

Refinement of the Crystal Structure of Mullite

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42 parameters of the crystal structure of 1.83/1-mullite have been refined by the least-squares method. The intensities of 1817 independent diffractions have been estimated visually, the final R -factor is 0.113 (0.080). The results of the refinement confirmed the scheme of the mullite structure previously determined [1, 2, 4, 5], especially the distribution of the electron density in the neighborhood of the oxygen position, linking the Si and Al tetrahedra in the direction perpendicular to the c -axis, as suggested in [2]. The interatomic distances and bond angles as well as the review of the apparent thermal vibrations of the individual atoms are also given.

The problem of the statistical model of the crystal structure of mullite $\text{Al}[\text{Si}_{2-x}\text{Al}_x\text{O}_{(11-x)/2}]$ has been basically solved in two, mutually independent works of Ďurovič [1] and Sadanaga, Tokonami and Takéuchi [2]. In both works mullite was found^b to have the space group $Pbam$, lattice constants $a \doteq 7.5$, $b \doteq 7.7$, $c \doteq 2.9$ Å (the exact values depend on the chemical composition and, probably, on the thermal history of the given mullite) and the basic scheme of the mullite structure was determined as follows:

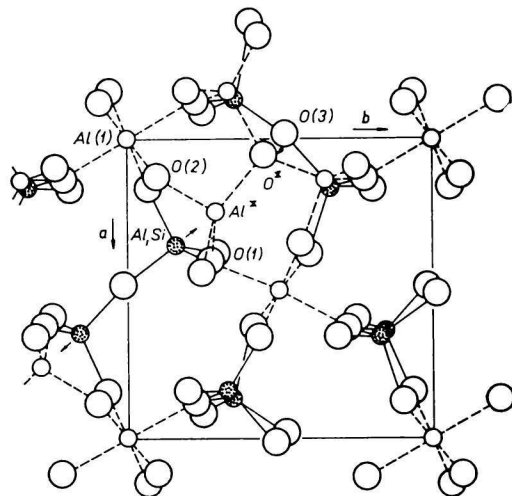


Fig. 1. The scheme of the mullite structure as derived from that of sillimanite.

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^b In this paper we shall deal exclusively with the statistical model of the mullite structure without respecting possible substructures with particular occupation of the individual atomic positions.

The mullite structure can be „derived“ from that of sillimanite $\text{Al}[\text{SiAlO}_5]$ [3] by substituting some Al atoms for the tetrahedrally coordinated Si atoms. The preservation of electro neutrality demands the removal of a corresponding amount of the O atoms from the positions O(3), linking the Si and Al tetrahedra (Fig. 1). Since the adjoining tetrahedra would then remain open, the corresponding central atoms are transferred from their original Al,Si positions into new, in sillimanite vacant, Al* positions. As a result, the O(3) atoms that close the coordination tetrahedra around these new Al* sites, increase their coordination number from two to three. It must be kept in mind, however, that this „derivation“ of the mullite structure from that of sillimanite serves only for a better understanding of the mullite structure and has nothing in common with the particular processes of the crystallization of mullite from melt or, of the mullitization of sillimanite, caused *e.g.* by elevated temperatures.

Although both papers [1] and [2] agree in the basic principles of the mullite structure, they are not unified in the interpretation of the Al* and O(3) positions (Fig. 1). Paper [1] admits the occupation of the Al* position by both Al and Si atoms, paper [2] only by Al atoms. According to the paper [1], the O(3) position is occupied by the pair of O atoms around the symmetry center at $(0\frac{1}{2}\frac{1}{2})$ (plus other equipoints), in paper [2] one can find more complicated interpretation: the O(3) atoms with twofold coordination remain in the symmetry centers, whereas those O(3) atoms with threefold coordination are shifted into the O* positions. Since the results of both papers are based on the copper-radiation diffractions, the resolution power is insufficient to decide about the correct interpretation.

In an effort to clear the above inconsistencies, a revision of the statistical model of the mullite structure has been undertaken. In the meantime, however, *Burnham* [4, 5] published his structural study of mullite (based on molybdenum-radiation diffractions), that confirmed the Japanese [2] interpretation of the O(3) position but left some ambiguity concerning the occupation of the Al* site.

Burnham used in his work 792 (564 non-zero) counter-measured diffractions and the chemical composition of his mullite was $1.91\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$. In our case 1817 (1276 non-zero) Mo-radiation diffractions have been used and the intensities of the individual diffractions were estimated visually. The specimen had the composition $1.83\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$. It was, therefore, decided to publish the results of our work and to compare them with those of *Burnham*.

Experimental

A single crystal of an arc-fused mullite (chemical composition 24.32% SiO_2 , 74.68% Al_2O_3 , 0.15% TiO_2 , 0.85% Fe_2O_3 ; this, if Fe and Ti are assumed in the sixfold coordination, corresponds to the 1.83/1-mullite) in the shape of a regular rectangular prism of the dimensions $0.4 \times 0.4 \times 1$ mm, was selected for this study. The equi-inclination *Weissenberg* method, multiple-film technique and zirconium-filtered molybdenum radiation was used. The diffraction patterns of 6 levels ($hk0-hk5$) were obtained; the value of $(\sin \theta/\lambda)_{\text{max}}$ reached almost the theoretical value of 1.41 \AA^{-1} . For each level a special intensity scale was prepared and developed simultaneously with the films. The intensities of the individual diffractions were estimated visually (all equivalent diffractions on all three films for each level were measured), brought to the intensity scale of the first film

and their standard deviations were estimated. The non-observable diffractions were assigned the values of $I_{\min}/3$ as well as the relative standard deviation of 100%. The intensities of the strongest diffractions were measured by the micro-densitometer from the integrated *Weissenberg* films. The data from different levels were then approximately brought to the absolute scale using the model of the mullite structure from the previous paper [1] and corrected for the *Lorenz* and polarization factors. A Fortran data reduction programs *DTRDA* and *DTRDB*, written by *Burnham* [6] were used for this purpose, the absorption correction being neglected ($\mu R \approx 0.2$). This calculation as well as others, were carried out on an IBM 7044 computer.

