

## BRIEF COMMUNICATIONS

## THE CRYSTAL STRUCTURE OF PYROSMALITE

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Pyrosmalite has been assigned to the layer silicates on the basis of morphology and physical features. The *c* parameter of pyrosmalite is a multiple of that of kaolinite-type minerals, but the *a* parameter places it in an entirely special position [1]. This makes the structure of some interest.

This rare silicate was first found in the USSR in 1964, in Central Kazakhstan [2]. M. M. Kayupova made available specimens of this. It proved impossible to select a good single crystal, so the x-ray patterns were of poor quality. The layer lines were recorded with a KFOR-4 camera. The cell parameters were found as  $a = 13.37$ ,  $c = 7.11 \text{ \AA}$ , with  $\bar{3}m$  diffraction symmetry; no systematic absences, no piezoelectric effect observed. The shortest translation in the (0001) plane was parallel to the twofold axis, so the most likely space group is  $P\bar{3}m1$  [3]. The unit cell contains two formula units of composition  $(\text{Mn, Fe})_8\text{Si}_6\text{O}_{15}(\text{OH, Cl})_{10}$ .

A characteristic feature is the prominent repeat of  $a/4 = 3.34 \text{ \AA}$  along the *x* axis; only isolated weak reflections with  $h, k \neq 4n$  are observed, so the structure of the pseudocell was first determined. This contains one Mn atom, roughly three O

atoms, and  $3/4$  Si. Patterson projections gave the Mn octahedron and the mean position of Si. The vertical Si-O distance is very close to that found in other layer silicates [4, 5], but the position of one O atom in the unit cell could not be determined. The structure factors were then calculated for structures with ABA and ABC packings; ABA gave much the better result ( $R = 0.21$ ). A start was then made on deducing the true structure; but then the abstracts from the Sixth International Crystallography Congress were published [6], which include a communication on pyrosmalite. However, this gave only an idealized form of the structure, so an attempt at refinement was made. The poor quality of the crystals set a natural limit to the refinement.

First the Japanese model [6] was tested. Only the projection of the tetrahedral net on 0001 is given, from which the coordinates of Si and O in the bases of the tetrahedra were found. The coordinates I used for the O atoms in the Mn octahedron correspond to an undistorted octahedral layer with  $a = 3.34 \text{ \AA}$  in hexagonal packing. The coordinates of the O atoms were deduced for close pack-

TABLE 1. Coordinates of the Basal Atoms in Pyrosmalite

Atoms	Group of equivalent atoms	Found			Calculated	
		<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>
Mn <sub>1</sub>	1 <i>a</i>	0	0	0	0	0
Mn <sub>2</sub>	6 <i>g</i>	0.250	0.000	0	0.250	0.000
Mn <sub>3</sub>	6 <i>i</i>	0.250	0.750	0	0.250	0.750
Mn <sub>4</sub>	3 <i>l</i>	0.500	0.000	0	0.500	0.000
Si	12 <i>j</i>	0.097	0.430	0.392	0.111	0.444
Cl	2 <i>d</i>	0.333	0.667	0.150	0.333	0.667
OH <sub>1</sub>	6 <i>i</i>	0.083	0.917	0.155	0.083	0.917
OH <sub>2</sub>	6 <i>i</i>	0.833	0.167	0.155	0.833	0.167
OH <sub>3</sub>	6 <i>i</i>	0.583	0.417	0.155	0.583	0.417
O <sub>1</sub>	12 <i>j</i>	0.083	0.417	0.155	0.083	0.417
O <sub>2</sub>	6 <i>h</i>	0.354	0.000	0.500	0.333	0.000
O <sub>3</sub>	6 <i>i</i>	0.208	0.792	0.465	0.222	0.778
O <sub>4</sub>	6 <i>i</i>	0.431	0.569	0.465	0.444	0.556

TABLE 2. Structure Factors for Pyrosmalite

$hkl$	$F_O$	$F_C$	$hkl$	$F_O$	$F_C$	$hkl$	$F_O$	$F_C$	$hkl$	$F_O$	$F_C$
10 $\bar{1}$ 0	44.9	52.1	48 $\bar{1}$ 20	54.9	59.3	04 $\bar{4}$ 1	459.0	417.0	04 $\bar{4}$ 6	49.2	69.8
20 $\bar{2}$ 0	31.9	24.2	88 $\bar{1}$ 60	63.9	63.1	04 $\bar{4}$ 1	67.9	113.0	08 $\bar{8}$ 0	49.2	71.5
40 $\bar{4}$ 0	134.7	135.5	0001	303.0	262.0	04 $\bar{4}$ 2	278.5	272.0	08 $\bar{8}$ 1	155.5	178.7
80 $\bar{8}$ 0	85.8	139.3	0002	351.5	355.0	04 $\bar{4}$ 2	230.5	180.0	08 $\bar{8}$ 2	110.2	102.2
12.0. $\bar{1}$ 2.0	101.8	91.4	0003	120.5	75.0	04 $\bar{4}$ 3	220.0	274.0	08 $\bar{8}$ 2	120.5	115.2
11 $\bar{2}$ 0	51.9	55.3	0004	49.2	87.5	04 $\bar{4}$ 3	163.4	160.0	08 $\bar{8}$ 3	49.2	66.9
12 $\bar{3}$ 0	32.9	29.6	0005	184.0	149.5	04 $\bar{4}$ 4	155.5	128.0	08 $\bar{8}$ 3	129.9	129.0
2240	68.8	49.7	0006	110.2	96.8	04 $\bar{4}$ 4	196.8	222.0	08 $\bar{8}$ 4	67.9	111.5
44 $\bar{8}$ 0	366.6	338.0	0440	139.3	130.0	04 $\bar{4}$ 5	139.2	132.8			

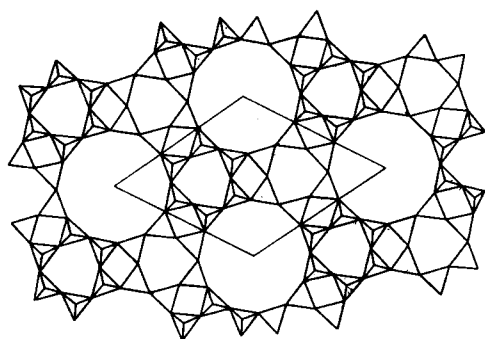


Fig. 1. Tetrahedral net in pyrosmalite.

ing with allowance for the observed mean inter-atomic distances in the pseudocell.

The agreement between the calculated and observed structure factors improved for the  $0kl$  reflections but deteriorated for the  $hk0$  ones, which thus indicated the direction of distortion: the atoms are displaced from the positions indicated by the Japanese model towards those for ABA packing. The structure factors were calculated for several possible positions. Table 1 gives the values chosen for the coordinates, and also those indicated by the Japanese model. The notation for the groups of equivalent atoms is as in [7]. Table 2 gives  $F_C$  and  $F_O$ ,  $R_{hk0} = 0.134$ ,  $R_{0kl} = 0.150$ ,  $\sin \vartheta/\lambda \leq 0.6$ ,  $B_m \sim 5.0$ . The figure shows the tetrahedral net, whose characteristic feature is a new twelve-sided

ring formed by alternate four- and six-sided rings. This type of ring occurs also in karpinskite [8]. The six-sided rings are distorted to ditrigons, as for other layer silicates [4, 5]. The temperature factor is large, and remained so at all stages of the analysis, which is evidently due to the openness of the structure.

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