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An electron microscopic investigation of oxides related to ß-alumina*

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High resolution electron microscopic (HREM) investigation of potassium β-alumina and the related gallate and ferrite has revealed that whereas the aluminate and gallate are highly disordered, consisting of random sequence of β and β'' units, the ferrite is more ordered. The aluminate and gallate are sensitive to electron beam irradiation exhibiting beam-induced damage similar to sodium β''-alumina. Significantly, the ferrite is beam-stable, the difference in behaviour amongst these related oxides arising from the different mechanisms by which alkali metal nonstoichiometry is accommodated. Barium hexa-aluminate and hexaferrite are both highly ordered; specimens prepared by the barium borate flux method exhibit a new $\sqrt{3}a \times \sqrt{3}a$ superstructure of the hexagonal magnetoplumbite cell.

1. Introduction

Ceramic oxides collectively known as β-aluminas and possessing the ideal formula $MAl_{11}O_{17}$ (M = Na, K, Ag etc.) crystallize in a layered structure comprising spinel slabs, four oxygens thick, separated by conduction planes containing M atoms and oxygen [1–3]. Two variants of this structure are common, β and β'', crystallizing respectively in the hexagonal and rhombohedral systems. In the β-structure, the spinel slabs are superimposed in such a way that the conduction plane is a mirror plane; in the β''-structure, the spinel slabs are rotated 120° with respect to each other and the conduction plane is not a mirror plane. Sodium-containing β-aluminas have been investigated by a variety of techniques because of their importance as fast sodium ion conductors [3, 4]. Although the ideal composition of sodium β-alumina is $NaAl_{11}O_{17}$, the actual composition varies between $Na_2O:5.33Al_2O_3$ and $Na_2O:8.5Al_2O_3$. β''-alumina, which is also composed of a stacking of spinel slabs of the same type as in β-alumina, is metastable being stablilized by small quantities of magnesium or lithium; the composition range of sodium β''-alumina is $Na_2O:7Al_2O_3$–$Na_2O:8.5Al_2O_3$. Electron microscopic investigations [5–7] of sodium β- and β''-aluminas have revealed several interesting structural features which include $(0\,0\,l)$ intergrowth between β- and β''-aluminas, presence of spinel blocks of different widths, stacking faults and dislocations. A high-resolution electron microscopic (HREM) study of β''-alumina [8, 9] has revealed a new type of "blocking" defect which hinders sodium ion conduction. This study has also shown that the material is sensitive to electron beam irradiation resulting in an exodus of Na_2O followed by collapse of the structure.

Electron microscopy carried out hitherto on β-aluminas has been essentially confined to sodium-containing systems and there has been little or no work reported on isostructural ferrites and gallates. We considered it most worthwhile to carry out a comparative HREM study of such a family of isostructural solids. In the present paper, we describe a systematic study of potassium β-alumina and the corresponding gallium and iron derivatives. In view of the close structural relationship

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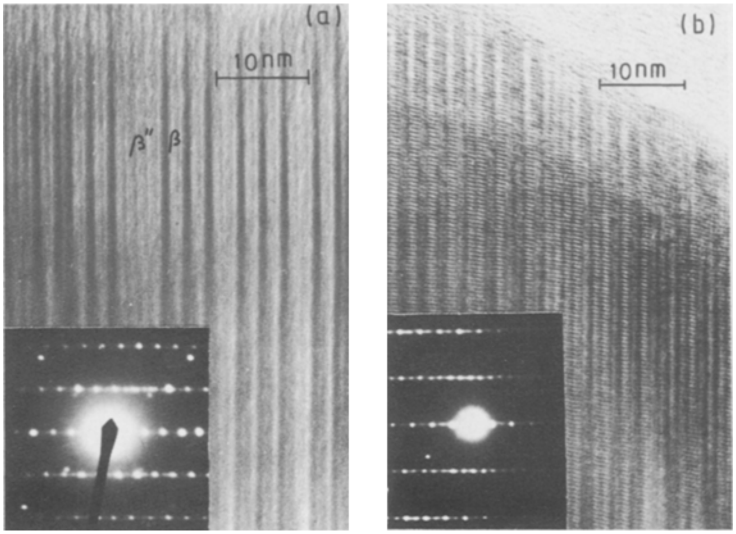

Figure 1 Electron microscopic images of crystals of potassium β-alumina (a) and sodium β-alumina (b) recorded with beam parallel to [100]. Disordered sequence of β and β'' units is seen. Insets show the respective diffraction patterns.

existing between β-alumina and barium aluminate and ferrite possessing the magnetoplumbite structure [10, 11], we have also investigated barium hexa-aluminate and barium hexaferrite for purpose of comparison. The present studies have revealed several interesting features of the solids investigated.

