

The crystal structure of sinhalite¹

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[Taken as read 11 March 1965]

Summary. The Ceylonese gemstone sinhalite, AlMgBO_4 , is isomorphous with olivine and chrysoberyl. Aluminium and magnesium are octahedrally coordinated and boron occupies slightly distorted tetrahedra. Because of size differences, the smaller Al ion can be assigned to the inversion symmetry sites, with Mg in mirror plane positions. Least-squares refinement based on single crystal X-ray data gave an accurate set of atomic coordinates with mean interatomic distances: Al-O 1.90, Mg-O 2.10, B-O 1.49 Å.

PRIOR to the work of Claringbull and Hey (1952), sinhalite was erroneously classified as olivine. Various physical measurements, together with chemical analysis, showed it to be a new mineral, AlMgBO_4 . Two subsequent publications describe the morphology of Ceylonese sinhalite (Payne, 1958) and a second occurrence of the mineral in Warren County, New York (Schaller and Hildebrand, 1955).

Sinhalite crystallizes in the orthorhombic system with a 9.878, b 5.675, c 4.328 Å, and $z = 4$ (Claringbull and Hey, 1952). The following space groups were suggested: $Pnma$, $P2_1ma$, and $Pm2a$. The cell dimensions and X-ray powder patterns are almost identical to those of chrysoberyl but the symmetry appears to differ; chrysoberyl and the isomorphous olivine belong to $Pnma$. The structure analysis reported in this paper resolves the ambiguity and provides an accurate description of the structure.

A brown Ceylonese specimen obtained from Mr. G. Bruce was used in the X-ray experiments. The optical spectrum of this crystal shows a broad, intense absorption near 1μ , similar to olivine and commonly attributed to divalent iron. Gravimetric measurements gave a specific gravity of 3.4944 ± 0.0006 , consistent with a chemical composition $\text{AlMg}_{0.95}\text{Fe}_{0.05}\text{BO}_4$.

Long-exposure Weissenberg photographs were taken about the three

¹ Supported by the U.S. Air Force, Aeronautical Systems Division, under Contract AF 33 (616)-8353, and by Advanced Research Projects Agency, Department of Defense, through Contract SD-90.

major axes to check the space group assignment. Systematic absences occur for $hk0$ reflections with h odd, and for $Ok\bar{l}$ reflections with $k+l$ odd, narrowing the choice to $Pnma$ or $Pn2_1a$. Satisfactory refinement of the structure was achieved assuming $Pnma$ to be correct.

The intensities of 473 $h0l$, $h1l$, and $hk0$ reflections were estimated visually from multiple-film Weissenberg photographs taken with filtered

TABLE I. Sinalite atomic coordinates and temperature factors

	x	y	z	B (\AA) ²
Al (i)	0	0	0	0.06
Mg (m)	0.2762	$\frac{1}{4}$	-0.0164	0.16
B	0.0884	$\frac{1}{4}$	0.4057	0.10
O ₁	0.0798	$\frac{1}{4}$	0.7418	0.25
O ₂	0.4450	$\frac{1}{4}$	0.2559	0.21
O ₃	0.1487	0.0410	0.2658	0.22

Mo- $K\alpha$ radiation. Beginning with the chrysoberyl coordinates (Farrell *et al.*, 1963), eight least-squares cycles reduced the R -factor from 0.41 to 0.11. Weak reflections having an intensity below the observational limit were omitted from the refinement. Scattering factors were taken from Vol. III of the 'International Tables for X-ray Crystallography'. The final atomic coordinates for sinalite (table I) changed by less than 0.002 \AA during the eighth least-squares cycle. Tables of the observed and calculated structure factors are available on request.

The bond lengths, oxygen-oxygen distances, and their standard deviations are given in table II. The BO_4 tetrahedra are somewhat irregular since B-O₂ is significantly larger than the other three distances. Other tetrahedral borates (Christ *et al.*, 1958, and Zachariasen, 1963) give mean B-O distances close to the value of 1.49 \AA found in sinalite.

