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Dunbar P. Birnie III

Department of Materials Science and Engi-
neering, Rutgers University, 607 Taylor Rd,
Piscataway, NJ 08854-8065, USA

Correspondence e-mail:
dunbar.birnie@rutgers.edu

The β''-alumina structure is examined in detail and an analysis is presented of the three-dimensional integrity of the lattice. The layer structure that is responsible for the very high sodium conduction rate is the specific focus. Rigid layers that are derived from the cubic spinel structure are interleaved by more open honeycomb pathways where rapid ion diffusion takes place. The three-dimensional rigidity of the spinel block in this structure makes it possible to accurately quantify the conduction layer thickness based only on the hexagonal unit-cell dimensions, as suggested originally by Harbach [(1983), *J. Mater. Sci.* **18**, 2437–2452]. His calculation is tested rigorously against the many single-crystal structure determinations that have been made on the β''-alumina family compounds and excellent correlation is found.

1. Introduction

The β''-alumina structure is based on a stacking of oxygen close-packed layers that builds an overall hexagonal structure (Sudworth & Tilley, 1985; Lu *et al.*, 2010). The basic repeat unit consists of two parts: a four-layer *ABCA* stack that is spinel-like in its structure and a conduction slab that has fewer O atoms and more room for sodium-ion motion. One full unit cell then requires three sets of this pairing. Fig. 1 shows how the *ABCA* oxygen layer stacking sequence creates the spinel and conduction blocks of the structure. The distance D is a measure of the thickness of the spinel block. The distance H is the spacing between spinel blocks and contains the hexagonal honeycomb of sites that are important for sodium conduction. Note that the naming of the A, B and C type layers is some-what arbitrary. Fig. 1 shows this sequence increasing upward on the page. The first block is *ABCA*, the second spinel block is *CABC* because the conduction layer has some oxygen sites occupied – actually ones that are positioned as B sites, which is why the next block starts with C.

At a rigorous crystallography level then β''-alumina is identified as having the space group $R\bar{3}m$ (#166) from *International Tables* (Hahn, 2005); this is rhombohedral in symmetry and is usually represented by coordinates referenced to a hexagonal cell. As discussed further below, there have been a number of detailed X-ray and neutron diffraction studies that have determined atom locations within the unit cell to high accuracy. Most compositions of the β''-alumina type are actually stabilized by the addition of some divalent ions that substitute for aluminium and enhance the amount of sodium in each formula unit, resulting in a general idealized chemical formula of

$$Na_{(1+x)}Mg_xAl_{(11-x)}O_{17} \rightarrow \text{Mg-stabilized-Na-}\beta''\text{-Alumina},$$

(1)

Table 1
Unique atom site locations as determined by Bettman & Peters (1969).

Atom	Site identity	x fractional coordinate	z fractional coordinate	'Ideal' z coordinate
Na	6c	–	0.1719	–
Al1	3a	–	0.00 (by definition)	–
Al2/Mg†	6c	–	0.3501	–
Al3	18h	0.3362	0.0708	–
Al4	6c	–	0.4498	–
O1	18h	0.1562	0.0339	1/30 = 0.03333
O2	6c	–	0.2955	9/30 = 0.30000
O3	6c	–	0.0961	3/30 = 0.10000
O4	18h	0.1657	0.2357	7/30 = 0.23333
O5	3b	–	0.50 (by definition)	15/30

† Neutron diffraction studies have confirmed the Al2 site as the stabilizer substitution location (Brown *et al.*, 1981; Jorgensen *et al.*, 1981).