2. Experimental techniques

Potassium aluminate and potassium ferrite corresponding to the nominal composition $K_{1.6}M_{11}O_{17.3}$ (M = Al or Fe) were prepared by decomposing the respective nitrate mixtures taken in the required molar proportion, followed by sintering the solid mass at 1570 K for 24 h. Potassium gallate (nominal composition $K_2O \cdot 5Ga_2O_3$) was prepared [12] by reacting potassium oxalate and Ga_2O_3 at 1470 K for 12 h. X-ray powder diffraction revealed that, while the aluminate and the ferrite were mainly of the β-type, the gallate was of the β''-type. Lattice parameters of the three preparations are listed in Table I. Attempts to prepare a sample of potassium β-gallate by heating the components at 1770 K [12] resulted in considerable volatilization of potassium, the solid residue being mainly Ga_2O_3.

TABLE I Unit cell parameters of potassium β-alumina, β-ferrite and β''-gallate

Nominal composition	a (nm)	c (nm)
$K_{1.6}Al_{11}O_{17.3}$	0.560	2.276
$K_{1.6}Fe_{11}O_{17.3}$	0.588	2.374
$K_{2.2}Ga_{11}O_{17.6}$	0.582	3.520

A JEOL JEM-200 CX transmission electron microscope, operated at 200 kV and equipped with ultra high-resolution objective pole piece ($Cs = 1.2$ mm) in the top-entry configuration, was used in the present study. Crystallites were dispersed in a holey carbon grid by standard technique. Thin crystals projecting through the holes in the carbon grid were selected and brought to the required orientation using the goniometer. Through-focus images with defocus values up to 100 nm were recorded at a primary magnification from 3×10^5 to 5×10^5. A 40 μm objective aperture was used to combine the primary beam with about 30 diffracted beams to produce the image.

3. Results and discussion

3.1. Potassium β-alumina and the corresponding gallium and iron derivatives

Selected-area electron diffraction and lattice imaging reveal that both potassium β-alumina and -gallia are highly disordered. The diffraction pattern, obtained with the beam parallel to [100], of an aluminate crystal (Fig. 1a) shows strong spots with a 1.15 nm periodicity in the c^*. In between strong spots there is considerable streaking and, in certain regions, clear superlattice spots corresponding to larger periodicities are seen. The corresponding image (Fig. 1a) reveals that the structure is nonuniform in the c-direction. The image is similar to the once-dimensional (00*l*) image of sodium β-alumina reported by Bovin and O'Keeffe [13] consisting of dark and white contrast. The β and β'' regions can be readily identified

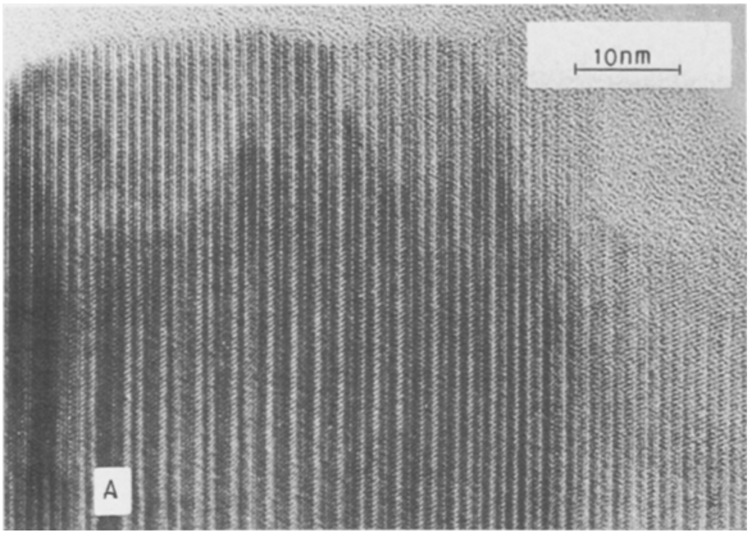

Figure 2 HREM image of a crystal of potassium β-alumina recorded with the beam parallel to [100]. A "blocking" defect is seen in the region marked A.

from the contrast. The β structure shows alternating dark and light contrast while β'' shows uniform contrast for the spinel slabs. We see from the image (Fig. 1a) that the β and β'' sequences are present randomly across the crystal. For purpose of comparison, we have recorded an image of sodium β-alumina (Fig. 1b) which shows similar features.

