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Kaolinite–mullite reaction series: a TEM study

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The kaolinite–mullite reaction series in single crystal kaolinite has been characterized by transmission electron microscopy. The exotherm observed at 980° C is attributed to the formation of a spinel phase. Mullite crystallites have also been observed with the spinel phase and both phases have a composition near that of 3:2 mullite. Subsequent heat treatment leads to the growth of mullite crystallites on the original kaolinite plates with the c-axis perpendicular to the plate.

1. Introduction

The kaolinite–mullite reaction has been studied by a number of researchers for several decades (e.g., see references 1–6). It is well known that on heating, kaolinite loses structural water between 500–600° C transforming into *meta*-kaolinite. The most significant structural change in this endothermic reaction is the transformation of octahedrally coordinated aluminium in kaolinite to tetrahedrally and pentahedrally coordinated alumina in *meta*-kaolinite [7]. The *meta*-kaolinite retains amorphous sheets of disordered SiO_4 and AlO_4 tetrahedra from the kaolinite. On heating kaolinite to higher temperatures a sharp exothermic peak is observed at 980° C. On further heating a second exothermic peak is observed in the vicinity of 1250° C due to the growth of mullite and a third exothermic peak is observed beyond 1300° C due to the formation of crystobalite. The positions of the second and third exothermic peaks are very sensitive to the presence and extent of impurities [8].

Although most of the reaction sequence is well understood, a controversy has centered around the nature of the first exothermic peak at 980° C. Reasons ranging from the formation of gamma alumina [1], a spinel phase [3, 6] a mullite phase [2], a spinel and mullite phase [4], through a spinodal decomposition [9] have been proposed for the occurrence of the first exothermic peak. Another unanswered question is the composition of the phase that forms at 980° C.

This study was undertaken to establish the cause of the first exothermic peak. It has been proposed that the different results reported by various researchers might have arisen due to differences in starting materials and compositions. Johnson and co-workers [8, 10] have documented the effect of impurities on the kaolinite–mullite reaction series. Therefore the approach used in this work was to start with kaolinite single crystals of high purity so as to minimize structural and compositional effects.

2. Experimental details

The starting material was single crystal kaolinite, ranging in size from 5–10 mm as shown in Fig. 1a. Figure 1b shows a bright field electron micrograph of the kaolinite crystals and the associated single crystal diffraction pattern is shown in Fig. 1c. The kaolinite crystals were heat treated in a Mettler DTA-TGA unit at $10^\circ C\,min^{-1}$ heating rate up to 1020°, 1200° and 1270° C. The heat treatment within the DTA-TGA unit ensured accurate temperature control and reliable experimental conditions. Figure 2a shows the heating curve for the 1270° C sample.

A part of the sample heated to 1020° C was chemically etched in 10% NaOH solution at 96° C for 15 minutes. This was done in order to remove the exsolved silica. Subsequently, one half of the etched sample was heated to 1250° C and a second to 1300° C. The DTA curve corresponding to the latter (1300° C) sample is plotted in Fig. 2b.

Conventional and analytical electron microscopy were carried out in a Philips 400T electron microscope operated at 100 kV and equipped with a Si(Li) X-ray detector and Kevex 8000 Analyst microanalysis system. High resolution electron microscopy was carried out on a JEOL 200CX electron microscope operated at 200 kV, at the National Center for Electron Microscopy (NCEM), Berkeley, CA.

3. Results

Transmission electron microscopy observations have been made at 750° C, 1020° C, 1200° C and 1300° C (*A*, *B*, *C* & *D* respectively in Fig. 2a). Figure 3 shows a bright field micrograph from a sample after heating at 750° C(*A*) i.e. between the endothermic peak and first exothermic peak. As can be seen from the corresponding diffraction pattern, the *meta*-kaolinite that forms after the first endothermic peak is completely amorphous. Figure 4 shows a dark field electron micrograph corresponding to the sample heated at 1020° C(*B*),

