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Planar [00.*l*] disorder in sodium beta alumina

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00.*l* and 01.*l* lattice images are used to show the presence of [00.*l*] disorder in β alumina. It is shown that both stacking sequence faults and β'' intergrowth are present. The faults are believed to be introduced in the early stages of sintering when spinel block ledges are added out of sequence during growth in the [00.*l*] direction. The observations show that the planar disorder observed by Bevan *et al.* [4] cannot be attributed solely to heterophase intergrowth.

1. Introduction

Transmission electron microscopy of polycrystalline sodium beta alumina readily reveals that this solid electrolyte contains a multitude of imperfections. Dislocations in the basal place were observed by Stevens [1]; complex faults resulting from partial dislocation climb or order–disorder transformations were reported by De Jonghe [2] and be LeCars *et al.* [3]; β'' intergrowth was described by Bevan *et al.* [4]; low-angle tilt boundaries revealing dislocation of the type $\frac{1}{2}[00.l]$ were discussed by De Jonghe [5]. In this paper we discuss further the [00.*l*] disorder that leads to the formation of (00.*l*) planar faults between the spinel blocks [6] of the sodium beta alumina structure. In particular, we report some observations with 00.*l* and 01.*l* lattice images that distinguish between β'' intergrowth and stacking sequence faults between the spinel blocks.

2. Experimental

Polycrystalline specimens of sodium beta alumina were prepared by pressureless sintering in air at 1750° C. In some samples silica was added as sodium silicate prior to sintering*. Electron transparent foils were prepared by ion milling. The foils were observed in a Siemens 101B transmission electron microscope operating at 125kV.

3. Planar disorder and heterophase intergrowth

To simply represent the spinel block planar disorder in the [00.*l*] direction of sodium β and β'' alumina the following symbolism is adopted:

$$\ldots AA'AA'AA' \ldots\!: \text{Na } \beta \text{ alumina}$$

where A is the oxygen plane sequence (ACBA) and A′ is the oxygen plane sequence (ABCA) in the spinel blocks, and

$$\ldots ABCABCA \ldots\!: \text{Na } \beta'' \text{ alumina}$$

where A is the oxygen sequence (ACBA), B is the oxygen sequence (BACB), C is the oxygen sequence (CABC) in the spinel blocks. Each letter thus represents a particular spinel block in this symbolism. One must further distinguish between stacking sequence faults† (SSF) of the type

$$\underset{\text{SSF}}{AA'AA'A/AA'AA'}$$

and a fault produced by a partial dislocation of the type $a/6\langle 1\,1\,\bar{2}\,0\rangle$ between two adjacent spinel blocks. Indeed, an $a/6\langle 1\,1\,\bar{2}\,0\rangle$ translation does not transform A into A′, B or C, since a rearrangement of the oxygen and aluminium ions is necessary to achieve such transformation.

*The effect of silica on sodium beta alumina solid electrolyte properties will be reported shortly.
†The SSF fault is identical to a reflection twin boundary.

The $a/6\ \langle 1\,1\,\bar{2}\,0\rangle$ translation between two spinel blocks will produce a cation fault only. Faults of this type have been discussed by De Jonghe [2] and by LeCars *et al.* [3] when they occur in planes normal to the basal plane. These fualts were termed "complex planar faults". In the present case the habit plane of these faults is the conduction plane. To distinguish these faults from a stacking fault involving the oxygen lattice, we will call it a CP fault. The presence of a fault of the type $a/6\ \langle 1\,1\,\bar{2}\,0\rangle$ (CPF) is then indicated by a subscript, as for example in

$$\underset{\text{CPF}}{\mathrm{AA'AA'/A_1A_1'A_1A_1'}}$$

where A and A_1 or A' and A_1' only differ in the cation positions. If the above notation is adopted, it is possible to describe $[00.l]$ spinel block disorder in a simple manner.

(1) CP fault (lowest energy fault)

$$\underset{\text{CPF}}{\mathrm{\ldots AA'AA'/A_1A_1'A_1A'\ldots}}$$

(2) Stacking sequence faults: SSF

(a) Low energy (nearest neighbour fault only)

$$\underset{\text{SSF}}{\mathrm{AA'AA'A/AA'AA'AA'}}$$

(b) Higher energy faults. This involves combinations of SSF and CPF.

$$\underset{\text{SSF + CPF}}{\mathrm{AA'AA'A/A_1A_1'A_1A_1'A_1A_1'}}$$

(3) Disorder involving β'' intergrowth

(a) Low energy intergrowth

$$\mathrm{AA'AA'\underline{ABC}AAA'A'\ldots}$$
$$\beta \quad \beta \quad \beta'' \quad \beta \quad \beta$$

This is a low energy β'' intergrowth in β, since no nearest neighbour spinel block faults are present.