Fig. 2 shows the image of another crystal of potassium β-alumina, again revealing considerable disorder in the stacking sequence across the crystal. Bovin [8, 9] has shown that images of thin crystals obtained with an underfocus of about 60 to 100 nm exhibit the right contrast betweeen the spinel slabs and the conduction planes, the spinel slabs appearing as dark fringes and the conduction planes as white lines in between. The image given in Fig. 2 shows this type of contrast at the edge where the crystal is thin. In region A of this picture, we see two white lines from the top (edge) disappearing as we go down. This feature probably represents a "blocking" defect of the type seen by Bovin [8, 9] in β''-alumina.

We have investigated the effect of electron beam irradiation on potassium β-alumina by irradiating the crystal for about 10 min in the microscope. Fig. 3 is the image after irradiation of the crystal whose image was shown in Fig. 2. The picture shows that the crystal is considerably damaged due to beam irradiation. We see regions of extreme dark and white contrast in the image coexisting side by side. In bands of dark contrast,

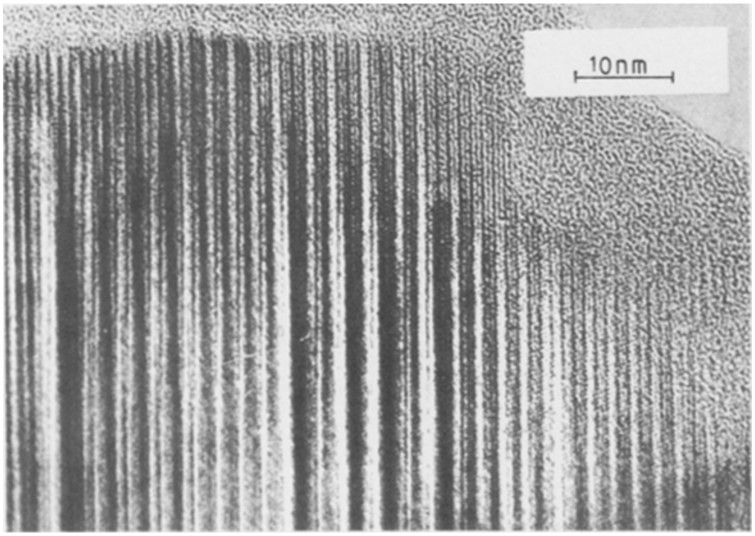

Figure 3 HREM image of the crystal shown in Fig. 2 after ~ 10 min of electron beam irradiation.

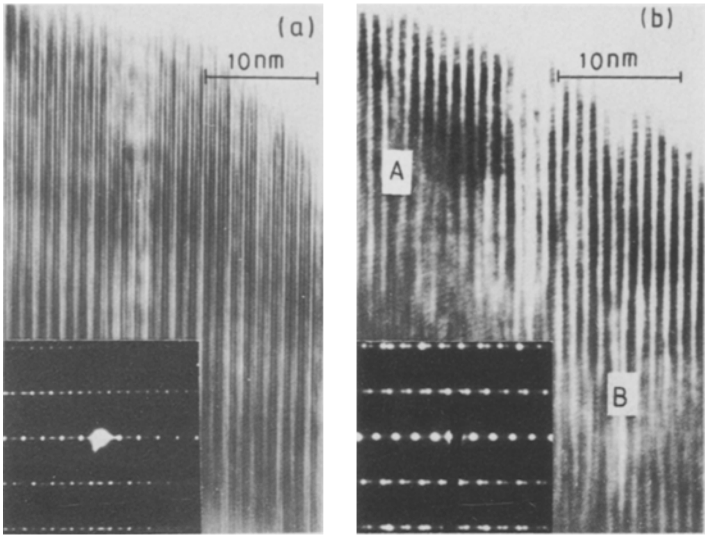

Figure 4 (a) HREM image of a crystal of potassium β''-gallate showing considerable disorder. The beam direction is parallel to [1 0 0]. (b) HREM image of a crystal of potassium β''-gallate showing "blocking" defects in the regions marked A and B.

we see the disappearance of white fringes (conduction planes) on going from the edge to the interior. The feature probably corresponds to electron beam-induced removal of K_2O from the conduction planes, forming thicker spinel slabs, the behaviour being similar to that reported by Bovin [8, 9] in sodium β''-alumina. It is, however, significant that the damage caused by beam irradiation is selective, being restricted to those regions of the crystal which are already defective consisting of "blocking" defects and so on.

