

The Ca²⁺ Distribution in Ca²⁺ β''-Alumina

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Abstract. Idealized formula: Ca_xMg_{2x-1}Al_{12-2x}O₁₇, *M_r* for $x = \frac{2}{6}$ is 600.40, rhombohedral, *R*3̄*m*. In hexagonal cell: *Z* = 3, *a* = 5.613 (1), *c* = 33.270 (5) Å, *V* = 907.8 (3) Å³, *D_x* = 3.295 (1) Mg m⁻³, *Mo Kα*, λ = 0.71069 Å, μ = 1.36 mm⁻¹, *T* = 295 K, *F*(000) = 885. Final *R* = 0.048, *wR*(*F*²) = 0.110 for 1757 *F*². The Ca²⁺ ions lie distributed along edge-linked hexagonal pathways with maxima at 6(*c*) and 9(*d*) sites (*R*3̄*m* notation). Best least-squares fit for a non-centrosymmetric distribution of Ca²⁺ ions with occupations at successive 6(*c*), 9(*d*), 6(*c*), ... sites in the approximate ratios 2:1:1:2, ..., respectively. The Ca²⁺-ion distribution near the 6(*c*) sites is best described by a vibrational model involving third-rank cumulants (*γ*_{*ijk*}'s). The column oxygen O(5) is disordered over six 18(*h*) positions, each displaced by 0.51 Å from the 3(*b*) position ($\frac{1}{3}, \frac{2}{3}, \frac{1}{6}$). The refined *x* value in the structure formula is 0.95 (3), suggesting a 45% substitution of Al(2) if Mg is assumed to enter the structure only at this site. The rigid centrosymmetric spinel-block framework is retained from Na⁺ β''-alumina.

Introduction. The divalent β''-aluminas are the first family of high-conductivity solid electrolytes for divalent cations. They are also ideal systems for modelling the complex relationship between structure, ionic-transport mechanism and ionic conductivity in solid electrolytes. This paper reports one of a series of studies in which divalent cations of different radii and electronic configurations have been introduced into the spinel host lattice of β''-alumina.

The ionic conductivity of Ca²⁺ β''-alumina has been reported by Dunn & Farrington (1980), and found to be quite similar to that of Ba²⁺, Sr²⁺ and Cd²⁺ β''-alumina. The purpose here is to determine the detailed distribution of Ca²⁺ ions in the conduction plane of Ca²⁺ β''-alumina. Similar studies are also in progress for other divalent systems (Sr²⁺, Cd²⁺, Pb²⁺, etc.). The Ba²⁺-ion distribution in Ba²⁺ β''-alumina has recently been studied (Thomas, Aldén, McIntyre & Farrington, 1984) and found to display distinct evidence of short-range ordering in the Ba²⁺-ion

distribution. A detailed knowledge of the ionic distributions for a series of ions of different radii (and different electronic configurations) in an otherwise virtually identical host system can lead to a better understanding of the conduction mechanisms involved in solid electrolytes [*r*(Ca²⁺) = 0.98, *r*(Sr²⁺) = 1.18, *r*(Ba²⁺) = 1.35 Å].

Experimental. Single crystals of Ca²⁺ β''-alumina were prepared by ion exchange from Na⁺ β''-alumina crystals grown at 1963–1998 K. The exchange was performed in a CaCl₂ melt at 1043 K for 24 h. The remaining Na⁺ content was shown to be <0.1%, using a ²²Na radioactive isotopic form of Na⁺ β''-alumina to monitor the exchange (Farrington & Dunn, 1982).