(b) High energy intergrowth – This disorder involves the combination of β'' intergrowth and CPF faults or stacking sequence faults. examples are:

$$\mathrm{AA'AA'/\underline{A_1B_1C_1}A_1A_1'A'A_1'\ldots}$$
$$\beta \quad \beta\text{CPF} \quad \beta'' \quad \beta \quad \beta$$

$$\mathrm{AA'AA'\underline{ABC}/A'AA'A\ldots}$$
$$\beta'' + \text{SSF}$$

$$\mathrm{AA'AA'/\underline{BCA}/AA'AA'\ldots}\quad \text{etc.}$$
$$\text{SSF} \quad \beta'' \quad \text{SSF}$$

We do not consider the possibility of β''' intergrowth at this time.

Planar disorder of the type described above arises most likely in the early stages of sintering when "spinel block" ledges are added during thickening of a crystallite in the $[00.l]$ direction. During subsequent growth of this crystallite in basal plane directions the faults that were produced will continue to grow with the crystallite. We believe evidence of such a process can be seen

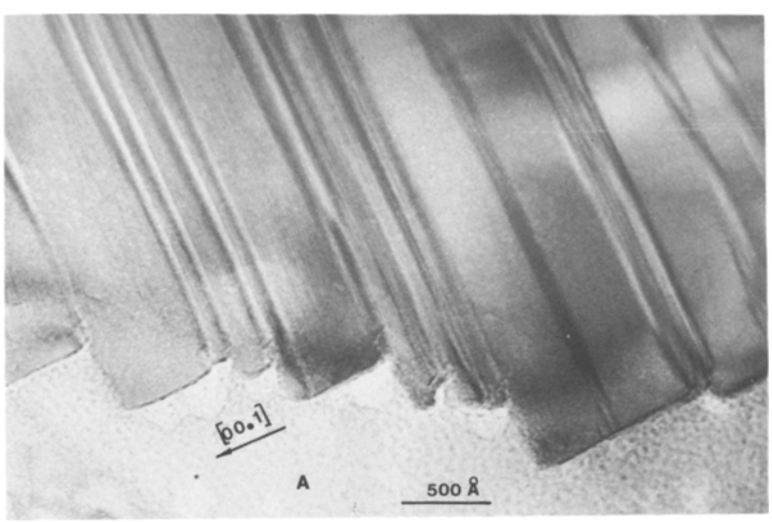

Figure 1 Stepped β/silicate interface in silica containing sodium β alumina. Note that the planar $(00.l)$ faults correlate with the steps in the β/silicate interface. The silicate phase is marked A.