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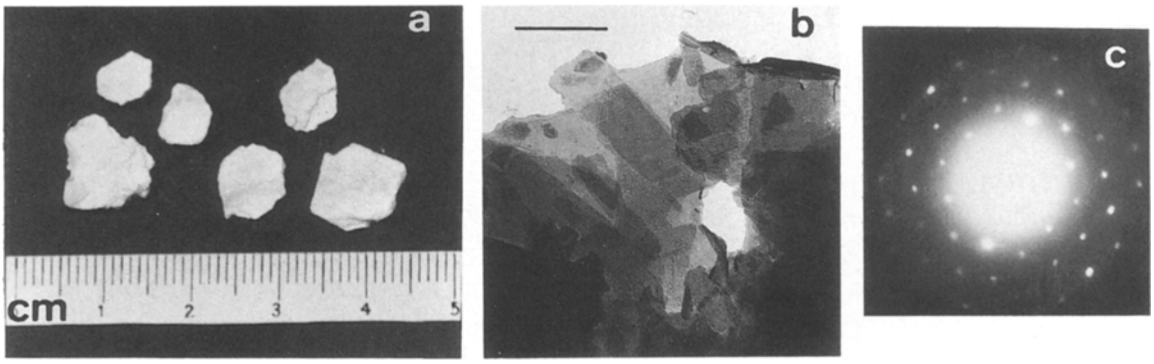

Figure 1 (a) Kaolinite single crystals (b) TEM image of kaolinite single crystals (bar = 0.5 μm) (c) SAD pattern.

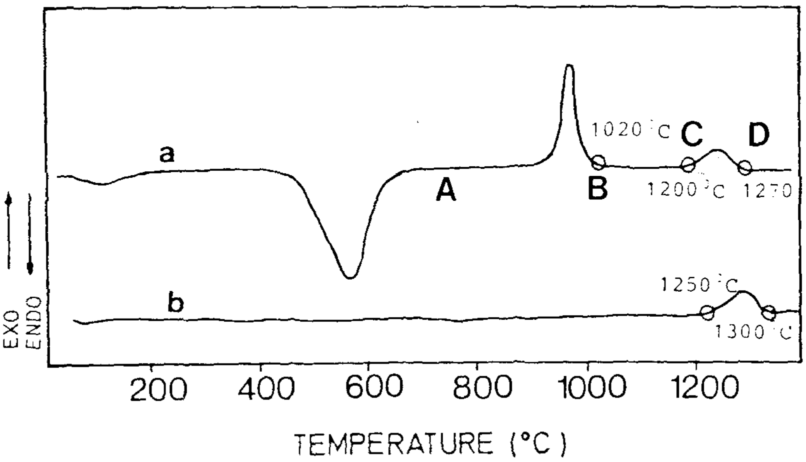

Figure 2 DTA curves for (a) kaolinite and (b) kaolinite heat treated at 1020° C and etched in 10% NaOH solution.