Figure 2
Reduction in conduction plane thickness, H, with increasing Mg content, x (replotted from Harbach, 1983).

where x is the extent of Al $\leftrightarrow$ (Na + Mg) substitution in the structure, typically saturating at approximately $x = 0.66$ or 0.70. For the $R\bar{3}m$ structure then there are actually three formula units of this composition in each unit cell. There are also typically five unique oxygen locations, four unique aluminium (plus magnesium) sites, and usually one or two unique sites for sodium (or for ions that have replaced the sodium). For example, the seminal structure determination by Bettman & Peters (1969) gave atom locations (for a composition assumed to have $x = 1$) as shown here in Table 1. For comparison with the measured coordinate values, an ideal fractional coordinate is also given for each of the oxygen
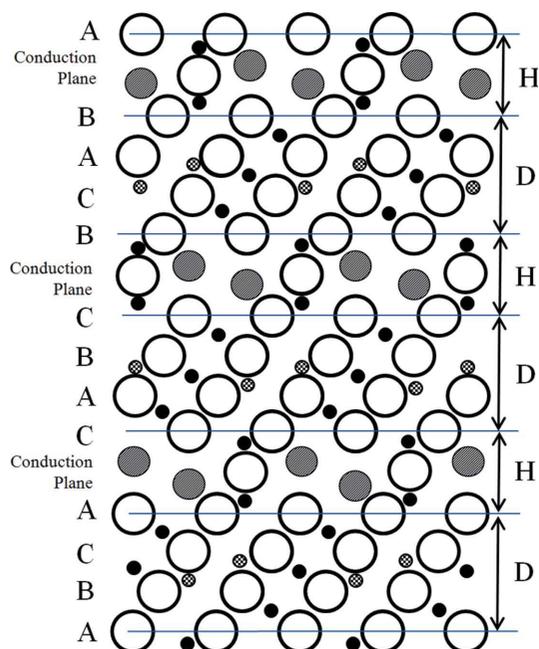
layers, which identifies what relative position these layers would occupy if they had perfect close-packing as found in the spinel structure, and if this stacking continued through the conduction plane *via* the O5 bridging atom. It is clear that the actual coordinates are close to their ideal hard-sphere packing spacing.

Note also that when stabilizer ions (Mg^{2+}, Li^+ *etc.*) are added then many studies have found that these are substituting onto the Al2 sites, which are tetrahedral in symmetry and are located near the center of the spinel block layers. These sites are identified in Fig. 1 by the small circles with the checkerboard pattern.

2. Structure analysis

Within the unit cell it is interesting to figure out how much space is available for conduction and how that space is modified when composition adjustments are made. Harbach first addressed this question by estimating how much space the conduction layer would occupy based on the assumption that the c-direction size of the spinel block part of the structure would be defined by the a-axis dimension of the β''-alumina. (Note that his assumption of isotropic expansion/contraction of this subunit of the structure is effectively being tested in the present work.) Since the a-axis unit-cell dimension is directed along close-packed rows of O atoms within each layer – and because the *ABCA* layers stack in such a way that the O atoms form rows diagonally upward in the structure (as they would in spinel), then we can actually use the a-axis unit-cell dimension to predict what the thickness of the spinel block would ideally be in the c-axis direction. Harbach did this derivation and arrived at this formula for 'H'[1]

Figure 1
Crystal structure of β''-alumina viewed from the side emphasizing the stacking arrangement of close-packed oxygen layers that make up the structure. Spinel-related blocks are identified with D and conduction slabs are identified by H. Large open circles are O^{2-}. Medium-sized shaded circles are Na^+. Small solid circles are Al sites. Checkerboard circles are the Al2 site where stabilizer ions substitute.
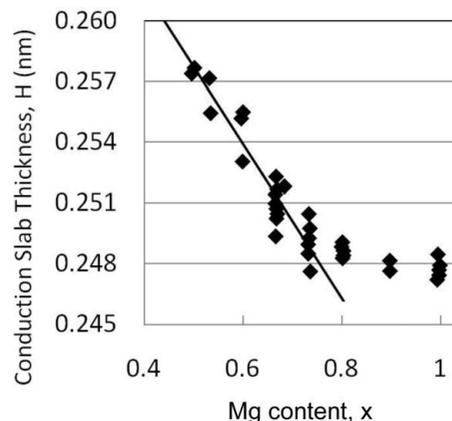
[1] Note that Harbach based his calculation on subtracting four thicknesses of close-packed oxygen from 1/3 of the c-axis dimension, as well as making an allowance for the distance that the adjacent O atoms stick into the conduction plane. If we examine distance D in Fig. 1 then we can see there are only three close-packed oxygen thicknesses spanned here. However, in a further discussion we preserve Harbach's equation, but recognize that there will be nearly a factor of two in conduction spacing thickness as an offset, with Harbach's numbers being almost two times smaller.

