

A comparative electron-diffraction study of sillimanite and some natural and artificial mullites

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(With Plates X and XI)

[Read 7 November 1963]

Summary. Electron-diffraction photographs of some natural and synthetic mullites and a typical sillimanite have been obtained and are interpreted using diffraction data due to Agrell and Smith. The position and diffuseness of mullite reflections ($h0l$) with $l = \frac{1}{2}$ have been re-studied. In such reciprocal lattice sections maxima are symmetrically disposed in pairs about the positions of sillimanite reflections with l odd. They lie on a^* rows and show different separations in the specimens studied. These diffraction conditions are closely analogous to those observed in the intermediate plagioclases (paired 'e' maxima) and in nepheline, and a similar explanation is envisaged in terms of antiphase domain structure. Intimate association of a mullite-type phase and sillimanite is shown to result from the breakdown of muscovite in a thermal metamorphic aureole, and a chemical analysis of a natural Fe,Ti-bearing mullite from a spinel-mullite buchite in the same aureole, is presented.

THIS study of mullite and sillimanite arose from an attempt to identify with certainty minute needle-like minerals (0.3×0.003 mm) that have grown on the breakdown of muscovites during thermal metamorphism of phyllites at the margin of the aureole of a dolerite plug at Sithean Sluaigh, Strachur, Argyllshire (plate X, figs. B and D).

Recently, Shears and Archibald (1954) and Agrell and Smith (1960) have reviewed the present state of knowledge of the minerals mullite and sillimanite. Bárta and Bárta (1956), using the flame-fusion method of synthesis, claimed to have obtained mullite ranging in composition between $5\text{Al}_2\text{O}_3.4\text{SiO}_2$ and $2\text{Al}_2\text{O}_3.\text{SiO}_2$ and suggested that there is actually a whole range of possible compositions between sillimanite and $2\text{Al}_2\text{O}_3.\text{SiO}_2$. More recently, Majumdar and Welch (1963) synthesized and investigated mullites ranging in composition between $3\text{Al}_2\text{O}_3.2\text{SiO}_2$ and $2\text{Al}_2\text{O}_3.\text{SiO}_2$. The suggested solid solution towards sillimanite has recently

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received support from Aramaki (1961), who reported sillimanite with excess alumina in metamorphosed sedimentary material found among the ejectamenta from the Asama volcano, north-west Tokyo. However, other workers consider that the possible compositional range is much smaller (e.g. Trömel, reported in Agrell and Smith (1960)).

Apart from the Al-silicates formed in altered muscovites at Sithean Sluaigh, the following specimens were examined: a sillimanite from a massive sillimanite rock, Mt. Crawford, South Australia (Alderman, 1942; Agrell and Smith, 1960); Agrell and Smith's 'Forster' mullite¹ (which has a composition $2\text{Al}_2\text{O}_3\cdot\text{SiO}_2$); and a natural Fe,Ti-bearing mullite from a spinel-mullite buchite at Sithean Sluaigh.

The natural Fe,Ti-bearing mullite was analysed chemically and its cell dimensions² obtained in the course of a detailed mineralogical study of the aureole of Sithean Sluaigh (to be reported later by one of us—D.G.W.S.). The results were: SiO_2 27.38, TiO_2 0.69, Al_2O_3 68.59, Fe_2O_3 3.18, MgO 0.31, sum 100.15%, leading to molecular percentages: 39.12, 0.74, 57.77, 1.71, and 0.66 respectively. The unit-cell dimensions are a 7.5461 \pm 0.0006, b 7.6976 \pm 0.0016, c 2.8912 \pm 0.0006 Å.

The natural Fe,Ti-bearing mullite contained bubbles of glass (the liquid from which it crystallized) and a few minute octahedra of pleonaste (see pl. X, figs. A and C). Although considerable attention was paid to the elimination of these impurities by various separation techniques, small amounts (probably not more than 2%) undoubtedly remained in the analysed material. Bearing in mind the limitations imposed by these contaminants it may be noted that there is no significant deviation from the formula $3\text{R}_2\text{O}_3\cdot 2\text{SiO}_2$, either towards sillimanite or towards corundum.