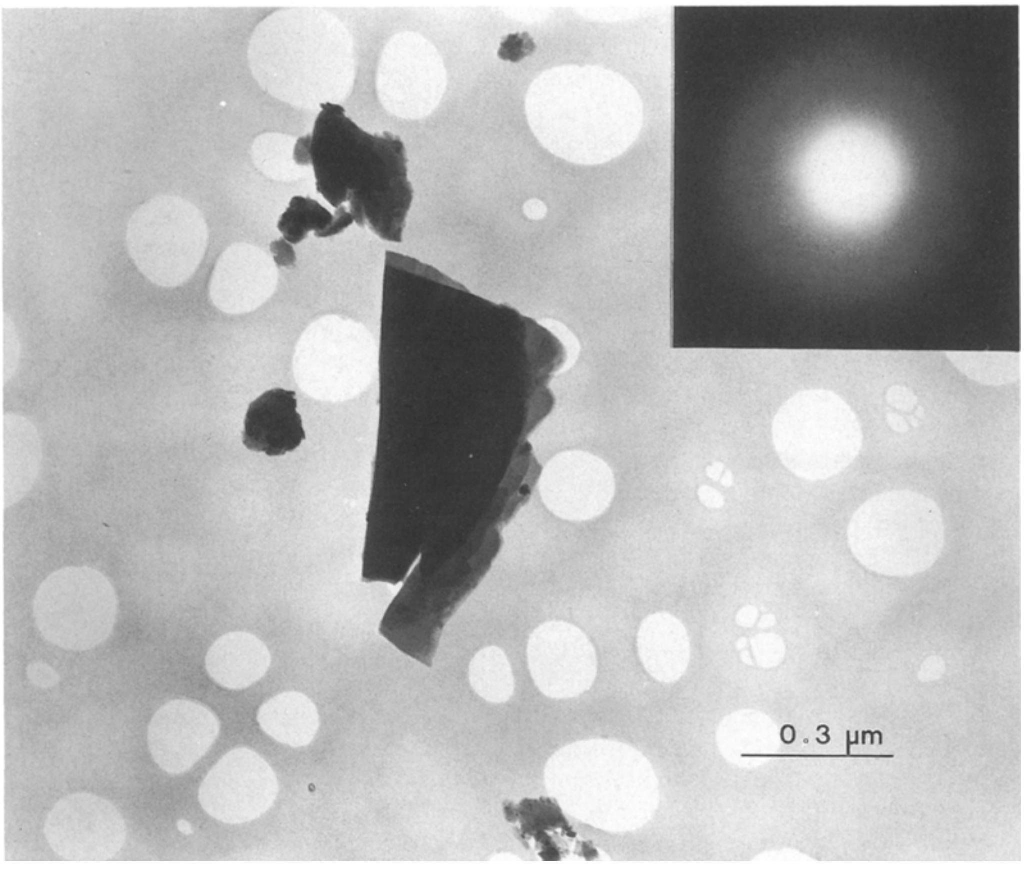

Figure 3 Bright field micrograph and SAD pattern of metakaolinite at 750° C showing its amorphous nature.

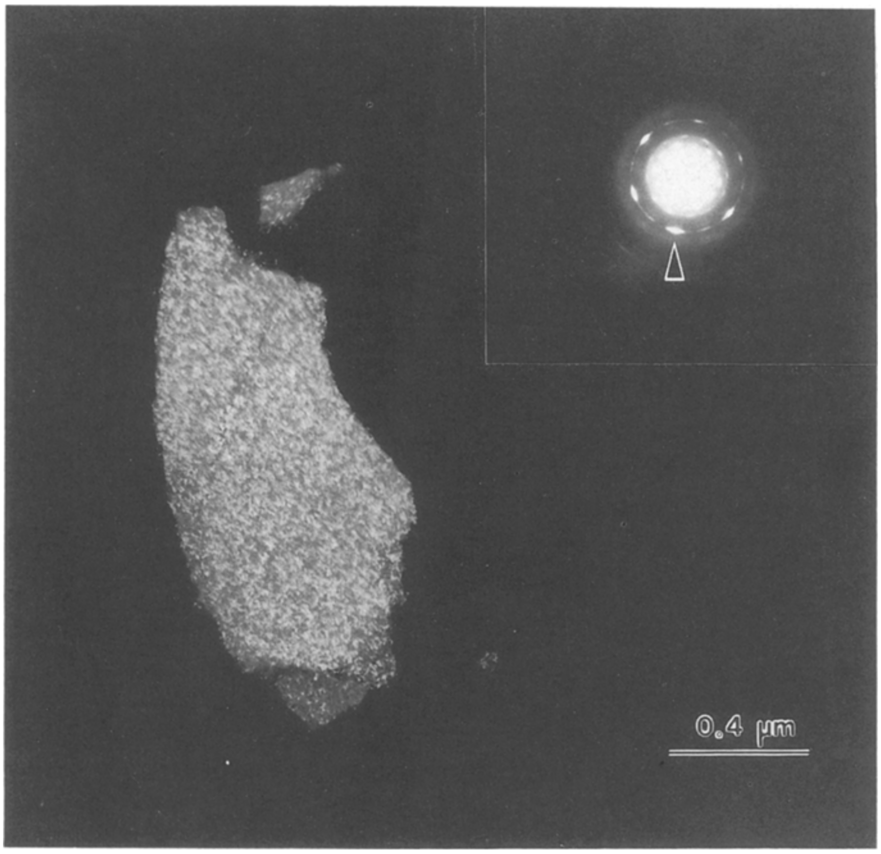

Figure 4 Dark field micrograph of the spinel phase taken at 1020° C after leaching and corresponding diffraction pattern.

after leaching. The image was taken from one of the bright spots (arrowed in the accompanying diffraction pattern). The diffraction pattern shown in the inset in Fig. 4 is a representative pattern of the major phase observed at 1020° C and it indicates a polycrystalline phase with a high degree of texture. Analysis of the crystal diffraction patterns, such as the one shown in Fig. 4, was carried out by coating the specimen with a