Table 2
Assembled structure determinations for β''-alumina phases.

Atoms in bold have been inserted *via* ion-exchange reactions for sodium. Entries are arbitrarily sorted in order of increasing $z(O3)$.

Composition	a_o	c_o	$z(O3)$	$z(O4)$
$\mathbf{Ga_{1.6}Li_{0.3}}Al_{10.7}O_{17}$[a]	5.5900	34.3805	0.0930	0.2361
$\mathbf{Ga_{1.6}Li_{0.3}}Al_{10.7}O_{17}$[a]	5.5951	34.3670	0.0932	0.2360
$\mathbf{In_{1.6}Li_{0.3}}Al_{10.7}O_{17}$[b]	5.6044	34.4807	0.0934	0.2368
$\mathbf{(NH_4^+)_{1.56}(H_3O^+)_{0.19}}Mg_{0.75}Al_{10.25}O_{17}$[c]	5.631	34.378	0.0940	0.2372
$\mathbf{K_{1.60}}Mg_{0.60}Al_{10.40}O_{17}$[d]	5.63	34.01	0.0951	0.2362
$\mathbf{Ba_{0.82}}Mg_{0.63}Al_{10.37}O_{17}$[e]	5.619	34.084	0.0952	0.2359
$\mathbf{(H_3O^+)_{1.09}}Mg_{0.49}Al_{10.36}O_{17}$[f]	5.625	34.18	0.0953	0.2368
$\mathbf{Zr_yLi_x}Al_{11-x}O_{17}$[g]	5.5994	33.7711	0.0960	0.2358
$Na_2MgAl_{10}O_{17}$[h]	5.614	33.85	0.0961	0.2357
$\mathbf{Eu_{0.65}}Mg_{0.67}Al_{10.33}O_{17}$[i]	5.600	35.380	0.0961	0.2353
$Na_{1.62}Li_{0.31}Al_{10.69}O_{17}$[j]	5.606	33.7376	0.0964	0.2356
$Na_{1.82}\mathbf{Co_{0.70}}Al_{10.2}O_{17}$[k]	5.6153	33.7120	0.0966	0.2353
$Na_{1+2x}Li_xAl_{11-x}O_{17}$[g]	5.6037	33.621	0.0967	0.2352
$\mathbf{Dy_{0.50}}Mg_{0.50}Al_{10.50}O_{17}$[l]	5.602	33.765	0.0968	0.2353
$\mathbf{Sr_{0.87}}Mg_{0.67}Al_{10.33}O_{17}$[m]	5.61	33.72	0.0970	0.2353
$Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$[n]	5.6230	33.536	0.0970	0.2350
$Na_{0.21}\mathbf{La_{0.44}}Mg_{0.72}Al_{10.34}O_{17}$[o]	5.614	33.525	0.0971	0.2349
$\mathbf{(UO_2^{2+})_{0.1}}Na_{1.47}Mg_{0.67}Al_{10.33}O_{17}$[p]	5.6206	33.703	0.0971	0.2352
$Na_{1.66}Mg_{0.67}Al_{10.33}O_{17}$[d]	5.61	33.54	0.0973	0.2350
$Na_{0.08}\mathbf{Pr_{0.44}}Mg_{0.54}Al_{10.48}O_{17}$[q]	5.611	33.479	0.0975	0.2347
$\mathbf{Zn_{0.87}}Mg_{0.74}Al_{10.26}O_{17}$[r]	5.623	33.517	0.0976	0.2347
$\mathbf{Gd_{0.46}}Mg_{0.38}Al_{10.62}O_{17}$[i]	5.6067	33.326	0.0977	0.2347
$\mathbf{Ho_{0.50}}Mg_{0.50}Al_{10.50}O_{17}$[i]	5.6143	33.537	0.0977	0.2348
$\mathbf{Mn_{0.77}}Mg_{0.54}Al_{10.46}O_{17}$[i,s]	5.6065	33.293	0.0977	0.2348
$Na_{0.03}\mathbf{La_{0.47}}Mg_{0.60}Al_{10.34}O_{17}$[t]	5.627	33.538	0.0977	0.2348
$Na_{0.01}\mathbf{Pr_{0.51}}Mg_{0.56}Al_{10.45}O_{17}$[q]	5.612	33.397	0.0978	0.2348
$Na_{1.72}\mathbf{Li_{0.30}}Al_{10.66}O_{17}$[u]	5.6101	33.4627	0.0979	0.2350
$Na_{1.72}\mathbf{Li_{0.30}}Al_{10.66}O_{17}$[u]	5.6071	33.4580	0.0981	0.2351
$\mathbf{Tb_{0.46}}Mg_{0.38}Al_{10.62}O_{17}$[i]	5.6091	33.303	0.0981	0.2346
$Na_{1.67}Mg_{0.67}(Al_{0.77}Ga_{0.23})_{10.33}O_{17}$[v]	5.6692	33.720	0.0981	0.2346
$Na_{1.67}Mg_{0.67}(Al_{0.59}Ga_{0.41})_{10.33}O_{17}$[v]	5.7185	33.920	0.0983	0.2343
$Na_{0.01}\mathbf{Pr_{0.53}}Mg_{0.72}Al_{10.31}O_{17}$[q]	5.631	33.342	0.0983	0.2344
$Na_{0.58}\mathbf{Nd_{0.36}}Mg_{0.67}Al_{10.33}O_{17}$[w]	5.627	33.39	0.0983	0.2341
$Na_{1.67}Mg_{0.67}(Al_{0.70}Ga_{0.30})_{10.33}O_{17}$[x]	5.6820	33.724	0.0983	0.2344
$\mathbf{Ag_{1.64}}Mg_{0.64}Al_{10.36}O_{17}$[y]	5.63	33.45	0.0985	0.2347
$\mathbf{Ca_{0.83}}Mg_{0.67}Al_{10.33}O_{17}$[z]	5.613	33.27	0.0987	0.2339
$\mathbf{Mn_{0.79}}Mg_{0.57}Al_{10.43}O_{17}$[r]	5.618	33.141	0.0988	0.2339
$\mathbf{Nd_{0.54}}Mg_{0.62}Al_{10.38}O_{17}$[aa]	5.628	33.259	0.0988	0.2341
$\mathbf{Eu_{0.54}}Mg_{0.62}Al_{10.38}O_{17}$[aa]	5.627	33.190	0.0990	0.2339
$\mathbf{Gd_{0.58}}Mg_{0.74}Al_{10.26}O_{17}$[aa,bb]	5.625	33.134	0.0992	0.2338