Potassium gallate shows a behaviour similar to potassium β-alumina. Crystals of the gallate are highly disordered showing a random sequence of β and β'' units (Fig. 4a), the latter being in larger proportion. Fig. 4b shows the image of another crystal of the gallate where we clearly see the presence of "blocking" defects in the regions marked A and B. Potassium gallate also undergoes beam-induced damage just as the β-alumina.

Potassium ferrite exhibits a different behaviour from the aluminate and the gallate. Electron diffraction and microscopy reveal that the crystals are more ordered consisting of a regular sequence of either β or β'' units. In some crystals, the two units are found to intergrow coherently. Fig. 5 shows the diffraction pattern and image of one such crystal. The diffraction pattern shows two sets of spots, one corresponding to the β-structure and the other to the β''-structure. The corresponding image (Fig. 5) reveals fringes with ~ 2.3 nm periodicity (β) as well as ~ 1.15 nm

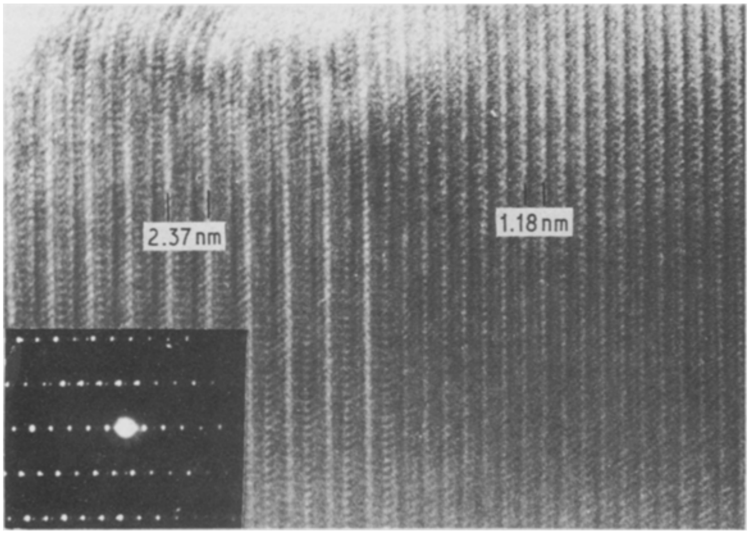

Figure 5 HREM image of a crystal of potassium β-ferrite exhibiting $(0\,0\,l)$ intergrowth of β (left) and β'' (right) phases. Inset shows corresponding diffraction pattern.

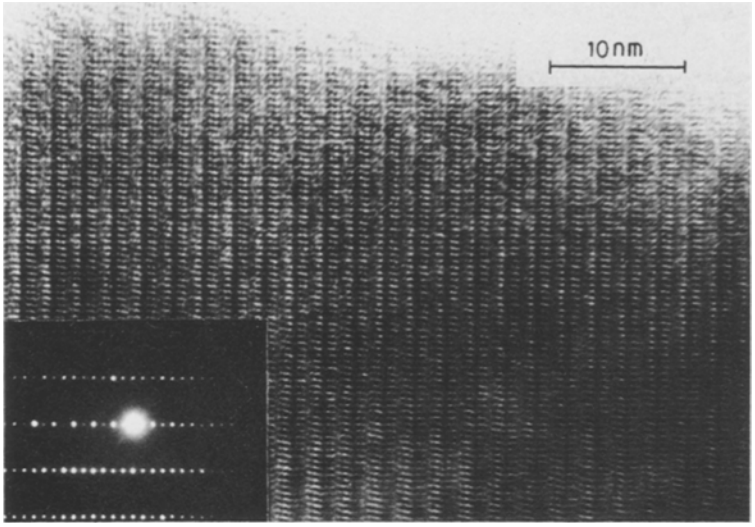

Figure 6 HREM image of a crystal of barium hexa-aluminate recorded with the electron beam parallel to [100], showing a regular periodicity of ~ 2.3 nm in the c-direction.

periodicity (β''). Unlike the aluminate and gallate systems, potassium ferrite crystals are stable to electron beam irradiation. Irradiation for 10 min produced no significant change in the image.

