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Crystal structure of paradamite

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Abstract

The crystal structure of paradamite, $Zn_2(AsO_4)(OH)$, the triclinic form of adamite, has been solved by direct methods and refined by full-matrix least-squares to R = 0.049. This study introduces anisotropic temperature factors for the As and Zn atoms in the crystal structure refinement of paradamite.

Paradamite was originally investigated by Switzer (1956), who described the mineral as a triclinic dimorphous form of adamite. Finney (1966) emphasized the isostructural relationship of paradamite with tarbuttite, which was confirmed in the present study. The structure of tarbuttite was described by Cocco *et al.* (1966). Most recently, the crystal structures of adamite and paradamite have been refined by Kato and Miúra (1977).

Kato and Miúra's (1977) least-squares refinement of paradamite concluded with a final residual factor of 0.102. The findings of this study confirm their structure and in addition contribute anisotropic temperature factors for As and Zn. A brief synopsis of the crystal structure analysis of paradamite follows.

The approximate structure of paradamite was determined independently by the symbolic addition method. This approximate structure was refined using the least-squares method with anisotropic temperature factors for the atoms As and Zn and isotropic temperature factors for the oxygen atoms. Corrections for anomalous dispersion of the As and Zn atoms and atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1968). After three cycles of least-squares refinement the final *R* index was 0.049. The observed and calculated structure factors are given in Table 1.[2] The final atomic coordinates and thermal parameters are given in Table 2. The interatomic distances and the bond angles are given in Tables 3 and 4.

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Table 2. Atomic coordinates and thermal (×100) parameters (A^{-2}). Anisotropic and isotropic temperature coefficients by Cruickshank's formula (1956)

Atom	X	Y	Z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	.7499(3)	.5008(3)	.3925(3)	1.95(14)	2.13(13)	2.19(14)	0.04(9)	0.05(8)	0.55(8)
Zn(2)	.2647(3)	.1869(3)	.0214(3)	1.64(13)	1.59(13)	2.25(13)	0.11(8)	-0.05(7)	0.41(8)
As	.7518(3)	.2760(3)	.8316(3)	1.15(12)	1.39(13)	2.17(13)	0.10(8)	0.02(6)	0.42(8)
O(1)	.032(2)	.140(2)	.764(2)	2.3(3)					
O(2)	.612(2)	.125(2)	.942(2)	2.4(3)					
O(3)	.614(2)	.333(2)	581(2)	2.3(3)					
O(4)	.253(2)	.498(2)	.956(2)	2.0(3)					
O(5)	.112(2)	.302(2)	.353(2)	1.7(2)					

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Table 3. Interatomic distances (A) in the oxygen polyhedra of paradamite

As - O(1)	1.689(11)	O(1) - O(3)	2.778(16)
As - O(2)	1.676(15)	O(1) - O(4′)	2.765(14)
As - O(3)	1.680(12)	O(2) - O(3)	2.739(20)
As - O(4′)	1.683(11)	O(2) - O(4′)	2.741(19)
O(1) - O(2)	2.720(18)	O(3) - O(4′)	2.736(16)
Zn(1) - O(3)*	2.015(15)	Zn(2) - O(1)*	1.963(11)
Zn(1) - O(3′)	2.147(11)	Zn(2) - O(2)*	2.015(12)
Zn(1) - O(4′)*	1.962(12)	Zn(2) - O(2′)	2.105(13)
Zn(1) - O(5)	2.211(10)	Zn(2) - O(4)	2.190(14)
Zn(1) - O(5′)*	1.980(11)	Zn(2) - O(5)*	2.000(10)
O(3) - O(3′) †	2.660(18)	O(1) - O(2)*	3.109(17)
O(3) - O(4′)*	2.872(16)	O(1) - O(2′)	2.720(18)
O(3) - O(5)	3.179(16)	O(1) - O(4)	2.935(18)
O(3) - O(5′)*	3.152(19)	O(1) - O(5)*	3.281(15)
O(3′) - O(4′)	2.736(16)	O(2) - O(2′)	2.550(20)
O(3′) - O(5′)	3.165(17)	O(2) - O(4)	2.859(16)
O(4′) - O(5)	2.979(16)	O(2) - O(5)*	3.588(18)
O(4′) - O(5′)*	3.081(19)	O(2) - O(5)	3.056(14)
O(5) - O(5′)	2.817(14)	O(4) - O(5)	3.081(19)

* Distances in the basal plane
† Shared edge

Table 4. Bond angles and their standard deviations in degrees

O(1) - As - O(2)	107.8(6)	O(2) - As - O(3)	109.4(6)
O(1) - - O(3)	111.1(6)	O(2) - - O(4′)	109.4(6)
O(1) - - O(4′)	110.2(5)	O(3) - - O(4′)	108.9(6)
O(3) - Zn(1) - O(3′)	79.4(5)	O(1) - Zn(2) - O(2)	121.5(5)
O(3) - - O(4′)	132.6(5)	O(1) - - O(2′)	99.6(5)
O(3) - - O(5)	96.9(5)	O(1) - - O(4)	89.8(5)
O(3) - - O(5′)	104.2(5)	O(1) - - O(5)	111.8(5)
O(3′) - - O(4′)	88.6(5)	O(2) - - O(2′)	76.4(5)
O(3′) - - O(5)	174.4(4)	O(2) - - O(4)	85.6(5)
O(3′) - - O(5′)	100.7(4)	O(2) - - O(5)	126.7(4)
O(4′) - - O(5)	90.9(4)	O(2′) - - O(4)	162.0(5)
O(4′) - - O(5′)	123.1(6)	O(2′) - - O(5)	96.2(5)
O(5) - - O(5)	84.3(4)	O(4) - - O(5)	94.6(5)

The hydrogen atom's coordinates were not directly determined. By calculating the sum of the electrostatic valencies (charge of cation/coordination) in the sites of the oxygen atoms, the oxygen coordination with hydrogen was obtained. It was noted that the O(1) and O(5) had a sum of 1.65 and 1.20 respectively. It can be concluded that the hydrogen atom is bonded with the O(5) atom and is in partial coordination with the O(1) atom per half unit cell. Comparison of Cocco *et al.*'s (1966) and Kato and Miúra's (1977) atomic coordinates with the coordinates given in the present paper shows that our oxygen atom O(5) corresponds to their OH group.

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