References: (*a*) Wilkinson (1997); (*b*) Cetinkol *et al.* (2007); (*c*) Thomas & Farrington (1983); (*d*) Boilot *et al.* (1980); (*e*) Thomas *et al.* (1984); (*f*) Roth *et al.* (1980); (*g*) Lomax (1992); (*h*) Bettman & Peters (1969); (*i*) Soetebier (2002); (*j*) Dunn *et al.* (1988); (*k*) Chen *et al.* (1986); (*l*) Soetebier (2002); (*m*) Aldén *et al.* (1985); (*n*) Brown *et al.* (1981); (*o*) Kohler *et al.* (1996); (*p*) Wolf *et al.* (1993); (*q*) Kohler & Urland (1996); (*r*) Carrillo-Cabrera *et al.* (1985); (*s*) Soetebier & Urland (2002); (*t*) Kohler & Urland (1997); (*u*) Jorgensen *et al.* (1981); (*v*) Edstrom *et al.* (1998); (*w*) Wolf & Thomas (1993); (*x*) Edstrom *et al.* (1998); (*y*) Kahn *et al.* (1980); (*z*) Aldén *et al.* (1984); (*aa*) Carrillo-Cabrera *et al.* (1988); (*bb*) Carrillo-Cabrera *et al.* (1983, 1988).