The mineral sillimanite, which is orthorhombic with unit-cell dimensions³ a 7.486, b 7.673, c 5.772 Å, can be assigned to space group *Pbnm*. The conditions for systematically absent reflections in this space group are $h0l$, $h+l$ odd, and $0kl$, k odd. In addition sillimanite shows strong pseudohalving of the c -axis repeat, which means that all reflections with l odd are very weak (Taylor, 1928).

Accordingly, the principal reciprocal-lattice sections of sillimanite can readily be recognised using the electron-diffraction technique. Repre-

¹ The writers wish to thank Dr. Agrell for making this material available.

² Cell dimensions obtained by the diffractometer method outlined by Agrell and Smith (1960) and best values arrived at using a programme written by Dr. C. H. Kelsey for the EDSAC II computer (in the Cavendish Laboratory).

³ The values given here refer to the Mt. Crawford sillimanite as reported by Agrell and Smith (1960).

sentative $h0l$ and hhl reciprocal-lattice sections of sillimanite from Mt. Crawford are illustrated in pl. XI, figs. A and B.

Using single-crystal diffraction photographs mullite may easily be distinguished from sillimanite by the absence of sharp maxima on intermediate layer lines normal to c^* in the positions occupied in sillimanite. Additional maxima do occur but comprise pairs, separated in the a^* direction, and symmetrically disposed about the position of sillimanite maxima with l odd. Data on these additional maxima in mullite have been presented by Agrell and Smith, who also describe a further group of diffuse maxima at $\frac{1}{8}$ and $\frac{5}{8}$ of the main c^* repeat. Agrell and Smith also noted that the degree of diffuseness of the paired maxima described above varied (they distinguished between S (sharp) and D (diffuse) mullites on this basis) and noted that the position of the maxima was not constant in different specimens.

Characteristic $h0l$ reciprocal-lattice sections of 'Forster' mullite and a natural iron-titanium mullite are illustrated in figs. E and F respectively of pl. XI. 'Forster' mullite represents the S type mullite of Agrell and Smith; the natural mullite is a D type. Measurement of the original diffraction plates shows that the separation of the paired maxima is different in the two mullites. The plates also show that the additional maxima in Forster mullite are less sharp than the primary Bragg maxima.

The separation of the additional maxima in mullite may conveniently be described relative to the a^* repeat. This procedure has been used, for example, in describing the additional paired maxima in the plagioclase feldspars (Bown and Gay, 1958) and in nepheline (McConnell, 1962). This separation relative to $2a^*$ was determined as 0.30 for Forster mullite and 0.37 for the natural iron-titanium mullite examined.

A general analogy may be drawn at this stage between the paired additional maxima in mullite and the paired 'e' type maxima in the low-temperature intermediate plagioclases (Bown and Gay, 1958). This analogy suggests that the position and degree of diffuseness of the paired maxima in mullite may be a function of chemical composition as in the plagioclases (Bown and Gay, 1958); the mullites examined possibly represent extremes of chemical composition. The mullite electron-diffraction photographs showed that in addition to the paired maxima further maxima occurred close to the primary c -axis layer lines. These regions of diffuse scattering were not studied in detail.

Examination of the breakdown products of the muscovite from Sithean Sluagh by electron-diffraction technique indicated the presence

of sillimanite and a mullite-type phase. Fig. c of pl. XI shows the $h0l$ reciprocal-lattice section of sillimanite as obtained from one crystal fragment; fig. D shows the mullite-type pattern. The separation of the additional paired maxima is greater than that of the other natural mullite studied and much additional diffuse scattering was noted.

The reason for the intimate association of 'mullite' and sillimanite in the decomposed muscovite is far from certain, but it may be that slight compositional differences from grain to grain in the original muscovite (such as the inclusion in some of flakes of hematite) stabilized the 'mullite' structure by the introduction of small amounts of ferric iron, whereas where it was absent the sillimanite structure was stable. On the other hand, there is in some of the decomposed mica grains a distinct tendency towards epitaxial arrangement of the Al-silicates, while in others they appeared to have grown radially or even randomly (pl. X). It seems possible that one of the minerals (i.e. 'mullite' or sillimanite) may develop metastably by the incorporation of pre-existing parts of the muscovite structure, while the other grows stably by more complete re-organization.