Differences in the structural behaviour of potassium aluminate and gallate, on the one hand, and potassium ferrite, on the other, may be traced to the different ways that these oxides accommodate nonstoichiometry, Dudley *et al.* [14] have shown that in $K_{1+x}Fe_{11}O_{17+x/2}$ ($0.09 < x < 0.65$), excess potassium ions in the conduction planes are charge-compensated by reduction of Fe^{3+} to Fe^{2+} in the spinel slabs. In the aluminate and gallate systems, alkali metal nonstoichiometry cannot obviously be accommodated by this mechanism. The work of Sato and Hirotsu [6] reveals that the existence of a solubility range for Na^+ in β- and β''-aluminas is due to a mixed intergrowth of spinel slabs of varying widths between the conduction planes rather than due to a change in sodium composition in the conduction planes.

Electron beam-induced damage of the aluminate and gallate phases probably arises from the removal of the alkali metal from the conduction planes. Bovin [8, 9] and Matsui and Horiuchi [15] have investigated the mechanism of electron beam-induced damage of sodium β''-alumina. The mechanism involves exodus of Na_2O from the conduction planes followed by collapse of the structure forming thicker spinel slabs. With β-ferrite the situation appears to be different: because of the possibility of easy reduction of Fe^{3+} to Fe^{2+}, beam irradiation probably results in reduction of Fe^{3+} in the spinel slabs rather than removal of alkali metal from the conduction planes. Accordingly, we do not see a change in the width of the spinel slabs on electron beam irradiation of potassium ferrite. A similar reduction cannot occur in the aluminate and the gallate obviously because Al^{3+} and Ga^{3+} cannot be easily reduced to the divalent state.

3.2. Barium aluminate and ferrite

As part of this study, we have investigated magnetoplumbite-type barium hexa-aluminate ($BaAl_{12}O_{19}$) and barium hexaferrite ($BaFe_{12}O_{19}$). Unlike the potassium aluminate, the structures of both barium hexa-aluminate and hexaferrite are highly ordered showing ~ 2.3 nm fringes in the images (Figs. 6 and 7). Specimens of the aluminate and ferrite prepared using barium borate flux, exhibit a new $\sqrt{3}a \times \sqrt{3}a$ superstructure of the magnetoplumbite cell, as revealed by selected-area electron diffraction. The lattice images of the superstructure phases do not, however, differ from the normal magnetoplumbite images. Iyi *et al.* [16], who have recently reported the formation of $\sqrt{3}a \times \sqrt{3}a$ superstructure in the barium hexa-aluminate system, have attributed it to the presence of two different kinds of Ba–O layers, normal and barium-rich, stacked alternately in the c-direction; the ordering of excess barium atoms at the anti-Beevers–Ross sites gives rise to the $\sqrt{3}a \times \sqrt{3}a$ supercell. We have found that the barium hexaferrite system behaves similarly to the barium hexa-aluminate system, forming the $\sqrt{3}a \times \sqrt{3}a$

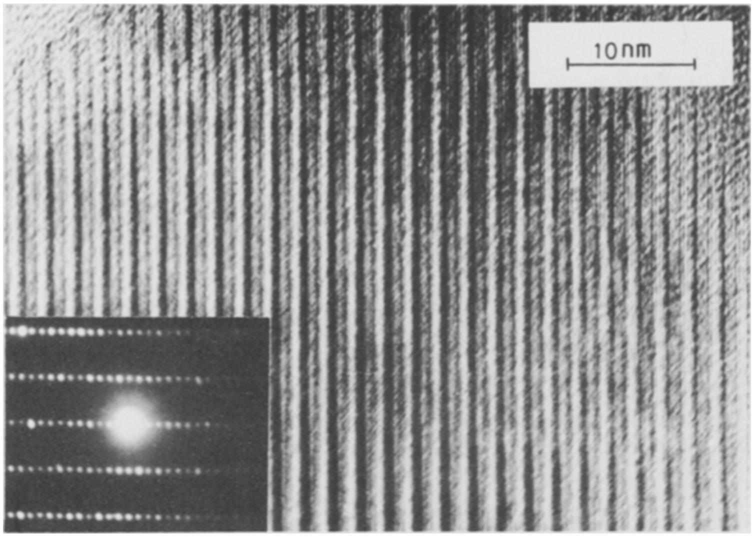

Figure 7 HREM image of a crystal of barium hexaferrite recorded with the electron beam parallel to [100], showing a regular periodicity of ~ 2.3 nm in the c-direction.

superstructure [17]. The new superstructure is formed in both the systems when the preparation is carried out under flux conditions with excess barium or similar ions (Pb^{2+}).

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