The lattice constants were determined from the silicon-calibrated diffractometer powder patterns with following results

$$a = 7.566(5), \quad b = 7.682(5), \quad c = 2.884(2) \text{ \AA}.$$

No density determination was made, since all previous papers [1, 2, 4, 5] found six Al + Si atoms plus the corresponding number of O atoms in the unit cell.

Refinement of the structure

The first electron-density calculation, using the signs of the structure factors calculated from the parameters published in [1], already showed that the interpretation of the Japanese authors [2] concerning the O(3) position, is correct. A Fortran full-matrix least-squares program *ORFLS*, written by *Busing, Martin and Levy* [7], the atomic scattering factors, published by *Cromer and Waber* [8] were then used for the refinement. Each observation was assigned a weight inversely proportional to the square of its standard deviation. The refinement was accomplished in 22 cycles with following strategy: in cycles 1–3 the scale factors for individual levels were refined, the atomic coordinates and an overall temperature factor coefficient, in cycles 4–5 the scale factors were refined

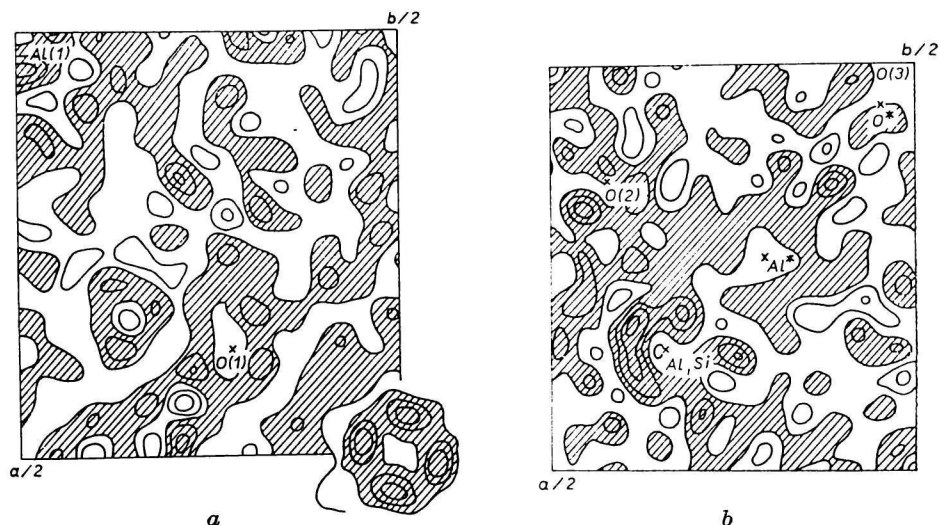


Fig. 2. Sections at $z = 0$ (a) and $z = 1/2$ (b) through the final residual electron-density function of mullite. Contour interval $1 e/\text{\AA}^3$. Negative areas shadowed.

Table 1

Observed and calculated structure factors for 1.83/1-mullite.
In the columns from left to right the values of h , F_o and F_c are listed. Undetectable diffractions are marked by n