X-ray diffraction data collected from a triangular platelet with well-defined faces and maximum dimension 0.13 mm; Stoe-Philips four-circle diffractometer with graphite-monochromatized *Mo Kα* radiation; 2371 $-h + k + l = 3n$ reflections of type ($\pm h, +k, +l$) measured with ω -2θ step scan, 50 steps, $\sin\theta/\lambda \leq 0.951 \text{ \AA}^{-1}$; three test reflections monitored. Small systematic decrease in intensity corrected for. Systematic absences ($-h + k + l \neq 3n$ in the hexagonal cell) indicate retention of *R*3̄*m* space-group symmetry of Na⁺ β''-alumina. Cell parameters determined from least-squares fit of θ angles measured for 14 reflections during the data collection. Intensity data corrected for background, Lp and absorption effects (μ = 1.36 mm⁻¹, assuming composition Ca_xMg_{2x-1}Al_{12-2x}O₁₇, $x = \frac{2}{6}$). Calculated transmission range: 0.85–0.98. Internal agreement factor for intensity control reflections ($\sum |I - \bar{I}| / \sum I$) = 0.012. Full-matrix least-squares refinement with *UPALS* (Lundgren, 1982). Function minimized: $\sum w(|F_o|^2 - |F_c|^2)^2$, where $w^{-1} = \sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (kF_o^2)^2$; *k* set empirically to 0.04; reflections with $F_o^2 < 2\sigma(F_o^2)$ together with four erroneously measured reflections removed from the refinements, leaving 1757 reflections.

The centrosymmetric average Ca²⁺ distribution in the conduction plane was obtained following the refinement of a scale factor and the positions of the

Al(Mg) and O atoms of the spinel block; starting values taken from the Na⁺ β''-alumina structure (Bettman & Peters, 1969). Δρ maps calculated in and near the $z = \frac{1}{6}$ plane showed that Ca²⁺ ions lie at both 6(c) and 9(d) sites. In the light of the earlier discovery of short-range ordering in the Ba²⁺ distribution in Ba²⁺ β''-alumina (Thomas, Aldén, McIntyre & Farrington, 1984), it was natural to suspect a corresponding effect here. While still retaining the $R\bar{3}m$ symmetry of the spinel block, the space-group constraint on the Ca²⁺ distribution was lowered to $R3m$, i.e. the local centre of symmetry was removed for the Ca²⁺ ions by making adjacent 6(c) sites non-equivalent. A significant improvement was obtained in the refinement, though not as dramatic as that in Ba²⁺ β''-alumina.

The trigonal distortion of the Ca²⁺-ion distribution at a 6(c) site towards neighbouring 6(c) sites could be well described by the introduction of a third-rank vibrational tensor (γ_{ijk}) (see *International Tables for X-ray Crystallography*, 1974). Evidence was also found to suggest a distribution of the O(5) column oxygen over six disordered 18(h) sites. The Mg occupation of the Al(2) site was not refined. An isotropic extinction parameter (g) was refined to the value 2310 (690) in the final stages of refinement (corresponding to an r.m.s. mosaic spread of 25''). All final shifts $< 0.1\sigma$. Final $R = 0.048$, $R(F^2) = 0.048$, $wR(F^2) = 0.110$. Form factors for Ca²⁺ and neutral Al and O atoms from *International Tables for X-ray Crystallography* (1974). No distinction was made between the X-ray scattering power of Al³⁺ and Mg²⁺ ions. All calculations made on the departmental NORD 100 computer or the IBM 370/155 computer at the Uppsala Computer Center. The programs used have been described by Lundgren (1982).

Discussion. The distribution of Ca²⁺ ions in the final ρ maps is shown in Fig. 1(a-c) and Fig. 2. Positional parameters are given in Table 1.*

Description of the structure

The spinel-block structure of Na⁺ β''-alumina (Bettman & Peters, 1969) is retained in Ca²⁺ β''-alumina. Al atoms are octahedrally and tetrahedrally coordinated by O atoms to form layers of spinel structure separated in the c direction by Al(4)–O(5)–Al(4) bridging bonds (see Table 2).