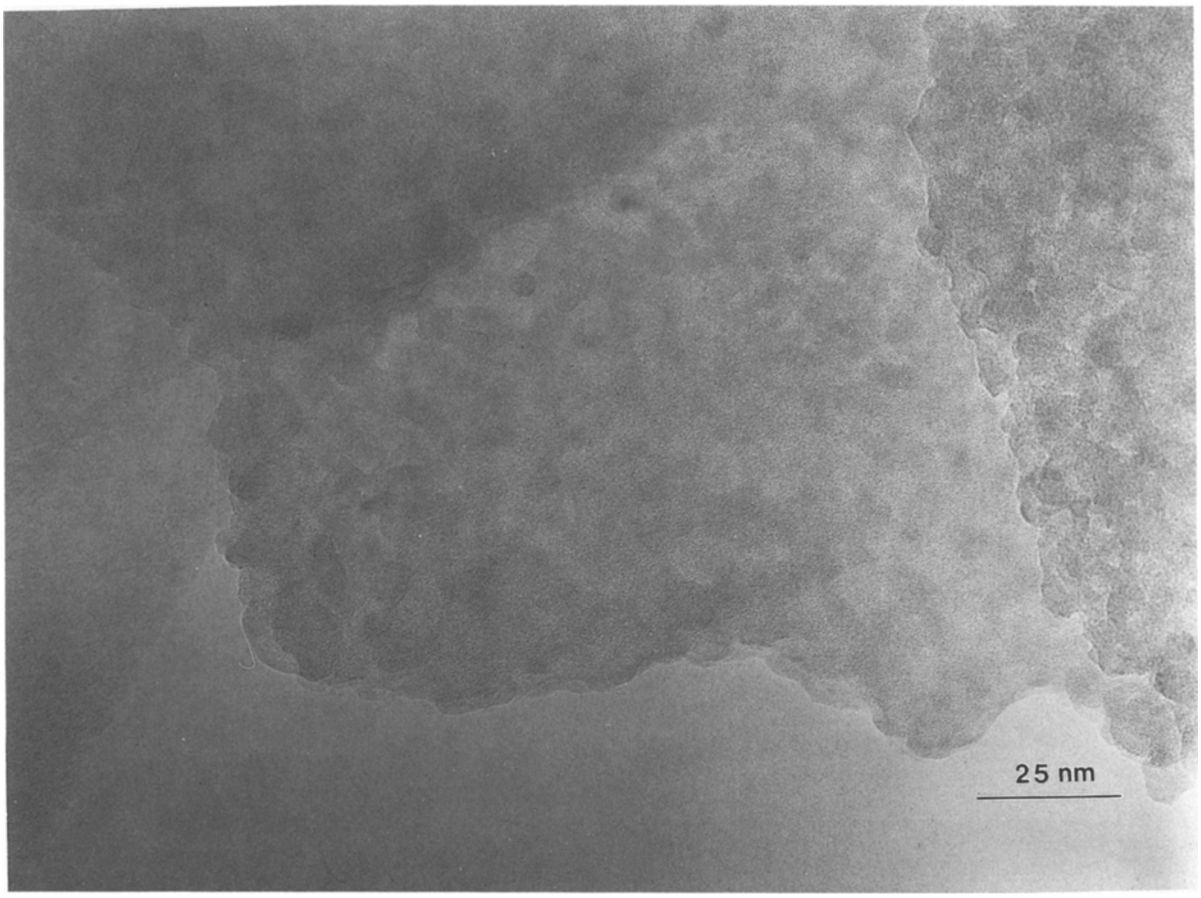

Figure 5 High magnification image of the spinel phase. The image is slightly underfocussed to enhance contrast.