	h 0 0	17 2.3 -2.4	2 11.9 11.1	13 2.9 -2.9	9 5.0 -4.8
		18 n 0.4 -0.4	3 32.1 33.4	14 n 0.4 0.3	10 n 0.4 0.1
2	7.7 6.8	19 3.2 3.1	4 7.2 -7.8	15 2.6 2.5	11 4.6 4.3
4	31.3 -29.8	20 n 0.3 0.3	5 14.1 14.4	16 5.6 5.1	12 n 0.4 1.3
6	34.0 35.1		6 7.3 -7.3	17 n 0.3 0.8	13 2.4 2.4
8	31.2 30.4	h 4 0	7 14.2 -13.3	18 0.7 1.3	14 3.8 3.7
10	12.7 -12.4		8 8.1 8.2		15 2.8 -2.7
12	4.0 4.0	0 12.1 12.4	9 8.2 8.2	h 11 0	
14	13.7 12.1	1 9.0 -8.9	10 n 0.4 0.4	1 5.0 5.2	h 15 0
16 n	0.4 0.8	2 23.2 23.4	11 11.5 11.3	2 5.2 -5.2	1 5.7 5.2
18	1.0 -1.0	3 n 0.2 1.0	12 4.9 -4.9	3 5.9 6.0	2 5.6 4.3
20	5.1 4.5	4 26.6 26.7	13 n 0.4 -1.1	4 3.7 4.1	3 n 0.4 -1.6
	h 1 0	5 4.2 -2.6	14 n 0.4 1.6	5 5.9 5.6	4 n 0.4 -1.0
1	19.4 18.6	6 n 0.3 0.3	15 0.8 -1.6	6 n 0.4 1.6	5 3.6 3.3
2	38.7 39.2	7 9.6 9.8	16 3.3 3.2	7 3.6 3.4	6 2.4 -2.4
3	5.7 6.6	8 8.8 8.8	17 6.3 5.7	8 2.4 -2.6	7 7.0 6.7
4	9.7 -10.0	9 0.6 -0.6	18 2.1 -1.9	9 0.7 1.7	8 2.9 2.7
5	7.3 7.0	10 14.7 14.7	19 n 0.3 0.9	10 n 0.4 0.3	9 0.9 -1.6
6	19.8 -19.9	11 3.7 -4.1		11 n 0.4 1.4	10 n 0.4 0.7
7	8.9 9.6	12 2.9 3.0	h 8 0	12 2.7 2.6	11 n 0.4 0.1
8	13.5 13.2	13 n 0.4 0.7	0 2.0 1.7	13 3.2 3.0	12 1.7 -1.6
9	10.8 11.1	14 n 0.4 -1.1	1 17.1 -17.3	14 2.7 -2.8	13 5.0 4.8
10	2.3 2.3	15 2.8 3.0	2 14.9 15.1	15 3.2 2.3	14 n 0.3 -0.2
11	5.7 5.9	16 6.6 5.7	3 4.0 -4.0	16 n 0.3 -0.1	15 1.1 1.6
12	5.3 -5.1	17 2.6 -2.5	4 12.7 13.0	17 n 0.3 0.5	
13 n	0.4 1.0	18 3.7 3.7	5 14.3 13.3	18 0.9 1.6	h 16 0
14 n	0.4 0.1	19 n 0.3 -1.2	6 4.4 5.0		0 3.4 -2.7
15	4.4 4.1	20 n 0.3 -0.8	7 n 0.4 1.1	h 12 0	1 n 0.4 0.8
16	3.8 3.2		8 5.3 5.1	0 12.9 12.1	2 5.3 5.1
17	2.2 2.7	h 5 0	9 8.6 -8.6	1 3.4 3.5	3 n 0.4 -1.6
18	2.2 -2.3	1 8.8 8.3	10 11.5 11.0	2 5.1 5.1	4 9.3 8.6
19 n	0.3 0.1	2 23.3 -23.7	11 4.9 4.6	3 n 0.4 -0.7	5 n 0.4 0.2
20 n	0.3 0.3	3 17.7 17.8	12 2.5 2.9	4 n 0.4 -1.6	6 n 0.4 0.4
	h 2 0	4 12.9 13.4	13 0.9 1.9	5 4.2 -4.0	7 n 0.4 0.5
0 n	0.1 0.2	5 6.4 5.9	14 n 0.4 0.6	6 12.3 11.5	8 n 0.4 -0.8
1	26.8 -29.9	6 7.9 7.9	15 2.9 -2.8	7 3.2 3.0	9 n 0.4 0.7
2	32.7 33.7	7 4.2 4.5	16 3.6 3.3	8 5.7 5.4	10 5.5 5.1
3	11.7 -12.8	8 14.6 -16.1	17 n 0.3 0.5	9 3.1 3.0	11 n 0.3 -1.1
4	31.3 30.9	9 8.0 8.2	18 2.9 2.7	10 n 0.4 -0.2	12 2.8 2.9
5	31.6 31.6	10 n 0.4 0.6	19 1.5 1.7	11 4.9 -4.1	13 n 0.2 1.0
6	12.4 13.7	11 6.8 7.1		12 4.5 3.8	
7	5.7 -6.3	12 11.0 10.5	h 9 0	13 n 0.4 0.1	h 17 0
8 n	0.3 1.4	13 n 0.4 -1.3	1 19.0 19.2	14 5.4 5.3	1 2.3 2.3
9	12.8 -12.4	14 4.6 -4.2	2 9.0 9.7	15 4.4 3.8	2 6.1 -5.9
10	12.1 11.4	15 3.9 3.1	3 5.3 -6.0	16 n 0.3 0.8	3 n 0.4 1.5
11	7.9 8.1	16 3.7 -3.7	4 4.1 -4.4	17 n 0.2 -0.3	4 3.2 2.9
12	6.0 5.9	17 3.2 3.3	5 n 0.3 1.5		5 1.6 2.3
13	4.0 4.2	18 4.7 4.3	6 5.2 -5.1	h 13 0	6 4.7 4.3
14	2.6 3.1	19 n 0.3 1.2	7 16.3 15.5	1 2.8 3.0	7 1.9 1.7
15	7.8 -7.0	20 n 0.2 0.9	8 3.1 3.7	2 n 0.4 0.9	8 3.6 -3.6
16	2.6 2.4		9 1.9 1.9	3 7.5 7.0	9 1.9 1.9
17 n	0.4 0.5	h 6 0	10 1.4 2.5	4 n 0.4 -1.5	10 n 0.3 -1.4
18	2.8 2.5	0 21.6 21.7	11 1.6 -2.2	5 1.8 1.8	11 1.6 1.7
19	3.6 3.5	1 13.9 15.4	12 3.7 -3.8	6 2.9 2.1	12 3.0 2.9
20 n	0.3 1.4	2 10.3 9.6	13 3.3 3.6	7 n 0.4 0.0	
	h 3 0	3 4.5 5.1	14 0.8 1.1	8 n 0.4 1.6	h 18 0
1	21.6 22.3	4 8.4 9.2	15 4.3 4.0	9 6.6 5.8	0 6.0 5.7
2	33.6 -32.3	5 3.4 -3.7	16 n 0.4 1.4	10 1.9 -1.9	1 n 0.4 0.7
3	10.3 -9.6	6 19.9 19.7	17 n 0.3 -0.2	11 2.8 2.5	2 1.9 2.6
4	0.8 0.9	7 4.2 -4.4	18 n 0.3 -0.7	12 n 0.4 -1.6	3 0.7 1.3
5	14.2 15.1	8 7.6 7.9	19 1.2 1.8	13 n 0.4 -1.3	4 n 0.4 0.3
6	12.5 13.1	9 7.6 7.5		14 2.8 2.8	5 2.4 -1.3
7	22.9 22.2	10 n 0.4 -0.7	h 10 0	15 n 0.3 1.7	6 3.0 3.3
8	4.2 -4.6	11 n 0.4 -0.1	0 1.6 2.0	16 n 0.2 -0.7	7 n 0.3 0.5
9 n	0.3 -1.1	12 9.9 8.7	1 13.4 12.7		8 2.3 2.7
10	4.6 -4.4	13 2.6 -2.5	2 7.8 8.3	h 14 0	9 n 0.3 0.7
11 n	0.4 -0.7	14 6.9 6.3	3 5.9 6.1	0 11.5 10.6	10 n 0.3 0.6
12	0.9 1.6	15 n 0.4 -0.6	4 16.1 14.8	1 6.6 -6.2	11 n 0.2 0.1
13	12.7 12.4	16 n 0.4 -1.2	5 11.7 -11.0	2 2.1 2.9	
14	3.9 3.6	17 n 0.4 1.5	6 n 0.4 -0.3	3 n 0.4 -1.3	h 19 0
15 n	0.4 1.2	18 n 0.3 1.1	7 n 0.4 -1.0	4 n 0.4 0.7	1 n 0.3 -0.5
16 n	0.4 -1.5	19 n 0.3 -0.2	8 7.5 6.6	5 5.2 5.1	2 n 0.3 1.2
	h 7 0	20 3.3 3.8	9 9.7 8.2	6 5.9 5.5	3 4.4 4.4
1	8.5 -8.7		10 9.1 8.5	7 0.8 -1.4	4 n 0.3 0.0
			11 1.0 -1.8	8 7.1 6.7	
			12 n 0.4 0.3		

Table 1 (Continued)