$$H = \frac{c_o}{3} - 1.5413a_o. \qquad (2)$$

Then, when comparing different compositions of Mg-stabilized β''-alumina he found that larger additions of Mg caused a gradual shrinkage of the conduction layer down to a minimum value which was interpreted as a point where the vertical Al—O5—Al bond distances could not be compressed any further. Fig. 2 shows the reduction in conduction plane width that he found. One might suppose that the additional positive charge placed in the conduction plane is electrostatically attracted to the compensating relative negative charge within the spinel blocks leading to a slight compression of the structure as more

stabilizer ions are added. A more rigorous measure of the width of this layer can be made using the single-crystal structure determinations where specific atom locations have been determined.

Next it is interesting to examine how different stabilizers and other structure additives can influence the lattice size, with specific emphasis on the conduction plane. As noted above, the addition of Mg enables increasing amounts of Na to sit in the conduction plane, while the added Mg^{2+} replaces Al^{3+} in the spinel-block tetrahedral sites. The general reduction in conduction plane width seen by Harbach (1983), as shown already in Fig. 2, was also seen in a more recent systematic study by Alden (1986).

The conduction slab thickness calculated by Harbach is based only on the external dimensions of the hexagonal unit cell (a_o and c_o). However, the actual thickness of the conduction slab can be calculated directly for every case where a full crystal structure determination has been done. If we look more closely at the atom identities presented in Table 1 and map them onto the side-view of the layer structure of the unit cell then we can label each of the O atoms as shown in Fig. 3. Of course, the O5 bridges adjacent spinel block layers and connects two tetrahedral Al4 atoms pointing up and down. Atoms O3 and O4 are two oxygen locations that define the rest of the local environment for atoms within the conduction plane of the structure. Atoms O1 and O2 are internal to the spinel block and do not have direct bonds to any atoms in the conduction plane.

So, if we use the z-coordinate for atoms O3 and O4 then we can obtain an exact measure of the distances D or H. Using O3 we obtain this conduction slab thickness

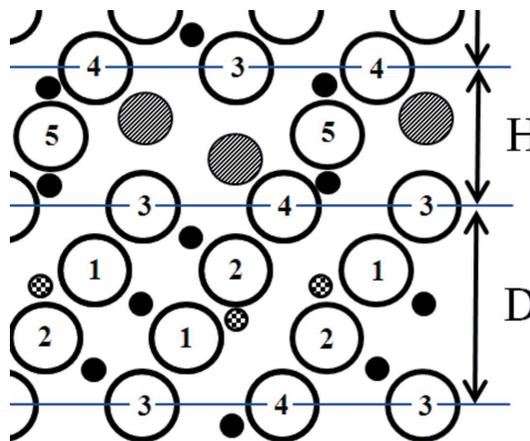$$H_3 = c_o\left[\tfrac{1}{3} - 2z(O3)\right]. \qquad (3)$$

Figure 3
Crystal structure of β''-alumina viewed from the side emphasizing the stacking arrangement of close-packed oxygen layers that make up the structure. Specific oxygen crystallographic sites are numbered in accordance with Table 1. O3 and O4 are used to calculate the conduction slab thickness.

Using the z-coordinate of the O4 atoms we obtain this measure of the conduction slab thickness

$$H_4 = c_o\left[2z(O4) - \tfrac{1}{3}\right]. \tag{4}$$

Edstrom *et al.* (1998) used this metric when comparing conduction plane sizes for Ga^{3+}–Al^{3+} solid-solution formation, although they found no trend even with large Ga^{3+} replacement. Both equations are based on the actual structure determinations, not on an assumed three-dimensional rigidity of the spinel-block that is implicit in Harbach's analysis.

3. Discussion

Now it is possible to examine how well the Harbach estimate works at specifying the conduction layer thickness. Table 2 assembles the numerous crystal structure determinations for β''-alumina family compositions, giving their unit-cell dimensions as well as the z-coordinate values for the O3 and O4 atom locations. It is interesting to compare the exact determinations (H_3 and H_4) with the conduction layer thickness first developed by Harbach. Figs. 4 and 5 show these two correlations. The fitted expressions for both cases are linear with correlation coefficients of 0.86 and 0.88. It can be seen that Harbach's macroscopic estimate is an excellent match to both O3- and O4-based values.