The planes containing the column-oxygen O(5) (at $z = \frac{1}{6}$, $\frac{1}{2}$ and $\frac{5}{6}$) are otherwise occupied only by Ca²⁺ ions and constitute the conduction 'planes' in the structure (Fig. 3). The Ca²⁺ ions move in the hexagonal

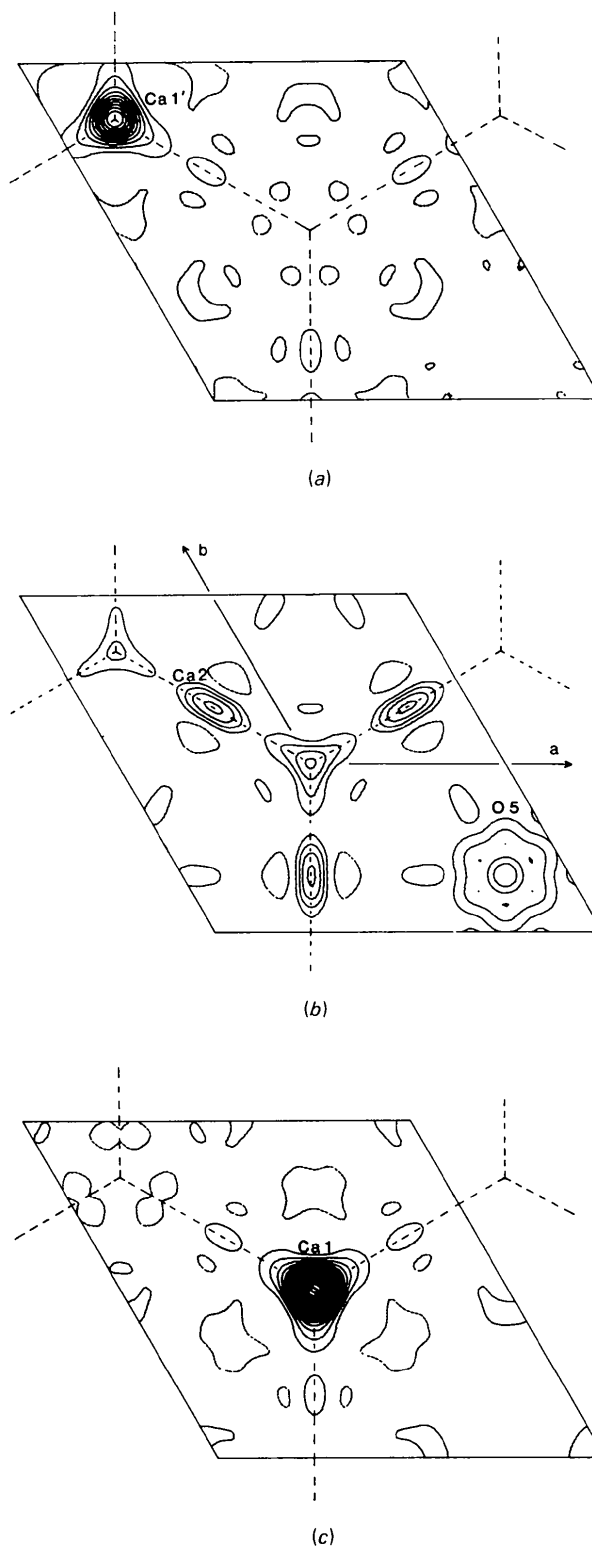


Fig. 1. ρ maps in and near the conduction plane in Ca²⁺ β''-alumina at (a) $z = 0.158$, (b) $z = \frac{1}{6}$ and (c) $z = 0.176$, with phases calculated for a non-centrosymmetric ($R3m$) Ca²⁺-ion distribution (contour interval: $1.5 e \text{ \AA}^{-3}$).

