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The Structure of Mullite, $2Al_2O_3 . SiO_2$, and Relationship with the Structures of Sillimanite and Andalusite

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A synthetic crystal of mullite, $2Al_2O_3.SiO_2$, was studied by X-ray diffraction methods. The structure was found to be describable as the result of the following changes imposed upon the structure of sillimanite: re-distribution of silicon and aluminium of tetrahedral coordination into a random way over the same set of positions, random removal of some of the oxygen atoms shared by the above cations, replacement of silicon by aluminium and shift of some of the cations of tetrahedral coordination into open sites. In terms of the structure thus described, decomposition of sillimanite and andalusite was interpreted as due to the formation of a stable arrangement of three aluminium atoms around an oxygen atom.

Introduction

Since Taylor (1928) published the results of his X-ray study on mullite, numerous X-ray and synthetic investigations have been reported on this mineral and the results may be summarized as follows. The crystal is orthorhombic and known to show a wide variation of chemical composition, ranging from $3Al_2O_3.2SiO_2$ to $2Al_2O_3.SiO_2$. Its X-ray diffraction pattern is in general very similar to that of sillimanite, suggesting a close resemblance between these two structures, but it is also observed that most of the specimens of mullite produce diffraction patterns with diffuse scattering either replacing the normal diffraction spots or appearing between them, and in some cases the crystals give rise to super-lattice lines. Presumably connected with these features, every specimen gives a fractional number of oxygen atoms in the unit cell.

In spite of its common occurrence in various ceramic products, these peculiarities seem to have been deterrent to the analysis, and the structure of the mineral has not completely been elucidated. The authors were fortunately afforded a synthetic crystal practically free from diffuse scattering and could draw interesting conclusions both on its structure and on the relationship with those of the kindred minerals, sillimanite and andalusite.

Experimental

The specimen used in this study is a synthetic crystal described by Roy & Aramaki (1961). It is a colorless fine prism and the composition is $2Al_2O_3.SiO_2$.

Weissenberg and rotation photographs were taken around the *c* axis with Cu *K* radiation. The reflections were recorded by means of the multiple film technique and their intensities were measured photometrically. The relative values derived after correction for the Lorentz and polarization factors were put on to an absolute scale by using Wilson's statistical method. Very faint diffuse scattering was observed only in the Laue photographs of considerable exposure times.

Unit cell and space group

The lattice constants determined from the powder diffractometer measurements by the above authors (Roy & Aramaki, 1961) are as follows:

$$a_0 = 7{\cdot}583 \pm 0{\cdot}002,\ b_0 = 7{\cdot}681 \pm 0{\cdot}002,$$
$$c_0 = 2{\cdot}8854 \pm 0{\cdot}0005\ \text{Å}\ .$$

This unit cell contains 6/5 of the formula unit, namely $Al_{4.8}Si_{1.2}O_{9.6}$, giving the calculated density of 3·13 g.cm.$^{-3}$ in comparison with the observed value, 3·16 g.cm.$^{-3}$ measured by Toshio Kato of this laboratory. Since the corresponding volume of sillimanite contains $Al_4Si_2O_{10}$, it was thus confirmed that while both structures have the same total number of cations per unit cell, the specimen under examination is short of oxygen content compared with sillimanite. This is in agreement with the conclusion given by Agrell & Smith (1960).

Reflections with *k* and *h* odd are missing in the *hk*0 and 0*kl* reflections respectively, no other systematic missing being observed. The space group was therefore determined to be *Pbam* (D_{2h}^9).

Structure determination

It was found that the intensity distribution of the *hk*0 reflections is almost the same as that of the corresponding reflections of sillimanite. Therefore, we started the analysis by seeking for deviations of the structure from that of sillimanite (Taylor, 1928), and made an $F_o - F_c$ synthesis by employing for each F_o an observed *hk*0 structure factor of the mullite and for F_c the

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corresponding calculated one of sillimanite. The result, as shown in Fig. 1 together with the atomic positions in the structure of sillimanite, revealed that quite marked depressions are observed at the Si, Al positions, a set of salient peaks at about (0·25, 0·30) and its equivalent points, and another set of depressions at the positions of O_{III}.

