Zeitschrift für Kristallographie, Bd. 130, S. 231–233 (1969)

Refinement of the structure of stranskiite

By C. CALVO and K. Y. LEUNG

Department of Physics and Materials Science Unit, McMaster University
Hamilton, Ontario

(Received 8 September 1967)

A number of recent structures containing tetrahedral AsO_4^{3-} have been reported. The average As—O bond distance has been found to be 1.69 Å in $Cu_3(AsO_4)_2$ (POULSON and CALVO, 1967), 1.70 Å in $Cu_2AsO_4(OH)_3$ (GHOSE, FEHLMANN and SUNDARALINGHAM, 1965),

Table 1. *Atomic parameters in stranskiite*
[Estimates standard deviations are in parentheses and the values of PLIETH and SÄNGER are in brackets.]

	x	y	z	$B(T)$
Cu	1/2	1/2	1/2	1.28(08)
	[1/2	1/2	1/2	1.6]
Zn	0.2285(7)	0.1858(3)	0.7347(7)	1.36(6)
	[0.2332	0.1855	0.7420	1.6]
As	0.8652(5)	0.2750(2)	0.1384(7)	0.90(5)
	[0.8607	0.2785	0.1360	1.6]
O(1)	0.1774(28)	0.3353(19)	0.1255(28)	0.54(22)
	[0.180	0.342	0.123	1.6]
O(2)	0.9097(35)	0.1217(20)	0.3352(40)	1.52(26)
	[0.892	0.116	0.339	1.6]
O(3)	0.6455(32)	0.1573(18)	0.8019(40)	1.09(28)
	[0.892	0.116	0.339	1.6]
O(4)	0.7280(28)	0.5055(19)	0.2920(33)	1.18(26)
	[0.748	0.527	0.283	1.6]

The scale constant applied to F_o is 1.006 for the $0kl$-type reflections and 1.015 for the $hk0$-type data. The weights were assigned as $\omega = [1.1 - 0.095F_o + + 0.021F_o^2]^{-1/2}$. Those weights whose calculated value would be negative with this function were set to zero.

Table 2. *Bond lengths and angles in stranskiite*

[Estimated standard deviations are in parentheses. The values of PLIETH and SÄNGER are in brackets]

CuO_4 group						
2 Cu—O(1)	2.014(13) Å	[2.01(4) Å]	O(1)—Cu—O(4)	88.7(5)°		
2 Cu—O(4)	1.893(15)	[2.07(5)]				
ZnO_5 group						
Zn—O(1)	2.064(11) Å	[2.03(4) Å]	O(1)—Zn—O(2)	124.1(7)°	O(2)—Zn—O(2)	81.2(7)°
—O(2)	2.030(13)	[2.09(4)]	—O($\bar{2}$)	96.5(7)	—O(3)	124.2(8)
—O($\bar{2}$)	2.097(17)	[2.02(4)]	—O(3)	110.9(6)	—O(4)	84.2(6)
—O(3)	2.022(16)	[2.10(4)]	—O($\bar{4}$)	89.5(6)	O(2)—Zn—O(3)	102.1(6)
—O($\bar{4}$)	2.171(14)	[2.00(5)]	O(3)—Zn—O($\bar{4}$)	88.2(6)	—O(4)	165.2(6)
AsO_4 group						
As—O(1)	1.700(15) Å	[1.75(4) Å]	O(1)—As—O(2)	111.6(8)°	O(2)—As—O(3)	111.3(8)°
—O(2)	1.667(12)	[1.75(4)]	—O(3)	106.9(9)	—O(4)	108.7(9)
—O(3)	1.627(14)	[1.78(4)]	—O(4)	109.6(7)	O(3)—As—O(4)	108.7(7)
—O(4)	1.716(15)	[1.74(5)]				

1.68 Å in $Cu_2(AsO_4)(OH) \cdot 3H_2O$ (FINNEY, 1966) and 1.75 Å in stranskiite (PLIETH and SÄNGER, 1967). Since this latter result is at variance with the others, it was felt that further refinement of the reported data would be worthwhile. The data reported by PLIETH and SÄNGER (1967) were refined using a full-matrix least-squares program prepared for the IBM 7040 by J. S. STEPHENS. Atomic form factors were taken from the International Tables (1962) and corrected for the effects of dispersion under the assumption that the data were taken with CuKα radiation. Reflections were weighted by ω so that $\omega \Delta F^2$ would be independent of F and the six unobserved reflections were given zero weight. Each layer line was given separate scale constants and the individual atomic thermal parameters were determined. The value of R dropped from 0.11 as reported by PLIETH and SÄNGER (1967) to 0.063 whereas the value of R_2 is 0.040. The values of the new atomic parameters are compared to the previous values in Table 1 and the new bond distances and angles are shown in Table 2. The average As—O value is 1.678 Å with a range extending from 1.627 Å to 1.716 Å and all the tetrahedral bond angles lie within 2.6° of the ideal value. As have been found in $Cu_3(AsO_4)_2$ the shortest As—O bond distance involves that oxygen atom with the lowest coordination number. The Cu^{2+} lying on a center of symmetry is roughly in a square-planar configuration with two pairs of additional Cu—O interactions at about 3.2 Å. The Zn^{2+} are in distorted trigonal bipyramids with average Zn—O bond distance of 2.08 Å. The estimated errors, as determined from the least-squares refinement, are likely to be somewhat optimistic in light of the fact that a limited amount of data, 146 reflections, were used.

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