

# On the crystal structure of $\kappa$ -alumina

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**The idealized structure of  $\kappa$ -alumina is determined on the basis of lattice images by high-resolution electron microscopy and by applying crystallographic considerations and constraints of crystal chemistry.**

$\kappa$ -Alumina was first observed in X-ray powder diffraction spectra of dehydration products of gibbsite by Stumpf *et al.*<sup>1</sup> in 1950. The unit-cell parameters as well as the space group of  $\kappa$ -alumina remained undetermined until 1991 when Liu and Skogsmo<sup>2</sup> performed electron diffraction on  $\text{Al}_2\text{O}_3$  material generated by CVD. These authors determined the crystal system to be orthorhombic crystallising in the space group  $Pna2_1$ . The number of formula units is  $Z = 8$  and a stacking sequence ABAC of closed-packed oxygen layers is the only possible one to be in accordance with that space group. Later, the lattice parameters were determined more precisely by means of X-ray powder diffraction to be  $a = 0.4834$ ,  $b = 0.8310$ ,  $c = 0.8937$  nm by Halvarsson.<sup>3</sup> However, the crystal structure of  $\kappa$ - $\text{Al}_2\text{O}_3$ , *i.e.* the cation distribution, was unknown up to now.

In the present study,  $\kappa$ - $\text{Al}_2\text{O}_3$  was produced by internal oxidation of a Nb–Al alloy with 5 atom% aluminium under the following conditions:  $T = 1450^\circ\text{C}$ ,  $p(\text{O}_2) = 10^{-4}$  mbar,  $t = 30$  min. Using this method,<sup>4</sup> aluminium is internally oxidized to give  $\text{Al}_2\text{O}_3$  precipitates within the metallic (Nb) matrix. Besides the modifications  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\theta$ - $\text{Al}_2\text{O}_3$ , plate-like precipitates of  $\kappa$ - $\text{Al}_2\text{O}_3$  were observed using transmission electron microscopy (TEM). In the course of our TEM study we confirmed the results obtained by Liu and Skogsmo.<sup>2</sup> Furthermore, we were able to obtain high-resolution lattice images of  $\kappa$ - $\text{Al}_2\text{O}_3$  in different zone axes in order to obtain information on the (projected) cation distribution. The point-to-point resolution of 0.2 nm of the electron microscope (Philips CM30 SuperTwin, operated at 300 kV) does not allow the cations to be imaged separately. However, applying crystallographic considerations, the large amount of possible structural models can be reduced to only five structures, as outlined in the following.

Applying the ABAC stacking sequence and setting oxygen to (0,0,0), the positions of all the other oxygen ions in the idealized (undistorted) closed-packed anion sublattice are fixed. The  $b$  axis is parallel to a closed-packed direction in the oxygen layer and its length is three times the oxygen diameter. The  $a$  axis corresponds to the distance between two oxygen ions perpendicular to the closed-packed direction, while the  $c$  axis is parallel to the stacking direction of the layers (see Fig. 1). Since only one general position with multiplicity  $M = 4$  exists in  $Pna2_1$ , four oxygen sites are symmetrically equivalent leaving six of the 24 anions in the unit cell symmetry-independent. This results in six independent octahedral sites and twelve tetrahedral sites, respectively. Owing to the stoichiometry, four of these independent interstitial sites have to be occupied resulting in 3060 principally possible structures calculated by combination theory. (i) First we stipulate that the number of cations between the pairs of oxygen layers A–B, B–A, A–C, and C–A are identical. (ii) We can also exclude face-sharing and edge-sharing of  $\text{AlO}_4$  tetrahedra with other tetrahedra as well as with  $\text{AlO}_6$  octahedra, such elements do not exist in the structural chemistry of aluminium oxides. (iii) Since in aluminium oxides, aluminium preferentially occupies octahedral sites, a maximum value of 1:1 as the ratio of the occupied tetrahedral to

octahedral sites is assumed. (iv) Cation layers showing exclusively tetrahedral occupation do not exist in the known aluminium oxides, and can be definitely excluded.

Following the boundary conditions (i)–(iv) for the cation occupation, five of the 3060 possible structures for  $\kappa$ - $\text{Al}_2\text{O}_3$  remain. Structures I–IV show only octahedrally coordinated aluminium, whereas structure V exhibits octahedral and tetrahedral coordination of aluminium with a ratio of 3:1. The latter structure is the structure we propose for  $\kappa$ - $\text{Al}_2\text{O}_3$ . One indication of this structure is the spacing of 0.2234 nm of the closed-packed layers of  $\kappa$ - $\text{Al}_2\text{O}_3$ , which corresponds better with the value of 0.2284 nm in the spinel aluminas relative to the value of 0.2165 nm in corundum. An even more substantial indication are the values of the Coulomb energies calculated for the five possible structure models and for corundum using the MAPLE program package.<sup>5</sup> The Coulomb energies are as follows. Structures I–IV: 3846–4024 kcal mol<sup>-1</sup>. Structure V: 4232 kcal mol<sup>-1</sup>. Corundum: 4354 kcal mol<sup>-1</sup> (cal = 4.184 J).