Since Harbach's number is based on both a_o and c_o, then it is valid to question whether there might already be a correlation between a_o and c_o that would naturally lead to the good correlation observed in Figs. 4 and 5. However, as seen in Fig. 6, the a_o and c_o parameters show only a very weak correlation. So, the absolute atom positions are not influenced by the general size of the lattice, but rather by the local atom occupancies and 'fit' of the structure.

Next, it is interesting to compare the O3 and O4 data since these are two different measures of the conduction slab
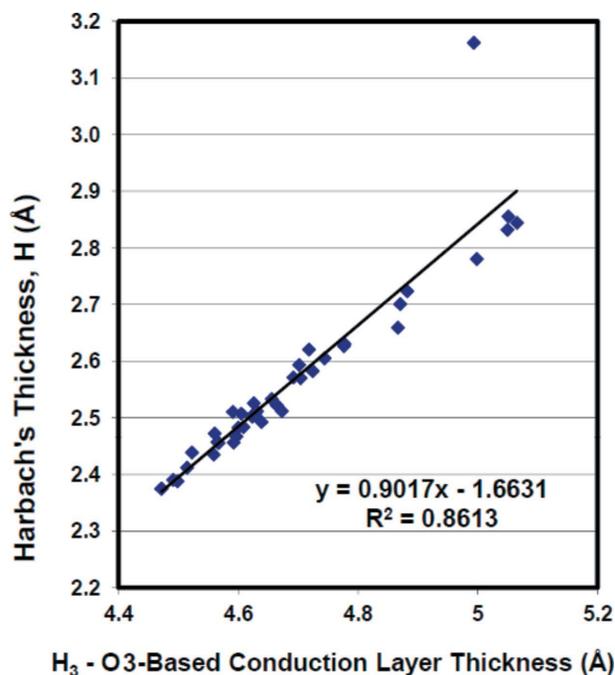

Figure 4
Harbach's calculation of the conduction layer thickness, H [equation (2)], plotted as a function of H_3, the O3-based rigorous determination of the conduction layer thickness [equation (3)].
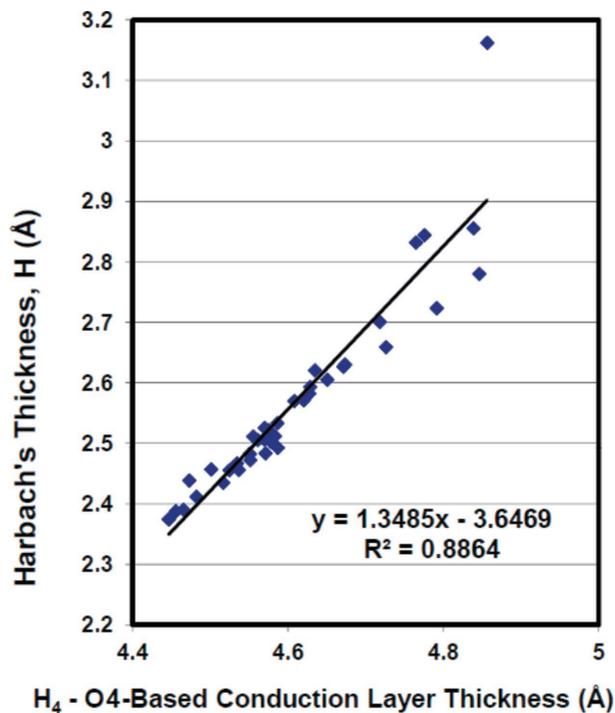