In conclusion, it may be noted that the electron-diffraction technique can be used to make a relatively rapid and positive distinction between mullite and sillimanite, using only small quantities of material, which can be of very fine grain size. Furthermore, the position and degree of diffuseness of the extra reflections in mullite can readily be determined. The data presented in this paper indicate that attempts to interpret the diffuse reflections in mullite patterns on the basis of their having truly fractional values of the accepted lattice spacing are unlikely to succeed, and it is possible that solid solution from mullite towards sillimanite and mullite towards corundum is reflected in the separation (and thus position) of the maxima, which are split about the sillimanite superlattice point on the intermediate layer lines. The presence of complex, weaker diffuse reflections close to the main layer lines is also noted as well as their tendency to be stronger and better developed in the natural mullites that were examined. Again it is thought unlikely that the positions of these diffuse reflections can be interpreted in terms of precise fractional values of the normal unit-cell dimensions.

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[*Manuscript received 3 February 1965*].

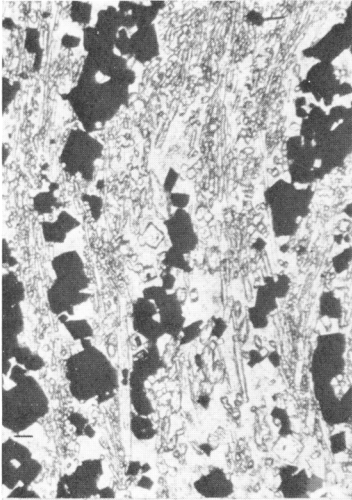
EXPLANATION OF PLATES X AND XI

PLATE X

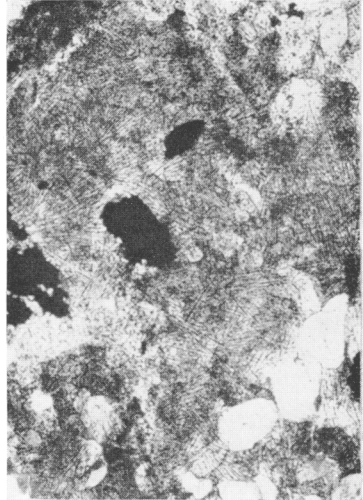
- FIG. A. A photomicrograph of a spinel-mullite buchite, showing the relatively coarse development of the Fe,Ti-bearing mullite. Plane polarized light $\times 50$.
- FIG. B. A photomicrograph of a thermally metamorphosed muscovite-chlorite-quartz-albite phyllite sectioned parallel to the foliation. Needles of either mullite or sillimanite or both can be seen in the basal sections of the decomposed muscovite. In places an epitaxial arrangement is suggested. Plane polarized light $\times 65$.
- FIG. C. A photomicrograph (highly enlarged) of mullite needles from the same spinel-mullite buchite, showing the numerous globular inclusions of glass. Plane polarized light $\times 255$.
- FIG. D. A photomicrograph showing the radial development of mullite or sillimanite needles in a flake of decomposed muscovite, from a rock similar to that in Fig. A. Plane polarized light $\times 240$.