5	1.7	1.7	16	0.7	-0.3	0	4.4	-3.9	10	1.9	-2.8	4	1.8	2.6									
6	n	0.3	-0.9	17	n	0.3	0.6	1	11	5.8	5.4	5	1.4	3.2									
7	n	0.3	-0.6	18	n	0.3	1.5	2	12	6.7	6.1	6	1.7	2.1									
8	n	0.3	-0.2	19	3.1	-3.3	3	5.8	5.8	13	n	0.4	-0.5	7	8.4	7.9							
9	2.2	2.5	20	2.0	2.5	4	19.3	18.8	14	n	0.3	-0.5	8	1.9	-2.8								
h 20 0			h 3 1			5	6.3	-6.2	15	1.8	2.5	9	2.3	2.8									
0	3.1	2.8	1	1.3	-1.8	6	n	0.3	0.3	16	1.9	-2.6	10	n	0.4	-0.6							
1	n	0.3	-1.0	2	n	0.2	-0.4	7	n	0.3	-1.0	11	1.2	1.7									
2	1.1	1.8	3	48.7	50.1	8	2.3	2.4	8	2.3	2.4	12	3.5	3.3									
3	n	0.3	-0.4	4	n	0.2	-0.1	9	n	0.3	-0.6	13	2.1	3.1									
4	1.9	2.5	5	16.8	16.8	10	11.6	9.6	h 10 1			14	n	0.3	-0.7								
5	1.7	2.0	6	2.2	2.2	11	2.9	3.1	0	15.5	15.8	15	1.8	1.8									
6	1.7	2.0	7	6.6	-8.2	12	1.2	1.6	1	5.5	-6.0	16	n	0.2	-0.2								
7	n	0.2	-0.9	8	4.3	4.2	13	n	0.4	-1.1	2	5.0	5.3	h 14 1									
h 21 0			9	13.3	12.9	14	n	0.4	0.6	3	n	0.3	0.2	0	2.3	2.2							
1	1.3	1.4	10	2.3	-2.4	15	3.9	4.1	5	5.4	5.7	1	8.2	7.3									
2	1.1	1.6	11	14.4	14.6	16	n	0.3	0.7	6	14.5	13.2	2	3.1	4.6								
3	n	0.2	0.9	12	n	0.3	-1.1	17	n	0.3	1.5	7	3.5	-3.2	3	3.4	3.3						
4	1.0	-1.2	13	3.5	-3.4	18	n	0.3	1.5	8	4.7	4.5	4	0.9	2.4								
h 0 1			14	n	0.4	0.3	19	n	0.2	0.8	9	3.6	-4.0	5	5.8	-5.3							
2	28.4	29.0	15	1.9	2.4	16	n	0.4	1.4	10	3.0	-3.3	6	0.8	2.1								
4	27.0	25.6	16	n	0.6	6.1	17	6.6	6.1	11	6.3	5.2	7	n	0.4	-0.7							
6	7.2	-7.0	17	6.6	6.1	18	1.0	-1.3	18	2.3	2.8	8	2.5	2.4									
8	1.7	2.1	18	1.0	-1.3	19	n	0.3	0.9	13	n	0.4	0.9	9	5.5	5.1							
10	21.0	23.8	19	n	0.3	0.9	20	n	0.2	-0.2	4	5.8	6.1	10	4.4	3.5							
12	n	0.3	-0.5	0	40.1	41.3	1	18.3	18.8	5	10.1	10.9	11	n	0.3	-1.8							
14	4.0	-4.2	1	9.1	-8.1	2	13.9	-13.5	2	2.0	-0.8	16	n	0.3	0.4								
16	7.9	7.1	2	8.1	7.9	3	2.0	-0.8	4	5.8	6.1	17	n	0.2	0.7								
18	4.3	4.1	3	11.8	-12.1	4	5.8	6.1	5	10.1	10.9	18	n	0.2	0.2								
20	3.1	-3.0	4	14.5	-14.7	5	10.1	10.9	6	9.1	9.6	19	n	0.2	0.7								
h 1 1			5	14.1	13.4	6	9.1	9.6	7	18.0	19.3	20	n	0.1	-0.6								
1	26.4	27.7	6	20.8	20.1	7	18.0	19.3	8	5.6	-5.7	h 7 1			1	18.3	18.8						
2	8.2	7.4	7	4.1	-4.2	8	5.6	-5.7	9	n	0.3	-1.1	2	13.9	-13.5								
3	18.9	19.0	8	13.6	15.4	9	n	0.3	-1.1	10	n	0.3	-1.7	3	2.0	-0.8							
4	8.0	7.8	9	4.5	-4.8	10	n	0.3	-1.7	11	1.3	2.0	4	5.8	6.1								
5	17.1	17.0	10	0.9	-2.0	11	1.3	2.0	12	3.6	3.4	5	10.1	10.9									
6	n	0.2	0.0	11	1.0	2.1	12	3.6	3.4	13	10.7	9.4	6	4.0	-4.1								
7	15.2	14.4	12	n	0.3	1.4	13	10.7	9.4	14	n	0.4	-0.3	7	4.0	-4.1							
8	10.9	-11.1	13	2.9	2.8	14	n	0.4	-0.3	15	3.2	3.4	8	4.7	4.5								