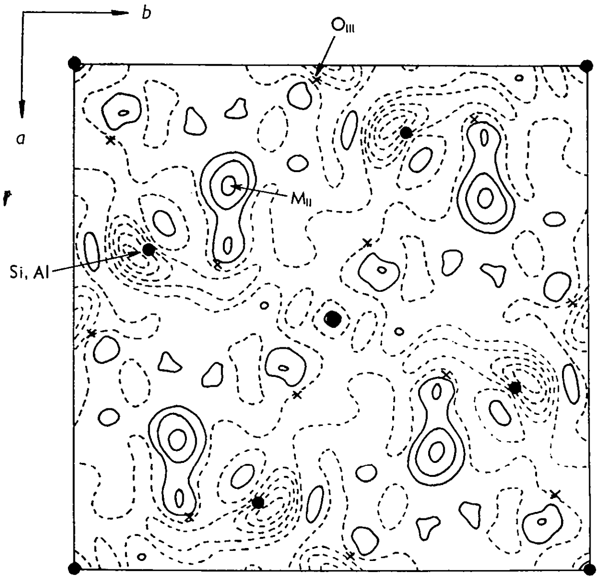

Fig. 1. $F_o - F_c$ synthesis derived by employing for F_o the observed structure factors of mullite, $2Al_2O_3.SiO_2$, and for F_c the calculated ones of sillimanite. Black circles and crosses indicate respectively cations and oxygen atoms in the structure of sillimanite.

From this diagram, the deviations of the structure from that of sillimanite were inferred to lie in that there are chances of migration of cations from the Si, Al positions into the places indicated by the peaks M_{II} in the $F_o - F_c$ diagram, and deficit of oxygen atoms takes place at the positions of O_{III}. Because of the fact that the c length of the mullite is half as long as that of sillimanite, it was further assumed that silicon and aluminium remaining at the Si, Al positions are randomly distributed over the positions.

Since the outline of the structure had thus been disclosed, we then proceeded to the refinement with the estimation from the $F_c - F_c$ diagram that one cation out of five, namely 0·8 atom per unit cell, be displaced from the Si, Al positions to M_{II} and its equivalent. After several cycles of refinement by means of the difference Fourier and the least-squares methods, we arrived at the final coordinates as listed in Table 1. The observed and calculated structure factors for the $hk0$ reflections are tabulated in Table 2. The isotropic temperature factor with $B \times 10^{16} = 1·2$ was employed

Table 1. *Coordinates of atoms in the structure of mullite*

Name of atomic site	Number of equivalent points	Atoms destributed over the equivalent points	Coordinates x	y	z
Al	2	Al_2	0·000	0·000	0·000
M_I	4	$Al_2Si_{1·2}$	0·351	0·159	0·500
M_{II}	4	$Al_{0·8}$	0·236	0·294	0·500
O_I	4	O_4	0·139	0·076	0·500
O_{II}	4	O_4	0·374	0·283	0·000
O_{III}	2	$O_{0·8}$	0·000	0·500	0·500
O_{IV}	4	$O_{0·8}$	0·053	0·447	0·500