The proposed structure of  $\kappa$ - $\text{Al}_2\text{O}_3$  is shown in Fig. 1. From this it can be deduced that the most promising orientation for determining the cation positions is lattice imaging along [100] because the channels in the structure can be imaged best. A lattice image of  $\kappa$ - $\text{Al}_2\text{O}_3$  along [100] is shown in Fig. 2. The image simulation for a crystal thickness of 3.9 nm and focus setting of  $-78$  nm shows very good matching with the observed image. Under these imaging conditions the brightest dots correspond to the channels between the octahedral double chains in the structure. The curved bright contrasts above represent the region of low atomic density, *i.e.* low scattering power along the chains of the  $\text{AlO}_4$  tetrahedra. The dark contrast in the image corresponds to a region of high scattering power, produced in particular by the Al atoms, and forming intersecting dark lattice fringes of the planes (011) and (0 $\bar{1}$ 1), respectively.

The crystal structure of  $\kappa$ - $\text{Al}_2\text{O}_3$  (Fig. 1) is isomorphous to that of  $\text{FeGaO}_3$ ,<sup>6</sup> where aluminium occupies the iron and

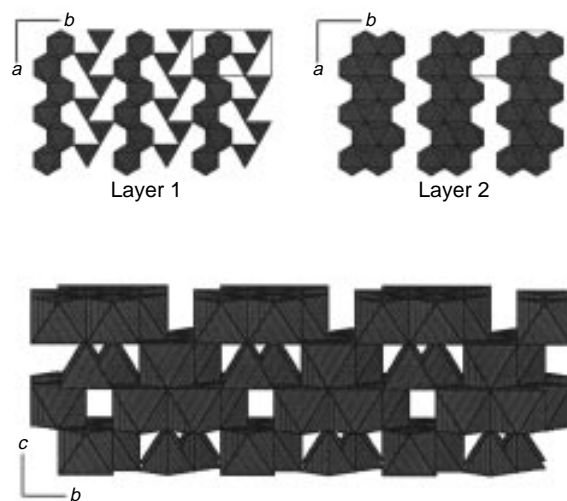
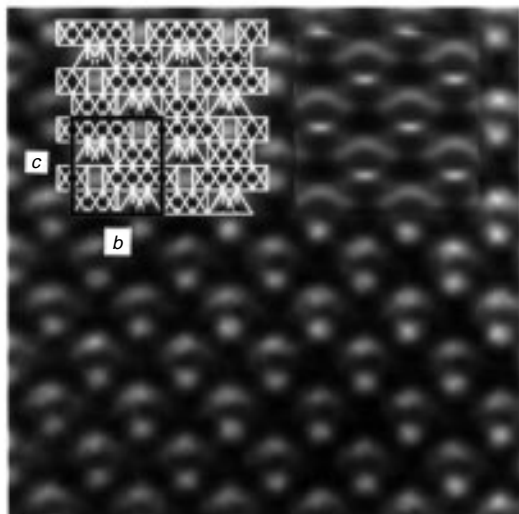


Fig. 1 The idealized crystal structure of  $\kappa$ - $\text{Al}_2\text{O}_3$

gallium sites in the iron gallium oxide structure. The structure can be described as constituted by two different layers 1 and 2, which are stacked alternately along the direction of the  $c$  axis. Layer 1 consists of single chains of edge-sharing  $\text{AlO}_6$  octahedra, which are connected *via* single chains of corner-sharing  $\text{AlO}_4$  tetrahedra. Layer 2 is built up by edge-sharing  $\text{AlO}_6$  octahedra, which are arranged as double chains parallel to



**Fig. 2** Lattice image of  $\kappa\text{-Al}_2\text{O}_3$  along  $[100]$  with inserted image simulation, aluminium atoms and unit-cell dimensions

the  $a$  axis, leaving channels of unoccupied octahedra in between. The repeat unit (length =  $c$  axis) contains four layers stacked as  $121'2'$ , where the layers  $1'$  and  $2'$  are distinguished from the layers 1 and 2 by a rotation of  $180^\circ$  around the  $2_1$ -screw axis. In this structure the channels of unoccupied octahedra in layer 2 are bridged by the chains of tetrahedra of the adjacent layer 1.

Further examinations using quantitative electron diffraction are currently being performed in order to evaluate the exact atomic coordinates of  $\kappa\text{-Al}_2\text{O}_3$ .

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