9	5.6	5.8	14	8.2	7.2	15	3.2	3.4	15	3.2	3.4	9	3.6	-4.0									
10	6.2	6.3	15	0.7	-1.9	16	n	0.3	-1.9	16	n	0.3	-1.9	10	3.0	-3.3							
11	3.9	4.1	16	n	0.3	1.2	17	3.3	-1.9	17	n	0.3	2.2	11	6.3	5.2							
12	3.6	4.0	17	n	0.3	0.8	18	n	0.3	1.4	18	n	0.3	2.2	12	2.3	2.8						
13	7.1	6.5	18	n	0.3	-0.1	19	3.3	3.2	19	3.3	3.2	13	n	0.4	0.9							
14	4.8	-4.3	19	n	0.3	1.0	h 8 1			10	1.4	2.2	14	n	0.4	-0.9							
15	1.8	2.5	20	2.2	2.4	0	17.4	17.9	11	6.7	6.6	10	1.9	2.4	15	5.5	5.1						
16	2.5	-2.5	h 5 1			1	7.0	7.0	12	4.1	-4.1	11	3.2	3.4	16	n	0.2	-0.7					
17	2.3	1.7	1	31.5	32.8	2	5.0	5.2	13	4.4	4.1	12	n	0.3	1.1	17	n	0.3	1.4				
18	4.5	4.3	2	34.1	34.8	3	4.0	4.1	14	n	0.3	1.7	13	n	0.3	0.1	18	n	0.2	0.1			
19	2.5	2.7	3	4.6	-4.8	4	3.9	4.0	15	n	0.3	0.1	14	n	0.3	0.1	19	n	0.2	-1.3			
20	n	0.2	-0.6	4	11.4	-11.5	5	4.5	4.6	16	2.2	1.8	h 16 1			0	5.5	5.0					
h 2 1			5	7.8	7.8	6	8.0	7.3	h 12 1			1	n	0.4	0.9	1	n	0.4	-0.6				
0	4.6	-3.5	6	15.6	-15.0	7	4.5	4.6	0	5.7	-5.5	2	n	0.4	1.1	2	n	0.4	1.1				
1	34.1	36.3	7	20.5	20.7	8	7.5	6.8	1	6.8	-6.6	3	0.6	0.1	3	0.6	0.1	3	0.6	0.1			
2	4.6	4.8	8	15.6	14.7	9	3.3	3.2	2	6.1	6.1	4	n	0.4	0.6	4	n	0.4	0.6				
3	19.5	19.3	9	8.0	8.6	10	n	0.3	0.1	3	2.8	-2.8	5	n	0.3	-0.7	5	n	0.3	-0.7			
4	25.2	25.7	10	4.0	4.0	11	8.3	-7.2	4	16.3	15.2	6	4.4	4.4	6	4.4	4.4	6	4.4	4.4			
5	35.2	-35.8	11	2.6	-2.2	12	3.4	3.4	5	7.5	6.6	7	n	0.3	0.9	7	n	0.3	0.9				
6	9.5	9.5	12	10.6	-9.2	13	3.4	3.4	6	4.2	-4.3	8	2.3	2.4	8	2.3	2.4	8	2.3	2.4			
7	3.4	3.1	13	7.5	6.6	14	3.3	2.9	7	n	0.4	0.9	9	n	0.3	0.5	9	n	0.3	0.5			
8	5.0	5.0	14	n	0.4	1.8	15	4.8	4.6	8	n	0.4	-1.3	10	n	0.3	-0.6	10	n	0.3	-0.6		
9	15.9	15.3	15	5.0	4.8	15	5.0	4.8	16	n	0.3	0.9	11	n	0.3	0.0	11	n	0.3	0.0			
10	2.9	2.8	16	3.8	3.3	16	n	0.3	0.9	17	0.5	-2.1	12	2.4	2.5	12	2.4	2.5	12	2.4	2.5		
11	7.0	-6.5	17	n	0.3	1.3	17	0.5	-2.1	18	n	0.2	1.4	13	n	0.2	-1.4	13	n	0.2	-1.4		
12	9.0	9.1	18	3.1	-2.9	18	n	0.2	1.4	19	1.5	-2.2	12	3.3	3.1	h 17 1			0	5.5	5.0		
13	6.8	-5.9	19	n	0.2	0.5	19	1.5	-2.2	13	n	0.3	1.3	14	3.2	-3.0	1	2.8	2.9	1	2.8	2.9	
14	3.0	3.1	20	n	0.2	-0.6	1	5.6	6.0	15	1.9	-1.6	15	1.9	-1.6	2	2.6	2.9	2	2.6	2.9		
15	7.3	6.5	h 6 1			2	10.5	-10.9	3	13.4	13.8	16	2.8	2.7	3	4.4	4.4	3	4.4	4.4	3	4.4	4.4
			3	13.4	13.8	4	6.0	6.0	4	6.0	6.0	17	n	0.2	-0.1	4	2.4	2.6	4	2.4	2.6		
			4	6.0	6.0	5	5.7	6.1	h 13 1			5	0.8	2.0	5	0.8	2.0	5	0.8	2.0			
			5	5.7	6.1	6	6.1	6.5	1	9.0	8.7	6	n	0.3	-1.3	6	n	0.3	-1.3				
			6	6.1	6.5	7	1.1	1.8	2	5.4	-5.3	7	n	0.3	1.5	7	n	0.3	1.5				
			7	1.1	1.8	8	5.5	-5.4	3	n	0.4	0.2	8	3.8	3.7	8	3.8	3.7	8	3.8	3.7		
			8	5.5	-5.4	9	12.4	11.0	4	9.0	8.7	9	2.5	2.7	9	2.5	2.7	9	2.5	2.7			
			9	12.4	11.0				5	5.7	6.1												