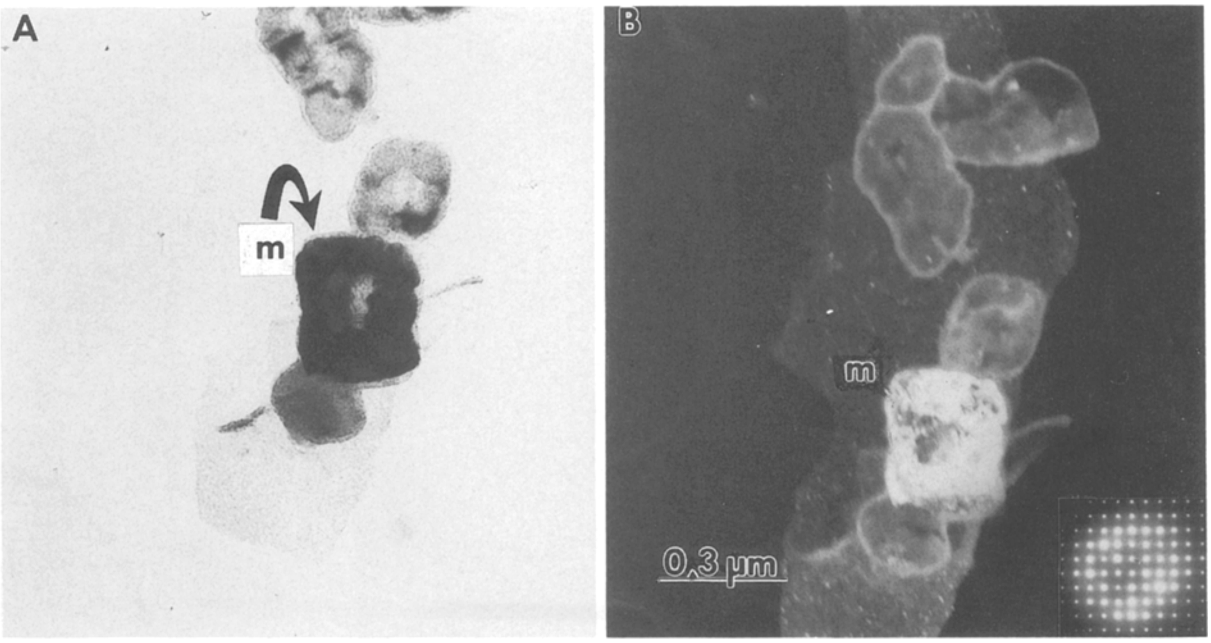

Figure 6 (A) Bright field (B) dark field and corresponding single crystal [0 0 1] zone diffraction pattern showing the presence of mullite (marked *m*).

thin layer of gold which acted as an internal standard. The analysis revealed the crystallites to be a spinel phase very close in lattice parameter ($a = 7.88$ nm) to that reported by Brindley and Nakahira [3] and several other researchers subsequently (e.g. Ref. 6). As is evident in the dark field micrograph (Fig. 4) the crystallites are very small in size (10–50 nm). This is further substantiated by the high magnification images (Fig. 5) which show some contrast on defocussing, but no crystallites can be resolved. At the same temperature, some mullite single crystals (Fig. 6a) were also observed, (marked *m*). This was confirmed by diffraction and dark field imaging (Figs. 6b and *inset*). These single crystals were much larger in average grain size than the spinel crystallites.

Energy dispersive X-ray spectroscopy revealed the spinel phase to have a composition very close to that of mullite (Fig. 7). On heating to temperatures beyond the second exothermic peak, the transformation to mullite goes to completion and acicular crystals of mullite such as in Fig. 8 form. The mullite crystals thus formed tend to have texture in that the *c*-axis lies out of the plane. This is understandable in terms of the fact that metakaolinite consists of sheets of alumina and silica tetrahedra and the mullite forms on these sheets. The *c*-axis is the smallest dimension of the