Figure 5
Harbach's calculation of the conduction layer thickness, H [equation (2)], plotted as a function of H_4, the O4-based rigorous determination of the conduction layer thickness [equation (4)].
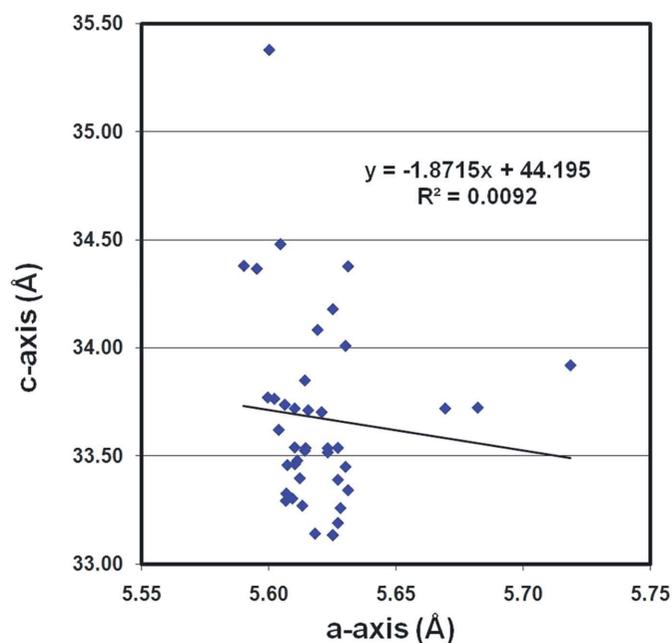

Figure 6
Test of the a-axis and c-axis lattice parameter correlation. No general relationship is found.
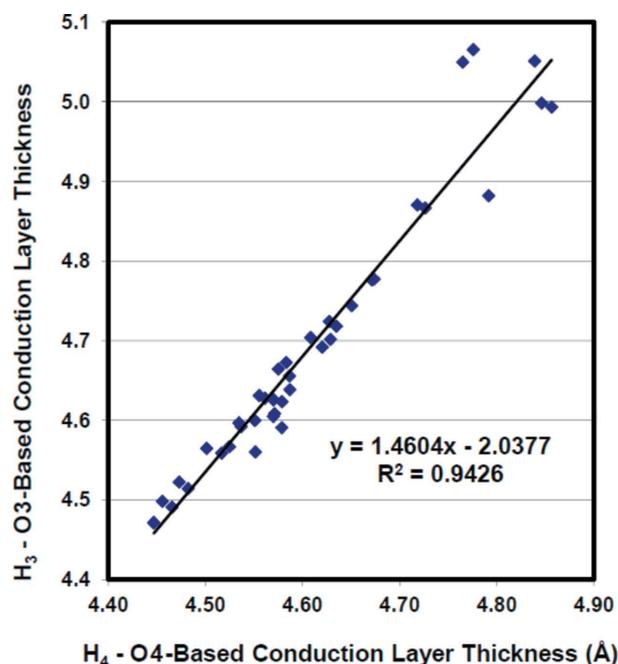
Figure 7
Comparison of H_3 and H_4, the O3- and O4-based conduction layer thickness values [from equations (3) and (4), respectively].

thickness. Fig. 7 shows a plot of H_3 *versus* H_4 and the correspondence is excellent. It can be seen that the H_3 values are almost always slightly larger than the H_4 values – and the slope of the regression line is quite a bit greater than unity showing that the O3 positions 'breathe' more when the structure is expanded. This makes sense because the O4 atoms form the base of the Al4 aluminium tetrahedra that are also connected to the O5-atom positions. Due to this bridging connection it is likely that the O4s will not have as much freedom to expand or contract as the contents of the conduction layer change (for example by ion exchange or by stabilizer cation substitution processes).

The good correlations shown above provide evidence that the Harbach formula works very well and is rooted in the inherent structural rigidity of the spinel blocks of the β''-alumina structure. This is a pleasing result since it is much simpler to measure the a_o and c_o lattice parameters for a structure than to do a full structure determination to find all lattice atom positions exactly.

4. Conclusions

Structure analysis of the β''-alumina family of compounds has been performed to extract the thickness of the conduction layer within the structure. Two formulae have been derived that are based on specific O-atom locations within the unit cell. These data have been compared with a simpler structural analysis from the literature with positive results. Together these correlations may be helpful when guiding compositional

adjustments that will lead to more open conduction planes and possible increases in conductivity for β''-alumina electrolytes.

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