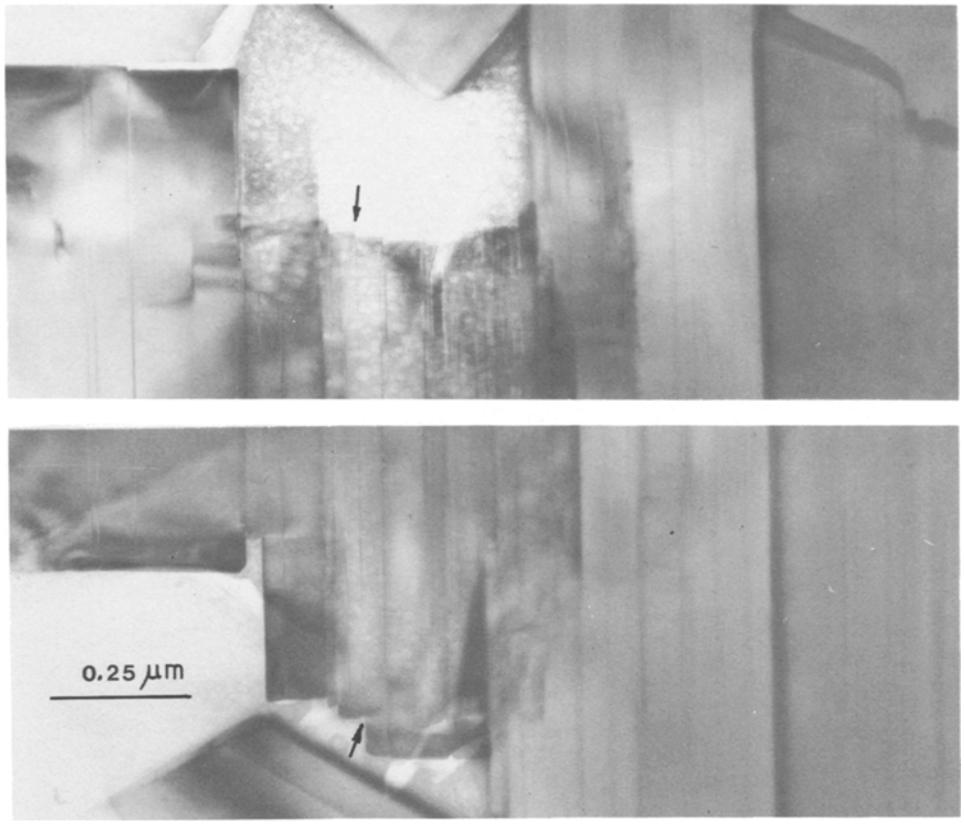

Figure 2 The steps on opposite sides of the same β alumina grains do not match in magnitude. One such offset is marked with an arrow. This indicates that the different grain segments are produced in the early stage of growth, and are not the result of extensive slip.

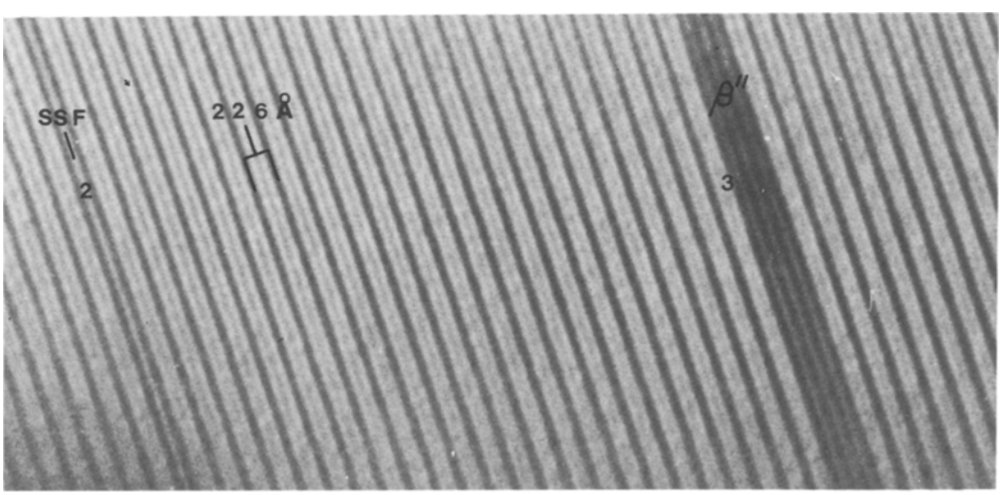

Figure 3 High resolution 00.*l* lattice imaging showing different nature of faults 2 and 3. A consistent interpretation of the images shows that 3 is β'' intergrowth, while 2 is a stacking sequence fault.