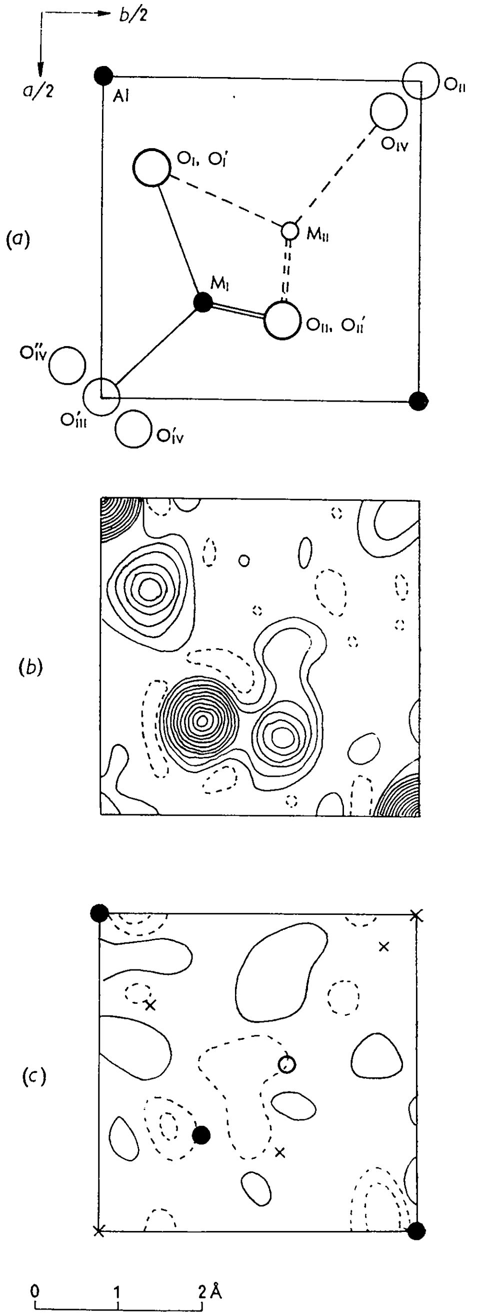

Fig. 2. Structure of mullite, $2Al_2O_3.SiO_2$, projected onto (001). (a) Atomic arrangement, (b) electron density and (c) final difference Fourier synthesis.

Table 2. *Observed and calculated structure factors for the hk*0 *reflections*

hk	F_o	F_c
00		156·0
20	7·6	7·3
40	26·3	−24·9
60	25·6	27·5
80	21·3	25·0
11	20·4	20·3
21	32·0	35·4
31	5·0	7·0
41	9·2	−8·6
51	6·2	5·5
61	16·5	−17·4
71	7·1	8·6
81	9·3	10·1
91	7·7	8·7
02	1·3	0·4
12	25·0	−25·8
22	27·2	31·9
32	12·4	−11·3
42	26·6	25·3
52	25·9	27·3
62	9·6	11·2
72	4·5	−5·4
82	0·0	0·8
92	8·0	−8·7
13	21·1	20·6
23	28·3	−28·0
33	7·4	−8·5
43	0·0	−0·7
53	12·2	13·7
63	8·2	12·2
73	15·2	16·8
83	3·2	−3·7
04	13·5	10·5
14	10·1	−7·9
24	21·9	19·8
34	0·0	0·6
44	20·7	22·9
54	4·1	−2·6
64	0·0	−0·2
74	9·3	9·7
84	7·2	7·2
15	7·9	8·4
25	23·7	−22·2
35	17·5	19·0
45	10·5	10·1
55	6·3	3·5
65	5·7	6·9
75	3·9	3·5
85	10·6	−10·1
06	21·0	18·4
16	15·4	13·7
26	7·7	7·8
36	3·1	3·1
46	7·7	7·5
56	2·0	−2·3
66	16·7	13·8
76	3·5	−3·3
17	6·5	−8·2
27	9·4	9·0
37	29·5	27·1
47	6·8	−5·6
57	12·3	12·2
67	6·6	−5·3
08	0·0	−1·5
18	15·5	−13·9
28	13·0	10·6
38	2·9	−3·1
48	11·0	10·6
58	10·9	8·6
19	17·5	13·3
29	7·5	7·2
39	4·6	−4·2