Table 1 (Continued)

5	10.3	-10.7	12 n	0.5	0.7	3 n	0.5	-1.0	h 10 5	h 13 5				
6	3.3	2.9	13 n	0.5	1.0	4 n	0.5	1.9	0	6.6	6.1	1	4.2	3.7
7 n	0.5	1.0	14	4.2	3.9	5	4.7	3.7	1	3.2	-2.7	2	2.5	-2.4
8 n	0.5	1.5	15 n	0.4	-0.9	6	4.3	3.7	2	2.8	2.3	3 n	0.5	0.5
9	6.7	6.4				7	6.9	7.9	3 n	0.5	-0.1	4 n	0.5	1.3
10 n	0.5	1.8		h 5 5		8	1.7	-2.2	4 n	0.5	-1.2	5 n	0.5	1.6
11	2.5	-2.8				9 n	0.5	-0.7	5	3.7	2.9	6 n	0.4	0.9
12	4.9	4.4	1	9.9	9.1	10 n	0.5	-1.0	6	6.4	6.0	7	3.7	3.6
13	3.0	-3.1	2	10.3	10.1	11 n	0.5	0.6	7 n	0.5	-1.4	8 n	0.4	-1.4
14 n	0.4	1.5	3	1.4	-2.0	12 n	0.5	1.7	8	2.3	2.1	9	0.6	1.5
15	3.7	3.5	4	4.2	-3.9	13	4.8	4.9	9	1.6	-2.3	10 n	0.3	-0.2
16 n	0.3	0.2	5	2.9	2.1	14 n	0.4	0.0	10 n	0.5	-1.2			
			6	6.1	-5.5				11	3.1	2.8		h 14 5	
	h 3 5		7	8.6	8.0		h 8 5		12 n	0.4	1.9			
1 n	0.3	-0.6	8	6.7	5.8				13 n	0.3	0.7	0 n	0.5	1.0
2 n	0.4	0.7	9	4.2	3.5	0	7.7	7.0				1	3.8	3.6
3	12.5	13.0	10 n	0.5	1.8	1	0.9	1.7		h 11 5		2	3.3	2.6
4 n	0.4	-0.5	11 n	0.5	-1.5	2 n	0.5	1.9	1 n	0.5	0.7	3 n	0.4	1.7
5	4.7	4.7	12	4.8	-4.5	3 n	0.5	-1.9	2	3.8	3.2	4	1.9	1.7
6 n	0.5	-0.2	13	4.0	3.4	4 n	0.5	1.2	3	4.6	4.6	5	2.8	-2.7
7	3.0	-2.8	14 n	0.4	1.1	5 n	0.5	-0.7	4	0.5	-1.8	6 n	0.4	1.2
8	1.7	2.2	15	2.4	2.6	6	3.8	3.5	5	4.7	4.3	7 n	0.4	-0.4
9	5.1	4.8				7 n	0.5	2.1	6 n	0.5	-1.7	8 n	0.3	1.4
10 n	0.5	-0.7		h 6 5		8	4.1	3.4	7 n	0.5	0.7	9	1.5	2.9
11	6.5	6.3	0 n	0.5	0.2	9 n	0.5	0.8	8 n	0.5	1.9		h 15 5	
12 n	0.5	-1.1	1 n	0.5	-0.3	10 n	0.5	-0.0	9 n	0.5	0.9	1 n	0.4	0.4
13 n	0.5	-1.6	2	4.9	4.5	11	3.8	-3.4	10 n	0.4	1.0	2 n	0.4	0.1
14 n	0.4	0.1	3	1.9	2.0	12	1.9	2.0	11	3.3	3.5	3	4.3	4.3
15 n	0.4	1.4	4	6.2	5.5	13 n	0.4	1.1	12	1.5	-2.0	4 n	0.4	0.4
16 n	0.3	1.0	5	3.0	-2.4	14	2.1	2.0				5	2.3	2.2
			6 n	0.5	1.1				h 12 5			6 n	0.3	-0.5
	h 4 5		7 n	0.5	-0.2		h 9 5					7 n	0.3	-0.5
0	10.8	11.3	8	0.9	1.8	1	2.5	2.5	0	2.4	-2.5		h 16 5	
1	1.3	-1.4	9 n	0.5	0.0	2	5.1	-4.8	1	3.3	-3.1			
2	3.6	2.9	10	4.4	3.7	3	5.4	4.5	2	3.8	3.0			
3	3.1	-2.8	11 n	0.5	1.2	4	2.7	2.6	3 n	0.5	-1.3	0	3.2	3.0
4	3.5	-3.9	12 n	0.5	0.9	5	2.4	2.3	4	8.5	7.6	1 n	0.3	-0.3
5	3.4	3.3	13 n	0.4	-0.5	6	3.5	3.2	5	3.6	3.2	2 n	0.3	0.9
6	7.5	6.9	14 n	0.4	0.9	7 n	0.5	1.1	6 n	0.5	-1.8	3 n	0.3	0.7
7 n	0.5	-1.3	15 n	0.3	-0.1	8	2.4	-2.8	7 n	0.5	0.3	4 n	0.3	0.5
8	6.2	6.2				9	5.0	4.7	8 n	0.4	-0.5			
9 n	0.5	-1.0		h 7 5		10 n	0.5	-1.6	9	1.0	-2.2			
10 n	0.5	-0.7	1	7.5	6.4	11	2.1	2.5	10	4.3	4.5			
11 n	0.5	0.5	2	5.4	-4.6	12	3.3	3.3	11 n	0.3	1.1			
						13 n	0.3	-0.0						

for individual levels together with the individual isotropic temperature factor coefficients, in cycles 6–18 all parameters, including the occupancy factors for individual atomic positions and all the individual anisotropic temperature factor coefficients were refined, and, finally, in cycles 19–22 all parameters but the occupancy factors for individual atomic positions were refined. Towards the end of the refinement the *R*-factor dropped to the value of 0.113 for all diffractions (0.080 for non-zero diffractions) and the final difference synthesis showed no significant features in the atomic positions, if neglecting the shallow rings around the Al(1) and Al,Si positions (Fig. 2). The maximum value of the residual electron density in these rings (about $3 \text{ e}/\text{\AA}^3$), however, is very small in comparison with the peak-density of $156 \text{ e}/\text{\AA}^3$ and $131 \text{ e}/\text{\AA}^3$ for Al(1) and Al,Si positions respectively, and suggests merely that the actual electron-density distribution around the above atomic positions cannot be fully allowed for with spherically symmetrical atomic scattering functions used [8]. The final electron-density distribution is in Fig. 3 (note the environment of the O(3) position, which is in full agreement with papers [2, 5]).

