite (Bayliss and Stephenson, 1968), arsenian ullmannite (Bayliss, 1977a), and pyrite (Bayliss, 1977b). Samples from the type locality of Shinkolobwe Mine, Katanga, Zaire were obtained from the British Museum, (BM 1971, 92) and the Smithsonian Institute (USNM 106811).

Experimental and results

Sample BM 1971, 92 was analysed by electron probe as previously described by Stout and Bayliss (1975). The analytical results and derived chemical formula based upon a $4AX_2$ model are presented in Table 1. This composition is close to the end-member composition of cattierite, except for the substitution of cobalt by nickel and iron.

A 114.6 mm Debye-Scherrer photograph was taken with Ni-filtered Cu radiation. A unit cell with $a = 5.5387$ Å was calculated by the Nelson and

* Dedicated to Prof. W. Nowacki on occasion of his 70th birthday

Table 1. Electron-microprobe analysis and atomic proportions

Atom	Weight % CoS_2	Weight % BM 1971, 12	Atomic proportions	
Co	47.9	38.6	0.80	1.00
Fe		4.9	0.11	
Ni		4.3	0.09	
S	52.1	52.4		2.00
	100.0	100.2		

Riley (1945) extrapolation method to $\theta = 90°$. This value is similar to 5.5346(5) Å, which is converted from the kX units used by Kerr *et al.* (1945), and to 5.5365(8) Å of Butler and Bouchard (1971), but slightly higher than 5.523 Å of Elliott (1960) for CoS_2. All reflection can be indexed in space group $Pa\bar{3}$.

A single crystal with dimensions of $136 \times 48 \times 18$ μm was selected because of its well-developed cube form {100}. This crystal was aligned along an a^* axis on a precession camera using Mo radiation. The $hk0$ and $h0l$ photographs recorded on polaroid film showed the systematic absences of space group $Pa\bar{3}$.

This crystal was accurately centered on a four-circle diffractometer with reflections 800, $\bar{8}00$ and 080 so that the a^* axis coincided with the diffractometer ϕ axis. Integrated intensities of 28 reflections, including 24 reflections forbidden by space group $Pa\bar{3}$, showed that sample BM 1971, 12 is similar to sample USNM 106811 (Table 2). Therefore only integrated intensities of all reflections from one hemisphere of BM 1971,12 were collected with MoK_α radiation and a graphite 002 monochromator. Within the range $5° < 2\theta < 60°$, 969 reflections were scanned in duplicate using the scan mode of $\omega : 2\theta$ at $1° 2\theta$ per minute over the scan width of $1.8° + \tan\theta$. Ten-second background counts were measured at both the beginning and end of each reflection. Where the total counts were less than 500, or if there was significant variation between duplicate reflections, then the reflection was measured again in duplicate. A standard reflection 020 was measured every 50 reflections throughout the data collection in order to check experimental stability.

Background, Lorentz, polarization, and absorption corrections were made following the method of Wuensch and Prewitt (1965). The linear absorption coefficient of this cattierite is $120.8\,cm^{-1}$, which results in transmission factors from 0.63 to 0.80 for this crystal. The extinction factor described by Zachariasen (1967), and extended by Coppens and Hamilton (1970), was calculated.

From 969 reflections, 82 symmetry-independent reflections with 73 above the 1σ level were calculated in space group $Pa\bar{3}$, which has systematic

Table 2. Intensities from BM 1971, 12 and USNM 106811

hkl	Intensity BM 1971, 12	Intensity USNM 106811	*hkl*	Intensity BM 1971, 12	Intensity USNM 106811
020	10000	10000	110	2	3
			101	2	4
001	2	4	011	2	4
003	1	2			
005	10	19	201	2038	2985
007	1	2	120	2236	4518
			012	2245	3995
010	2	3	102	1	3
030	1	2	210	2	3
050	1	2	021	2	2
070	1	1			
			301	1	2
100	4	14	130	1	2
300	9	15	013	1	2
500	1	2	103	1	2
700	1	1	310	1	2
			031	1	2

absences of $hk0$ with h odd, $0kl$ with k odd, and $h0l$ with l odd. All of these reflections were included in the refinement of the crystal structure by the least-squares program (Refine 4) of Finger and Prince (1975). All observations were weighted according to $\omega = 1/\sigma_F^2$, where σ_F is the standard deviation based upon counting statistics. Initial positional parameters were taken from Elliott (1960). The neutral-atom scattering factors and anomalous dispersion corrections were taken from Ibers and Hamilton (1974). The data were refined in space group $Pa\bar{3}$ to a R_ω value of 0.014 ($R = 0.015$). The positional parameters, isotropic temperature factors, and extinction parameter are listed in Table 3. Table 4 gives the interatomic distances and angles for this refinement as well as the interatomic distances of Elliott (1960) for comparison.

This R value indicates that the crystal structure is basically correct, although space group $Pa\bar{3}$ has systematic absences. The intensity and background of four reflections ($0k0$ with k odd from $k = 1$ to 7) were measured each for 60 s at every 5° as the crystal was rotated about the scattering vector. The reflection-to-background ratios, which were observed away from Renninger reflections, are 1.2 (010), 1.3 (030), 1.2 (050), and 1.2 (070). Of the 144 measured reflections that are systematically absent in space group $Pa\bar{3}$, only the 005, 033 and $0\bar{3}3$ are observed above the 1 σ level.

An attempt was made to refine this crystal structure in space group $P1$ similar to arsenian ullmannite (Bayliss, 1977a), but no refinement occurred. The R_ω value 0.028 of the $P1$ model with 969 reflections is similar to the R_ω value 0.028 of the $Pa\bar{3}$ model with 969 reflections including all reflections that

Table 3. Positional parameters, isotropic temperature factors, and extinction parameter

Atom	Site occupancy	x	B
Co	Co 0.400 Fe 0.055 Ni 0.045	0.00	0.38(2) Å^2
S	S 1.00	0.3900(2)	0.46(3)
Extinction parameter		−0.000011(1)	

Table 4. Interatomic distances and angles

Atoms	Distance, this study	Distance, Elliott (1960)	Atoms	Angle
S−S	2.112 Å	2.214 Å	S− S −Co	103.5°
S−Co	2.327	2.315	Co− S −Co	114.7
			S−Co−S	93.9
			S−Co−S	86.1

are systematically absent. In addition, a refinement was attempted with the $P2_13$ model, which allows for anion ordering with only systematic absences of $h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd. The R_ω value 0.0202 of the $P2_13$ model with 108 reflections is similar to the value 0.0211 of the $Pa\bar{3}$ model with 108 reflections.

Discussion

All the atoms in the structure of cattierite occupy special positions on one of the three-fold axes. The data indicate that there has not been any small displacement of any atom from a three-fold axis, which would cause the symmetry to disappear. In addition no anion ordering within the cubic model was detected.

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