PLATE XI

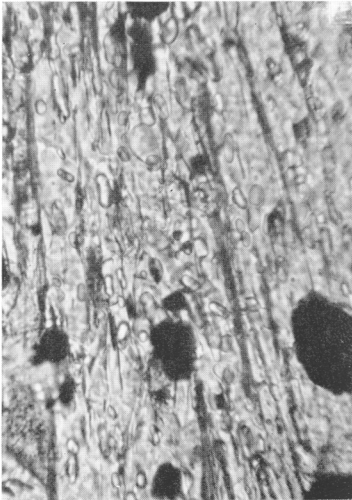
- FIG. A. $h0l$ reciprocal-lattice section of sillimanite from Mt. Crawford, S. Australia. Note the weak but sharp reflections with l odd.
- FIG. B. hhl reciprocal-lattice section of sillimanite from Mt. Crawford.
- FIG. C. hhl reciprocal-lattice section of sillimanite formed from muscovite during thermal metamorphism in the aureole of the dolerite plug at Sithean Sluaigh.
- FIG. D. $h0l$ reciprocal-lattice section of a mullite-type phase produced by thermal metamorphism of muscovite at Sithean Sluaigh.
- FIG. E. $h0l$ reciprocal-lattice section of 'Forster' (S type) mullite showing relatively sharp, paired additional maxima.
- FIG. F. $h0l$ reciprocal-lattice section of a natural Fe,Ti-bearing mullite from a mullite-pleonaste buchite at Sithean Sluaigh. The paired diffuse additional maxima have been indicated.



A



B

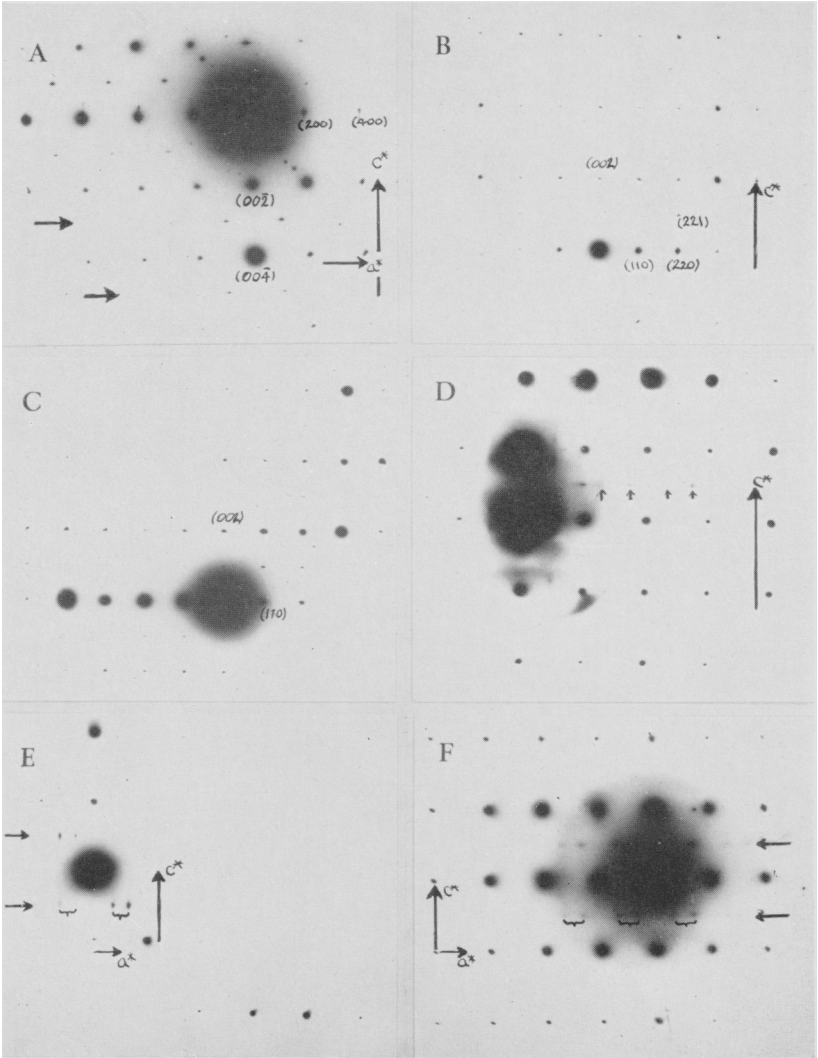


C



D

D. G. W. SMITH AND J. D. C. MCCONNELL: SILLIMANITE AND MULLITE



D. G. W. SMITH AND J. D. C. McCONNELL: SILLIMANITE AND MULLITE