The chemical composition of the mullite investigated was confirmed indirectly from the refined occupancy factors of the Al,Si, Al*, O(3) and O* positions. The Al* position was considered as occupied solely by Al atoms, the reason for this being crystallochemical

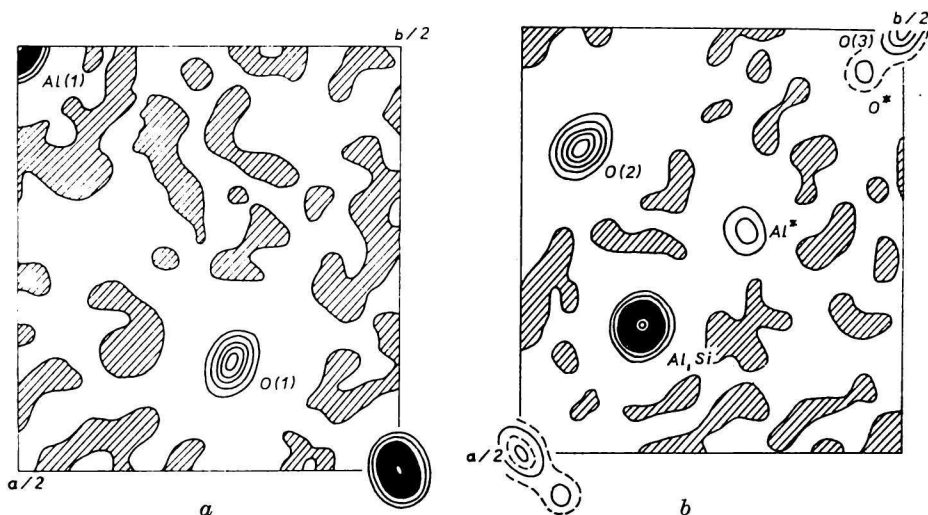


Fig. 3. Sections at $z = 0$ (a) and $z = 1/2$ (b) through the final electron-density function of mullite. Contour interval $10 \text{ e}/\text{\AA}^3$, supplementary contours in the O(3) position at 5 and $15 \text{ e}/\text{\AA}^3$. Negative areas shadowed.

(2nd Pauling's rule and the dimensions of the Al^*O_4 tetrahedron). The decision, whether this site may contain some Si atoms as well as Al atoms, however, cannot be made from the X-ray data alone and, thus, this question remains unanswered.

The final calculated structure factors together with the observed values are given in Table 1, the atomic coordinates, together with those of Burnham [5] are given in Table 2. Table 3 contains the weight analysis which turns out to be quite satisfactory.

Table 2

Final atomic coordinates in the structure of 1.83/1-mullite (1st line) and their comparison with the same values for 1.91/1-mullite [5] (2nd line). Standard deviations in parentheses

	x	y	z
Al(1)	0	0	0
	0	0	0
Al*	0.2380(4)	0.2945(4)	1/2
	0.2384(4)	0.2945(4)	1/2
Al,Si	0.3512(1)	0.1590(1)	1/2
(Al ₂ ,Si)	0.3512(1)	0.1596(1)	1/2
O(1)	0.3729(2)	0.2808(2)	0
(O _d)	0.3729(2)	0.2811(2)	0
O(2)	0.1420(2)	0.0777(2)	1/2
(O _{ab})	0.1415(2)	0.0779(2)	1/2
O(3)	0	1/2	1/2
(O _c)	0	1/2	1/2
O*	0.0509(11)	0.4482(9)	1/2
(O _c *)	0.0500(14)	0.4514(14)	1/2

Table 3

Weight analysis obtained in the last cycle of the refinement of the structure of 1.83/1-mullite (w is the weighting factor; $w = 1/\sigma^2$)

Interval ($\sin \Theta/\lambda$)	Number of diffractions	$\overline{w\Delta^2}$	Interval $ F_o $	Number of diffractions	$\overline{w\Delta^2}$
0.0—0.2	7	5.09	0.0—0.9	601	3.91
0.2—0.4	53	3.25	0.9—3.7	524	1.75
0.4—0.6	130	3.13	3.7—8.4	455	3.85
0.6—0.8	252	2.92	8.4—15.0	161	4.98
0.8—1.0	392	3.65	15.0—23.5	51	1.81
1.0—1.2	502	2.61	23.5—34.0	18	2.12
1.2—1.4	480	3.90	34.0—46.0	6	1.46

Discussion

For the calculation of the interatomic distances and bond angles as well as for the evaluation of the apparent thermal vibrations of the individual atoms a Fortran Crystallographic Function and Error Program (*ORFFE*), written by *Busing, Martin* and *Levy* [9] has been used. This program takes advantage of the magnetic tape containing the atomic parameters together with the variation-covariation matrix prepared in the last cycle of the least-squares refinement by the *ORFLS* program [7] and yields, in addition to the interatomic functions, their standard deviations.

The results of these calculations are given in Table 4 (the dimensions of the coordination polyhedra and the bond angles) and Table 5 (the dimensions and orientations of the ellipsoids of the apparent thermal vibrations of the individual atoms). Both tables contain, when available, the corresponding data of *Burnham* [5].

It can be easily seen that both sets of data (*Burnham's* and ours) are quite consistent. The dimensions of the coordination tetrahedra of the 1.91/1-mullite are slightly larger. Very interesting is the fact that the standard deviations calculated for the 1.83/1-mullite are almost identical with those for 1.91/1-mullite. This means that the visually estimated intensities, if properly handled (and, if they are at disposal in sufficient amount), may yield the results comparable with those obtained by counter methods.

Both amplitudes and orientations of the ellipsoids of the apparent thermal vibrations agree very well with those reported by *Burnham* [5] that are only slightly higher. In Table 5 the values of the equivalent individual isotropic temperature factor coefficients [10]

$$B_r = 4/3 \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

are also given, where β_{ij} are the coefficients of the individual anisotropic temperature factor of the r -th atom.

The strong anisotropy of the O(1) and O(2) atoms (see also Fig. 3) is a result of the positional disorder of these atoms caused by irregular alternation of Si atoms, Al atoms and vacancies in the Al,Si positions. It is, therefore, not to be assigned to the abnormally large thermal vibrations. Since the longest main axes of the corresponding ellipsoids are almost perpendicular to the directions Al(1)—O(1) and Al(1)—O(2)

Table 4

Interatomic distances and bond angles in the coordination polyhedra of 1.83/1-mullite and their comparison with analogous data for 1.91/1-mullite [5]. Standard deviations in parentheses

Octahedron AlO_6 , symmetry $.2/m$

	Multiplicity	1.83/1	1.91/1 [5]
		dist. [Å]	dist. [Å]
Al—O	2	1.939(2)	1.940(1)
	4	1.895(1)	1.897(1)
O—O	2	2.884(2)	2.890(1)
	4	2.722(2)	2.723(2)
	4	2.700(2)	2.704(2)
	2	2.458(2)	2.458(3)
	Multiplicity	angle [°]	angle [°]
O—Al—O	2	99.12(8)	
	4	89.55(7)	data not available
	4	90.45(7)	
	2	80.88(8)	