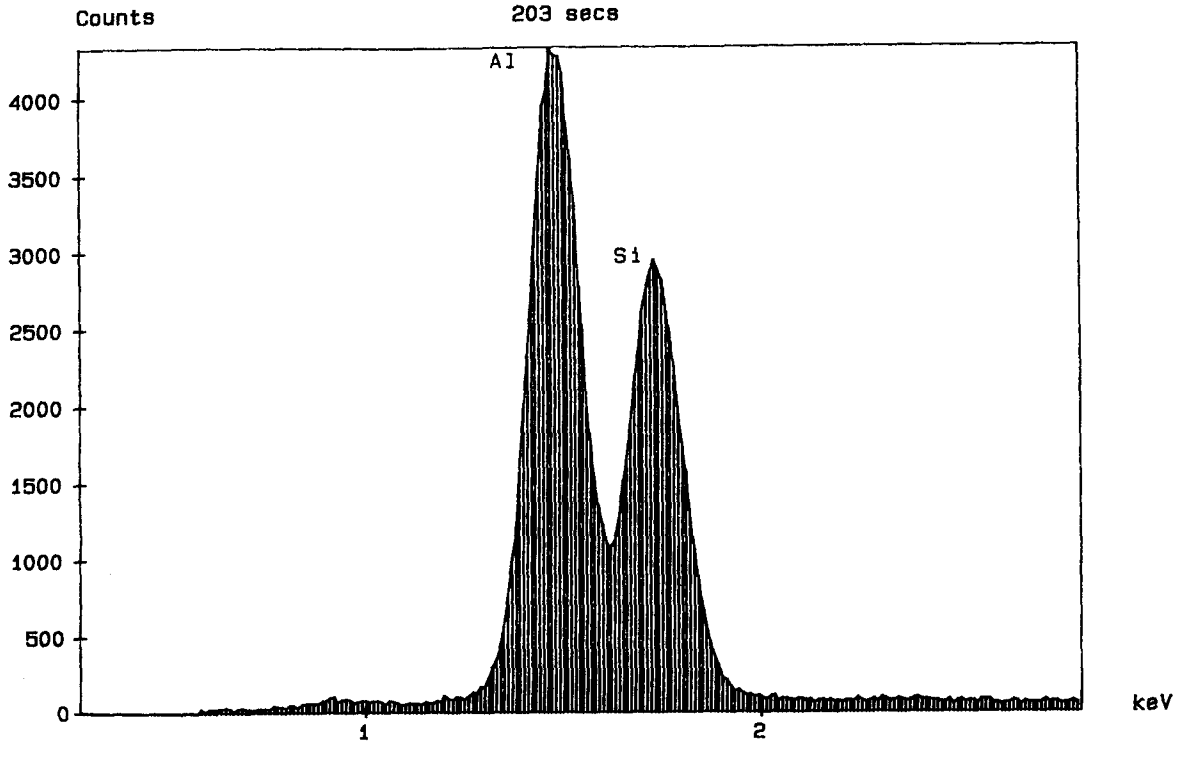

Figure 7 EDX spectrum showing the presence of alumina and silica in the spinel phase.