Since their scattering factors are almost identical, the aluminium and magnesium distribution is inferred from size considerations. The mean metal-oxygen distances for the inversion and mirror plane octahedral sites are 1.90 and 2.10 \AA , respectively. Recent refinements of chrysoberyl (Farrell *et al.*, 1963) and forsterite (Gibbs *et al.*, 1963) report average bond lengths of 1.91 \AA for Al-O and 2.12 \AA for Mg-O. It seems reasonable, therefore, to assign Al to the inversion symmetry sites and Mg to the mirror plane positions, in a fully ordered configuration. The result is consistent with those obtained for lithiophilite (Geller and Durand, 1960) and for $\text{Al}_{2-x}(\text{Cr,Fe})_x\text{BeO}_4$ solid solutions (Newnham *et al.*, 1964). In all three substances, the larger of the octahedral cations selects the mirror plane position; ionic size, rather than valence, seems to be the

TABLE II. Bond lengths and oxygen distances in sinhalite. Shared edges are denoted by an asterisk (*)

Al octahedron		Mg octahedron		B tetrahedron	
Al-O ₁	1.967 Å (2)	Mg-O ₁	2.212 (1)	B-O ₁	1.458 (1)
Al-O ₂	1.850 (2)	Mg-O ₂	2.042 (1)	B-O ₂	1.580 (1)
Al-O ₃	1.880 (2)	Mg-O ₃	2.118 (2)	B-O ₃	1.459 (2)
O ₁ -O ₂	2.848 (2)	Mg-O ₃	2.041 (2)	O ₁ -O ₂	2.528 (1)
O ₁ -O ₂	2.545* (2)	O ₁ -O ₃	3.159 (2)	O ₁ -O ₃	2.475 (2)
O ₁ -O ₃	2.790 (2)	O ₁ -O ₃	2.651* (2)	O ₂ -O ₃	2.338* (2)
O ₁ -O ₃	2.651* (2)	O ₂ -O ₃	3.158 (2)	O ₃ -O ₃	2.372* (1)
O ₂ -O ₃	2.338* (2)	O ₂ -O ₃	2.843 (2)		
O ₂ -O ₃	2.908 (2)	O ₃ -O ₃	2.372* (1)		
		O ₃ -O ₃	3.303 (1)		
		O ₃ -O ₃	2.984 (2)		

Standard deviations

$\hat{\sigma}(\text{Al-O}) = 0.004 \text{ \AA}$

$\hat{\sigma}(\text{Mg-O}) = 0.005$

$\hat{\sigma}(\text{B-O}) = 0.009$

$\hat{\sigma}(\text{O-O}) = 0.006$

Average values

Al-O 1.899 Å

Mg-O 2.095

B-O 1.489

O-O

O-O (shared edges)

O-O (unshared edges)

2.732

2.483

2.898

TABLE III. Average bond lengths for octahedrally coordinated cations in minerals isostructural with olivine

Mineral	Formula	Inversion site	Mirror site
Chrysoberyl (Farrell <i>et al.</i> , 1963)	Al ₂ BeO ₄	1.89 Å	1.94 Å
Fayalite (Hanke, 1963)	Fe ₂ SiO ₄	2.16	2.19
Forsterite (Gibbs <i>et al.</i> , 1963)	Mg ₂ SiO ₄	2.10	2.14
Lithiophilite (Geller and Durand, 1960)	LiMnPO ₄	2.17	2.20
Olivine (Hanke and Zemann, 1963)	(Mg,Fe) ₂ SiO ₄	2.10	2.14
Sinhalite (this paper)	AlMgBO ₄	1.90	2.10

determining factor. As shown in table III, the mirror plane site is slightly larger than the inversion site, even when the two cations are identical.

Acknowledgements. We wish to thank Dr. R. Mykolajewycz, Mr. R. Mills, and Mr. E. Farrell for their assistance in the experimental work. The least-squares analyses were carried out at the M.I.T. Computation Center using the Busing-Levy OR FLS programme.

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[*Manuscript received 5 June 1964.*]