Tetrahedron $(\text{Al,Si})\text{O}_4$, symmetry $.m$

I. Basic state: O(3) in twofold coordination

	Multiplicity	1.83/1	1.91/1 [5]
		dist. [Å]	dist. [Å]
(Al,Si)—O	2	1.727(1)	1.728(1)
	1	1.702(2)	1.711(2)
	1	1.661(1)	1.668(1)
	mean	1.704	1.709
O—O	1	2.884(2)	2.890(1)
	1	2.774(2)	2.784(2)
	2	2.768(2)	2.773(1)
	2	2.751(2)	2.759(2)
	Multiplicity	angle [°]	angle [°]
O—(Al,Si)—O	1	113.3(1)	
	1	111.1(1)	data not available
	2	109.5(1)	
	2	106.7(1)	

Table 4 (Continued)

2. Supplementary state (1): O* in threefold coordination			
	Multiplicity	1.83/1	1.91/1 [5]
		dist. [Å]	dist. [Å]
(Al,Si)—O	2	1.727(1)	1.728(1)
	1	1.721(8)	1.733(13)
	1	1.702(2)	1.711(2)
	mean	1.719	1.725
O—O	1	3.100(9)	3.107(11)
	1	2.884(2)	2.890(1)
	2	2.751(2)	2.759(2)
	2	2.644(7)	2.663(11)
	Multiplicity	angle [°]	angle [°]
O—(Al,Si)—O	1	129.9(3)	
	1	113.3(1)	data not available
	2	106.7(1)	
	2	100.1(2)	
3. Supplementary state (2): O* in threefold coordination			
	Multiplicity	1.83/1	1.91/1 [5]
		dist. [Å]	dist. [Å]
(Al,Si)—O	1	1.781(8)	1.768(13)
	1	1.702(2)	1.711(1)
	2	1.727(1)	1.728(1)
	mean	1.734	1.734
O—O	2	2.990(7)	2.976(11)
	1	2.884(2)	2.890(1)
	2	2.751(2)	2.759(2)
	1	2.527(8)	2.534(13)
	Multiplicity	angle [°]	angle [°]
O—(Al,Si)—O	2	117.0(1)	
	1	113.3(1)	data not available
	2	106.7(1)	
	1	93.0(1)	

Table 4 (Continued)

Tetrahedron Al*O ₄ , symmetry . . <i>m</i>			
	Multiplicity	1.83/1	1.91/1 [5]
		dist. [Å]	dist. [Å]
Al*—O	1	1.843(8)	1.870(8)
	1	1.817(4)	1.822(3)
	2	1.770(2)	1.772(2)
	mean	1.800	1.809
O—O	2	3.109(7)	3.131(7)
	1	2.929(8)	2.956(10)
	1	2.884(2)	2.890(1)
	2	2.751(2)	2.759(2)
	Multiplicity	angle [°]	angle [°]
O—Al*—O	2	118.7(2)	
	1	119.1(1)	
	1	106.3(3)	data not
	2	100.1(1)	
Al*—O—Al*	1	105.3(4)	available
	1	111.6(4)	
	1	143.1(5)	

Table 5

Magnitude and orientation of the apparent thermal vibration ellipsoids of atoms in the structure of 1.83/1-mullite (1st line) and their comparison with the analogous data of 1.91/1-mullite [5] (2nd line, the angular data derived from figures)

Principal axis	r.m.s. amplitude of vibration [Å]	Equivalent <i>B</i>	Orientation [°] with respect to		
			+ <i>x</i> axis	+ <i>y</i> axis	+ <i>z</i> axis
Al(1)	0.065(2)	0.40	90	90	0
	—		—	—	—
	0.066(1)	0.45	107(3)	162(3)	90
—	—		—	—	
	0.082(1)		18(3)	108(3)	90
	—		—	—	—

Table 5 (Continued)

Principal axis	r.m.s. amplitude of vibration [Å]	Equivalent B	Orientation [°] with respect to		
			+x axis	+y axis	+z axis
Al*	1	0.067(6) 0.08(1)	90 —	90 —	0 —
	2	0.077(5) 0.08(1)	142(18) —	51(18) —	90 —
	3	0.090(5) 0.08(1)	51(18) —	38(18) —	90 —
Al,Si	1	0.068(2) 0.072(2)	25(6) 14(7)	65(6) 76(7)	90 90
	2	0.076(3) 0.084(2)	90 104(7)	90 14(7)	0 90
	3	0.081(2) 0.090(1)	115(6) 90	25(6) 90	90 0
O(1)	1	0.081(2) 0.079(3)	47(1) 48(2)	43(1) 42(2)	90 90
	2	0.098(2) 0.114(2)	90 90	90 90	0 0
	3	0.142(2) 0.135(3)	43(1) 42(2)	47(1) 48(2)	90 90
O(2)	1	0.065(3) 0.080(3)	90 90	90 90	0 0
	2	0.082(2) 0.090(3)	144(1) 132(2)	126(1) 138(2)	90 90
	3	0.147(2) 0.154(2)	126(1) 138(2)	36(1) 48(2)	90 90
O(3)	1	0.091(6) 0.12(1)	62(7) 36(32)	28(7) 54(32)	90 90
	2	0.137(7) 0.14(1)	152(7) 126(32)	62(7) 36(32)	90 90
	3	0.143(7) 0.15(1)	90 90	90 90	0 0
O*	1	0.08(1) 0.08(2)	110(35) 55(35)	20(35) 35(35)	90 90
	2	0.10(1) 0.11(2)	160(35) 145(35)	110(35) 55(35)	90 90
	3	0.12(1) 0.12(2)	90 90	90 90	0 0

respectively, it can be supposed that, due to the irregularities in the occupation of the Al,Si, Al*, O(3) and O* positions, the octahedra AlO_6 adapt their positions by turning themselves around their twofold axes.

Neither are the extraordinarily big dimensions of the vibration ellipsoids of the O(3) atoms in the plane approximately perpendicular to the Al,Si—O(3)—Al,Si direction, caused by a thermal movement; it is probably a result of the tendency of the siloxan bond angle to be less than 180° [11].

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