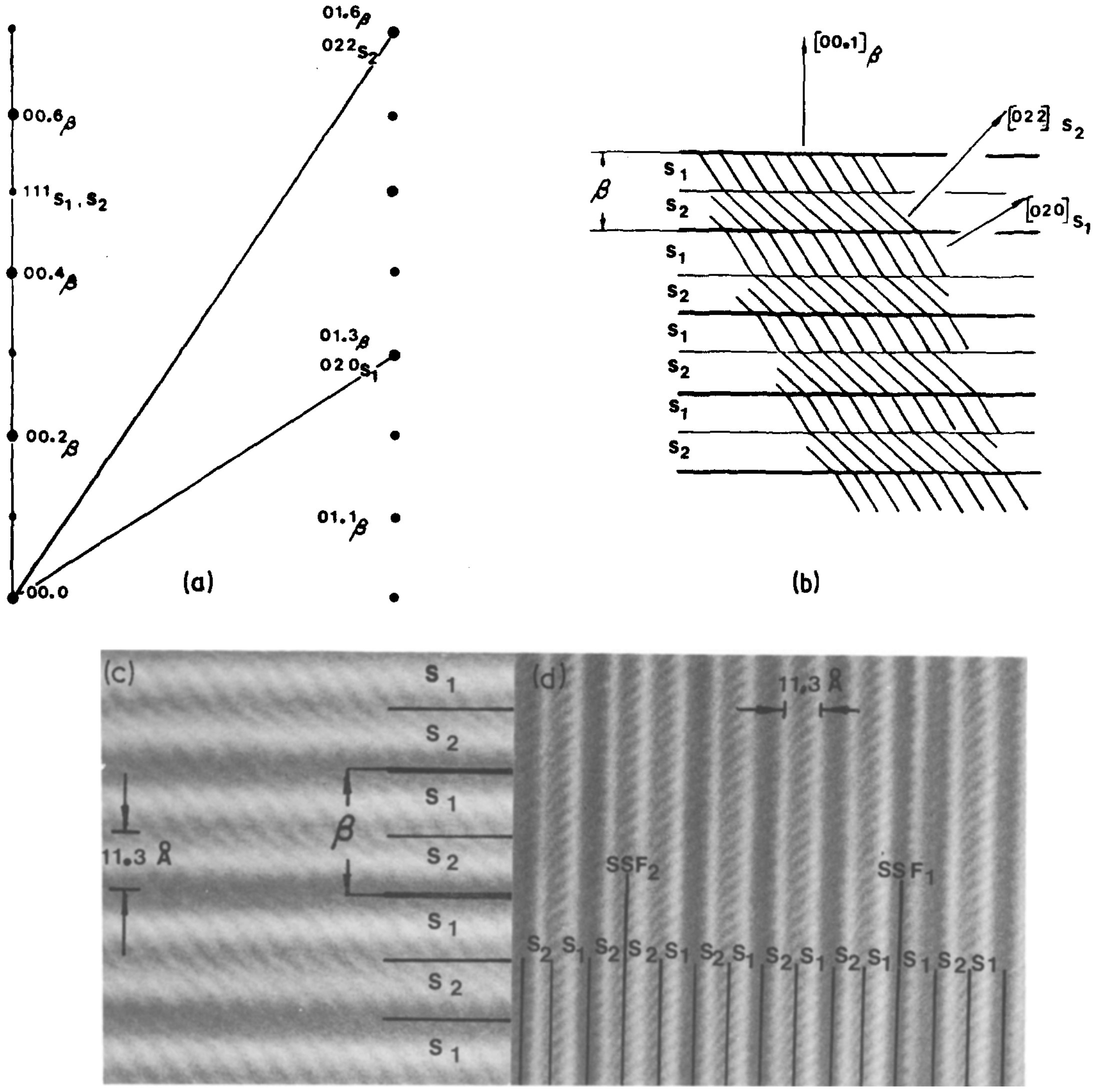

Figure 4 (a) Diffraction pattern labelled with the corresponding spinel block indices. (b) Expected fringe spacings and directions in the spinel blocks S_1 and S_2 of the β unit cell. (c) Experimental image with $00.l$ and 01.3_β $(=020_{S_1})$ and 01.6_β $(=022_{S_2})$ operating. (d) Two stacking sequence faults of opposite nature observed under the above diffracting conditions.

in the silica containing electrolyte. When silica is present in sodium beta alumina a glassy intergranular silicate phase is formed which is liquid at the sintering temperature, and which accumulates between grains as they grow. In many cases this silicate will prevent the direct contact of β alumina grains, revealing the shape of the unconstrained β/glass interface. Such an interface is shown in Fig. 1. The silicate phase is marked A in this micrograph. Note the stepped nature of this growth interface. Continuity of the Bragg extinction contours in such crystals indicates that the crystallite orientation is the same throughout, and that no rotations around $[00.l]$ occur at the faults. The steps in the growth interface correlate with faults. They are produced during the growth of the crystallites, and are not the result of extensive slip. This can be deduced from the block offsets which do not match in magnitude and direction on the opposite sides of the β alumina grains, as is shown in Fig. 2.

It is posssible, by an appropriate combination of diffracting conditions, crystal thickness, and defocus, to form lattice images which can elucidate the nature of the faults. Gratias *et al.* [7] have discussed how β'' can readily be distinguished from β alumina with direct lattice imaging of $00.l$ type reflections. If the β alumina is, for example, in an orientation containing $00.l$ and $01.l$, the double diffraction effects will produce the normally forbidden 00.1 reflection, leading to a fringe spacing of 22.6 Å rather than 11.3 Å. For β'' such effects cannot occur, and it shows 11.3 Å fringes even for thicker crystal foils. A one unit cell intergrowth of β'' in β can thus be observed as a set of identical 11.3 Å fringes next to the 22.6 Å fringes of the β alumina. A fault marked 3 in Fig. 3 is then identified as a β'' intergrowth. The fault marked 2 is, however, of a different nature. It is demonstrated below that the dark fringes may be associated with spinel blocks of the same types, indicating that fault 2 is stacking sequence fault.