Table 3. *Interatomic distances*

Tetrahedra			
$M_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{I}}$	1·73 Å	$\mathrm{O}_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{II}}$	2·79 Å
$M_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{II}}$	1·74	$\mathrm{O}_{\mathrm{II}}\text{–}\mathrm{O}_{\mathrm{II}}'$	2·89
$M_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{III}}'$	1·67	$\mathrm{O}_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{III}}'$	2·78
		$\mathrm{O}_{\mathrm{II}}\text{–}\mathrm{O}_{\mathrm{III}}'$	2·78
Mean	1·72 Å	Mean	2·81 Å
$M_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{I}}$	1·73 Å	$\mathrm{O}_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{II}}$	2·79 Å
$M_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{II}}$	1·74	$\mathrm{O}_{\mathrm{II}}\text{–}\mathrm{O}_{\mathrm{II}}'$	2·89
$M_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{IV}}'$	1·74	$\mathrm{O}_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{IV}}'$	3·19
		$\mathrm{O}_{\mathrm{II}}\text{–}\mathrm{O}_{\mathrm{IV}}'$	2·65
Mean	1·74 Å	Mean	2·83 Å
$M_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{I}}$	1·73 Å	$\mathrm{O}_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{II}}$	2·79 Å
$M_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{II}}$	1·74	$\mathrm{O}_{\mathrm{II}}\text{–}\mathrm{O}_{\mathrm{II}}'$	2·89
$M_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{IV}}''$	1·78	$\mathrm{O}_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{IV}}''$	2·54
		$\mathrm{O}_{\mathrm{II}}\text{–}\mathrm{O}_{\mathrm{IV}}''$	3·01
Mean	1·75 Å	Mean	2·84 Å
$M_{\mathrm{II}}\text{–}\mathrm{O}_{\mathrm{I}}$	1·83 Å	$\mathrm{O}_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{II}}$	2·79 Å
$M_{\mathrm{II}}\text{–}\mathrm{O}_{\mathrm{II}}$	1·78	$\mathrm{O}_{\mathrm{II}}\text{–}\mathrm{O}_{\mathrm{II}}'$	2·89
$M_{\mathrm{II}}\text{–}\mathrm{O}_{\mathrm{IV}}$	1·82	$\mathrm{O}_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{IV}}$	2·92
		$\mathrm{O}_{\mathrm{II}}\text{–}\mathrm{O}_{\mathrm{IV}}$	3·10
Mean	1·80 Å	Mean	2·93 Å
Octahedron			
$\mathrm{Al}\text{–}\mathrm{O}_{\mathrm{I}}$	1·88 Å	$\mathrm{O}_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{I}}'$	2·89 Å
$\mathrm{Al}\text{–}\mathrm{O}_{\mathrm{II}}$	1·91	$\mathrm{O}_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{I}}^{*}$	2·41
Mean	1·89 Å	$\mathrm{O}_{\mathrm{I}}\text{–}\mathrm{O}_{\mathrm{II}}^{*}$	2·70
		$\mathrm{O}_{\mathrm{I}}^{*}\text{–}\mathrm{O}_{\mathrm{II}}^{*}$	2·67
		Mean	2·67 Å

Asterisks indicate atoms in adjacent cells.

for the calculated structure factors, and the *R*-factor is 11·0%. The (001) projections of the atomic arrangement, of the electron density and of the final difference Fourier synthesis are shown respectively in (*a*), (*b*) and (*c*) of Fig. 2.

Description of the structure

The interatomic distances are listed in Table 3. These are derived from the *z* coordinates of atoms given according to the symmetry of the space group, *Pbam*. Because of the disordered nature of the structure, these distances may be looked upon as statistical averages.

As in the case of sillimanite, the structure consists of the chains of octahedral groups of oxygen atoms around aluminium. These chains run parallel to the *c* axis at each corner and the centre of the unit cell, and are bound together by silicon and aluminium atoms occupying tetrahedral positions.

80% of the positions corresponding to the Si, Al positions in sillimanite and denoted by M_{I} in Table 1 and 20% of the positions denoted by M_{II} are occupied by cations. Although both the positions are of tetrahedral coordination, the latter tetrahedra are definitely larger than the former as seen in Table 3. It may therefore be reasonable to suppose that the M_{II} positions are occupied by $\mathrm{Al}_{0\cdot8}$ per unit cell and M_{I} by $\mathrm{Al}_2\mathrm{Si}_{1\cdot2}$.

As to the oxygen atoms corresponding to $\mathrm{O}_{\mathrm{III}}$ in sillimanite, the elongated peaks in the electron density diagram, Fig. 2(*b*), may render several ways of interpretation. However, the atomic arrangement listed in Table 1, namely, with its $\mathrm{O}_{\mathrm{III}}$ and O_{IV} positions filled statistically with oxygen atoms at 40 and 20% respectively, has been adopted because not only does it produce an excellent agreement between the observed and calculated structure factors but also it offers an interpretation consistent with the distribution of cations as follows. If deficit of the oxygen content takes place in the crystal at the $\mathrm{O}_{\mathrm{III}}$ positions and in the ratio of 1 to 5, two cations on both sides of a dismissed oxygen atom will simultaneously lose their tetrahedral coordination, with the result that they are obliged to migrate into the M_{II} positions and will regain there another set of tetrahedral coordination by means of slight shifts of oxygen atoms from $\mathrm{O}_{\mathrm{III}}$ to O_{IV}.

Further details of the structure will be explained with reference to the structure of sillimanite as follows.