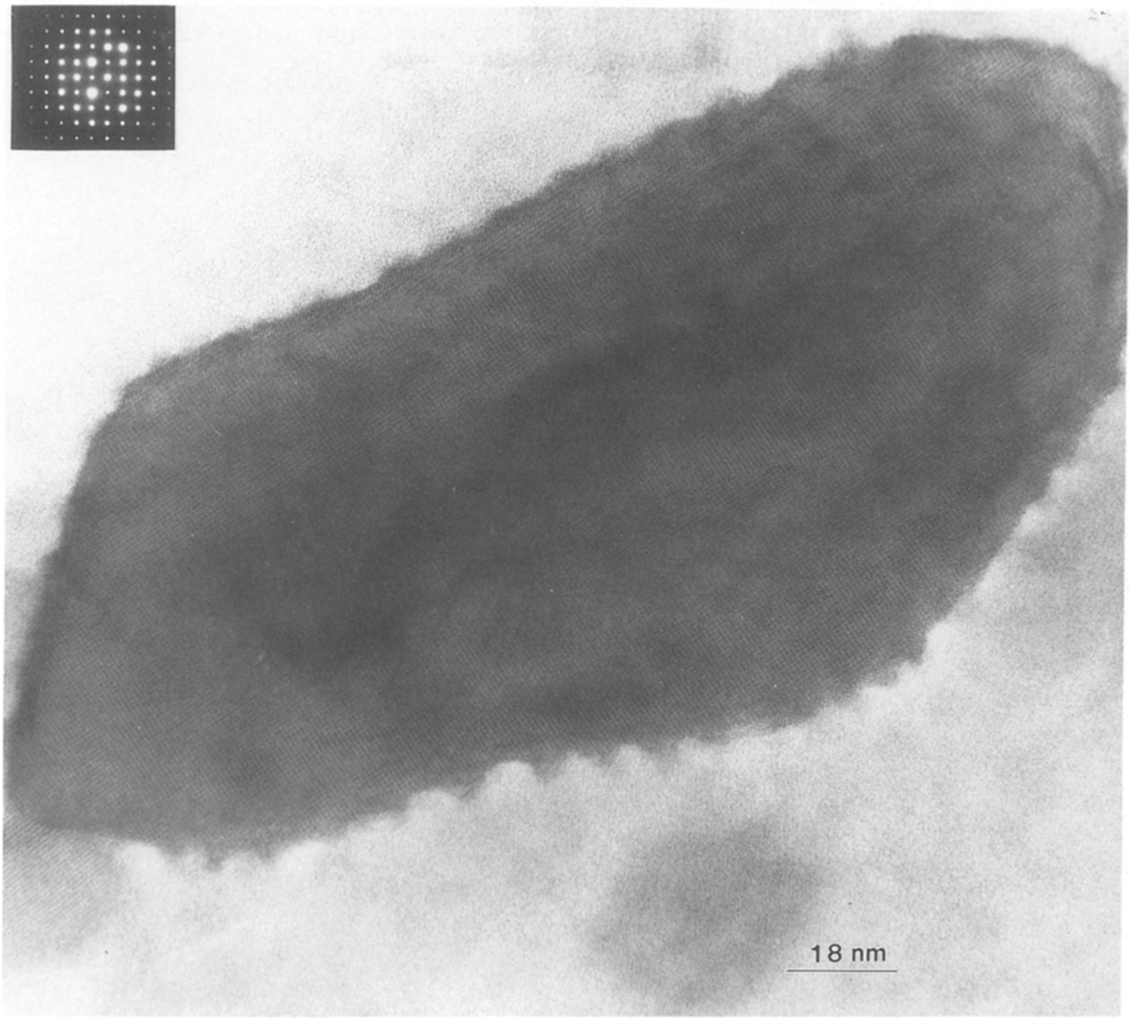

Figure 8 High resolution electron micrograph taken at 1200° C showing the formation of mullite and the corresponding SAD pattern (*inset*).

mullite unit cell. Therefore, energetically it would be favourable for it to lie perpendicular to the plane of the *meta*-kaolinite sheets.

4. Discussion

The two central questions in this reaction series are in relation to the structure and composition of the phase that forms around 980° C. The diffraction studies in this work unequivocally establish that the first phase to form is a spinel phase. This is in agreement with the recent findings of Sonuparlak *et al.* [6]. However these authors contend that the composition of this spinel phase is near that of pure γ-alumina. The technique used to determine the composition plays a crucial role in determining the answer to this question. These authors, as in this study, have etched the transformed *meta*-kaolinite with NaOH for various lengths of time. However the first crystallites to form at 980° C are very small as seen in Fig. 4 and therefore possess a very large surface to volume ratio. Prolonged etching would therefore necessarily lead to silica free compositions.

In this study, the fact that mullite crystals are observed simultaneously at 980° C (though in a much smaller fraction) with the spinel phase and the EDX results, together, support the contention that the spinel phase has a composition near that of mullite. The recent work of Sanz *et al.* [7] with ^{27}Al and ^{29}Si MAS-NMR indicated the presence of tetrahedral lines characteristic of mullite further substantiating our result.

5. Conclusions

Direct transmission electron microscopy observations of the kaolinite–mullite transformation series in single crystal kaolinite shows that the first exothermic reaction at 980° C is due to the formation of a spinel phase. A small amount of disordered mullite is also observed and both the spinel and mullite possess a chemical composition close to that of 3 : 2 mullite. Beyond the second exothermic peak, acicular mullite crystals are formed with the *c*-axis perpendicular to the original *meta*-kaolinite sheets.

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References

1. H. INSLEY and R. H. EWELL, *J. Res. Natl. Bur. Stand.* **14** (1935) 615–27.
2. R. ROY, D. M. ROY and E. E. FRANCIS, *J. Amer. Ceram. Soc.* **38** (1955) 198–205.
3. G. W. BRINDLEY and M. NAKAHIRA, *ibid.* **42** (1959) 311–324.
4. A. K. CHAKRABORTY and D. K. GHOSH, *ibid.* **61** (1978) 170–173.
5. K. J. D. MACKENZIE, I. W. M. BROWN, R. H. MEINHOLD and M. E. BOWDEN, *ibid.* **68** (1985) 293–301.
6. B. SONUPARLAK, M. SARIKAYA and I. A. AKSAY, *J. Amer. Ceram. Soc.* **70** (1987) 837–842.
7. J. SANZ, A. MADANI, J. M. SERRATOSA, J. S. MOYA and S. DE AZA, submitted to *J. Amer. Ceram. Soc.*
8. S. M. JOHNSON, J. A. PASK and J. S. MOYA, *ibid.* **65** (1982) 31.
9. J. A. HORNOR, W. A. MARTINEZ and V. A. GREENHUT, private communication.
10. S. M. JOHNSON and J. A. PASK, *Amer. Ceram. Soc. Bull.* **61** (1982) 838–842.

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