In Fig. 4a to d we consider the lattice images of β when $00.l$ is operating together with 01.3 and 01.1. The diffraction pattern is shown in Fig. 4a. It is useful to consider the β reflections in terms of the cubic indices of the respective spinel blocks S_1 and S_2 that would have a lattice parameter of 8.06 Å. The $00.l_\beta$ then corresponds to the common 1 1 1 directions of S_1 and S_2.

However, owing to the different oxygen stacking sequences in S_1 and S_2, the 020_{S_1}, corresponding to 01.3_β, is not identical to 020_{S_2}, and 022_{S_2} corresponding to 01.6_β is not identical to 020_{S_1}. The diffraction pattern thus has to be labelled as shown in Fig. 4a. The 020_{S_1} and 022_{S_2} fringes that should then show under the given diffracting condition are shown in Fig. 4b. The corresponding experimental lattice image is shown in Fig. 4c. It is evident from this image that it is valid to interpret the $00.l$ lattice fringes as if S_1 is associated with the dark $00.l$ fringe, and as if the lighter fringe is associated with S_2. The faults shown in Fig. 4d, imaged with identical diffracting conditions can thus be unambiguously interpreted as SSF faults, and are not a β'' intergrowth. Specifically, the fault SSF_1 is of the opposite type of fault SSF_2, i.e. fault 1 is of the type AA′A/AA′AA′, where $S_1 \equiv A$ and $S_2 \equiv A'$, while fault 2 is of the type AA′AA′/A′AA′AA′. This then clearly demonstrates the presence of stacking sequence faults in β alumina, and the validity of the interpretation of the fault labelled 2 in Fig. 3. It is interesting to note that the complex faults, reported earlier by De Jonghe [2]; and by LeCars *et al.* [3]; having a displacement vector of the type $a/6\ \langle 1\,1\,\bar{2}\,0\rangle$, often are seen to terminate on the planar disorder faults described here. This is shown clearly in Fig. 5, where some terminations have been marked with an arrow, indicating the possi-

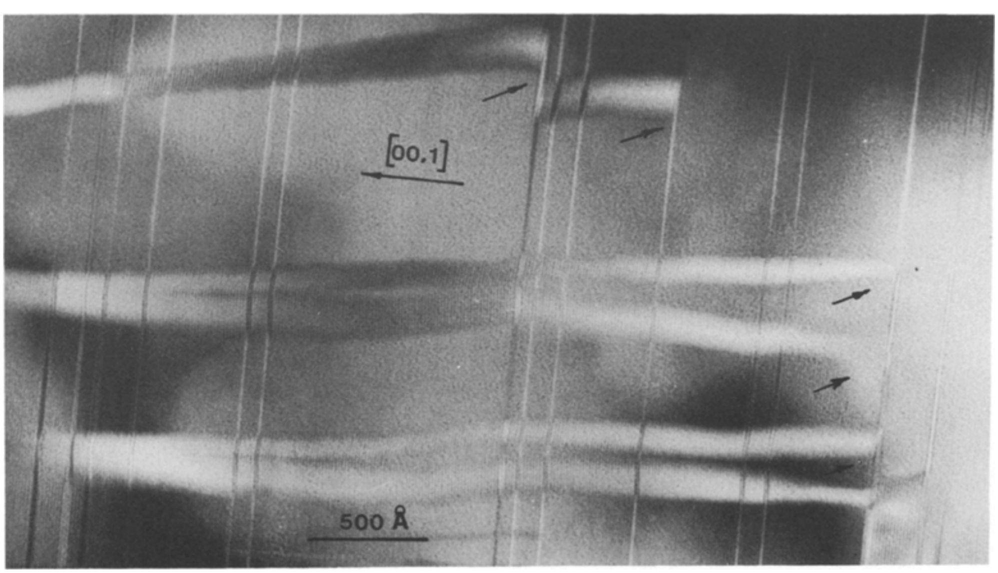

Figure 5 Complex faults of the type $a/6\ \langle 1\,1\,\bar{2}\,0\rangle$ terminating on $[00.l]$ disorder faults indicating the possibility of higher energy faults involving CPF with SSF and β'' intergrowth. Bright-field image.

bility of the presence of higher energy faults involving combinations of CPF with β'' or SSF planar [00.l] disorder.

4. Conclusions

It has been shown that not all planar [00.l] disorder as observed by Bevan *et al.* [4], has to be attributed to the presence of β'' intergrowth. From our observations it seems that stacking sequence faults are at least as likely as β'' intergrowth. We attribute the formation of such planar [00.l] disorder in sodium beta alumina to the early stages of sintering when spinel block ledges are added out of sequence during 00.l growth.

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