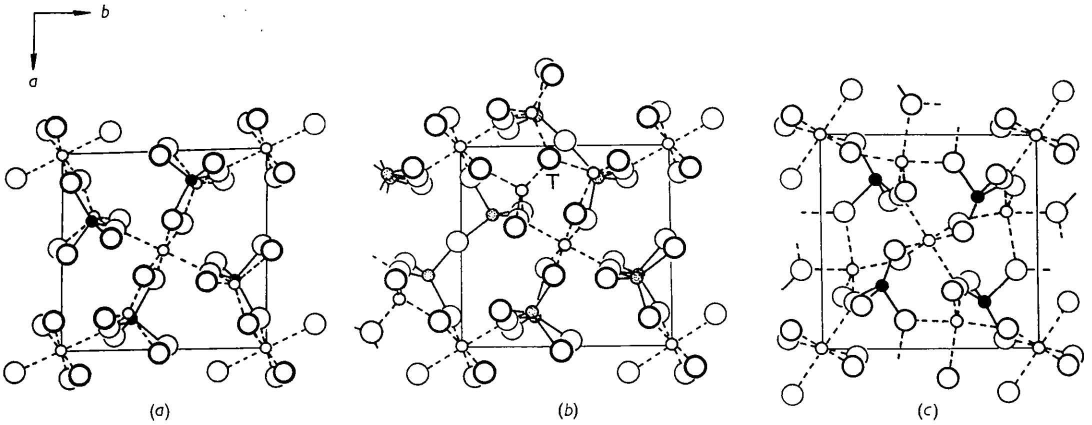

Fig. 3. Comparison of the structures of (*a*) sillimanite, (*b*) mullite and (*c*) andalusite. Small and large open circles indicate Al and O respectively throughout these figures, and the small black circles in (*a*) and (*c*) and the small shaded ones in (*b*) show Si, Al. For the structure of mullite in (*b*), a case is exemplified where the migrations of cations from $M_{\rm I}$ to $M_{\rm II}$ take place at the upper and lower left parts in and outside the unit cell respectively.

Structural relationship of mullite with sillimanite and andalusite, and the thermal decomposition of sillimanite and andalusite

The structural relationship of the mullite described here with sillimanite and andalusite will be visualized with the aid of Fig. 3. Namely, to derive theoretically the structure of the mullite from that of sillimanite, we must in the first place re-arrange the silicon and aluminium atoms at the Si, Al positions in the structure into the same set of positions but in a random way of distribution. Next, oxygen atoms should be removed from the $O_{\rm III}$ positions in the ratio of 1 to 5 but at random in regard to their positions, and at the same time, some of the silicon atoms must be replaced by aluminium atoms so as to compensate the change in valency due to the subtraction of oxygen atoms. Finally, if we shift the aluminium atoms, which have been attached to the oxygen atoms before the removal, into the $M_{\rm II}$ positions so that these cations may regain tetrahedral coordination of oxygen atoms around them, we can, apart from minor adjustments of atomic positions, arrive at the structure of the mullite.

On the other hand, if we transfer all the tetrahedral aluminium atoms in the structure of sillimanite into the $M_{\rm II}$ positions by retaining their ordered z coordinates, we can arrive, after adjustments of oxygen positions, at the structure of andalusite in Fig. 3(*c*) (Taylor, 1929). It may thus be regarded that structurally speaking, the mullite is a disordered phase intermediate between two ordered phases, sillimanite and andalusite.

The structural relationship described above will permit us to interpret the process of formation of mullite from sillimanite or andalusite as follows. It is a well known fact that sillimanite and andalusite, when heated, change to mixtures of mullite and silica. Now, when these minerals are heated, the thermal vibrations of atoms in the structures increase and will finally reach such a state as to allow some of the atoms to escape from their original positions into open sites in these structures. It seems, however, that the chains of octahedral groups of oxygen atoms around aluminium are so firmly built that they can mostly retain their configuration, though decomposed here and there, liberating some of aluminium and oxygen atoms. Under these circumstances, there may be in the structure of a heated crystal a chance for an oxygen atom at the $O_{\rm III}$ (or $O_{\rm IV}$) position to be surrounded by three cations, for example, as denoted by T in Fig. 3(*b*). This state will generally be unstable, as too much positive charge is concentrated upon the oxygen atom. However, if the three neighbours are all aluminium, the excessive charge toward the oxygen atom will be only $+\frac{1}{4}e$ and the arrangement of the atoms will be considerably stabilized. If this is true, we can assume that during the process of thermal agitation, aluminium atoms tend to be trapped around oxygen atoms, forming stable nuclei in the structure. In this way, an aluminium rich phase, mullite, will be derived, and excluded silicon atoms crystallize out with oxygen atoms as silica.

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