* Lists of structure factors, anisotropic thermal parameters, crystal dimensions and orientation matrix have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39605 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

toroid-like regions around the O(5) supporting oxygen atoms. The O(5) atom itself is systematically displaced from the 3(b) site it occupies in K^+ β' -alumina (Brown, Schwinn, Bates & Brundage, 1981) and in Ba^{2+} β' -alumina (Aldén, Thomas & Farrington, 1981) to six equivalent 18(h) sites. The distance between adjacent O(5) disordered sites and from the mean 3(b) positions is 0.51 Å. A similar effect has been noted in Ag^+ and Na^+ β' -alumina (Brown, Schwinn, Bates & Brundage, 1981). This distortion of the Al—O(5)—Al bridge can be related directly to the cation radius: small ions facilitate a closer approach of the spinel blocks, larger ions result in larger spacings and straighter more 'stretched' Al(4)—O(5)—Al(4) bonds. The presumably larger polarization of the O(5) oxygens by Ag^+ ions than by alkali-metal ions may also be a significant factor.

Neutron diffraction data on other β' -alumina systems suggest that charge compensation in the structure is achieved through Mg^{2+} substitution at the Al(2) sites alone (there is no realistic means of checking this with X-ray data; the scattering powers of Mg^{2+} and Al^{3+} are virtually identical). The refined Ca^{2+} occupations would thus imply, on average, a 45% substitution of Al(2) sites by Mg^{2+} , with the effective structural formula: $Ca_xMg_{2x-1}Al_{12-2x}O_{17}$, $x = 0.95$ (3). A value of $x = \frac{5}{6}$ would correspond to the ideal situation normally assumed. Current phase analysis work is aimed at establishing the homogeneity range for the β' structure, and thus at assessing whether such a discrepancy from $x = \frac{5}{6}$ can be meaningful. The mean Mg^{2+} substitution of Al(2) in NH_4^+/H_3O^+ β' -alumina has been found to be 37% in an accurate single-crystal neutron-diffraction study by Thomas & Farrington (1983). The degree of generality of the short-range ordering in the Mg substitution observed by neutron diffraction in Na^+ β' -alumina (Frase, Thomas & Farrington, 1983) is still unknown. However, should such an effect be present in the parent Na^+ β' -alumina crystal, it must surely be retained in the Ca^{2+} β' -alumina crystal examined here, and influence in some way the Ca^{2+} -ion distribution.

Table 1. Atomic positional parameters ($\times 10^5$) and equivalent isotropic thermal parameters (expressed as average r.m.s. amplitudes) in Ca^{2+} β' -alumina

	Site*	x	y	z	\bar{U} (Å)
Ca(1)	6(c)	0	0	17575 (15)	0.155
[Ca(1)']	6(c)	0	0	-17575 (15)	0.155
Ca(2)	9(d)	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	0.249
Al(1)	3(a)	0	0	0	0.077
Al(2)	6(c)	0	0	35027 (2)	0.085
Al(3)	18(h)	33420 (9)	x/2	7175 (1)	0.086
Al(4)	6(c)	0	0	45114 (3)	0.094
O(1)	18(h)	15368 (11)	2x	3483 (3)	0.097
O(2)	6(c)	0	0	29453 (6)	0.090
O(3)	6(c)	0	0	9870 (6)	0.095
O(4)	18(h)	16292 (11)	2x	23389 (3)	0.093
O(5)	18(h)	38611 (67)	-x	$\frac{1}{3}$	0.159

* $R\bar{3}m$ notation.

Table 2. Some interatomic distances (in Å) in Ca^{2+} β' -alumina

Contact	Distance	Mean	Mean in Ba^{2+} β' -alumina
Ca(1)—O(3)	2.563 (7) ($\times 1$)	2.516	2.697
Ca(1)—O(4)	2.500 (5) ($\times 3$)		
Ca(2)—O(3)	2.782 (3) ($\times 2$)	2.766	—
Ca(2)—O(4)	2.751 (3) ($\times 4$)		
Ca(2)—O(5)*	2.376 (3)	—	—
Al(1)—O(1)	1.891 (1) ($\times 6$)	1.891	1.890
Al(2)—O(1)	1.845 (1) ($\times 3$)	1.847	1.849
Al(2)—O(2)	1.854 (3) ($\times 1$)		
Al(3)—O(1)	1.988 (1) ($\times 2$)	1.913	1.916
Al(3)—O(4)	1.847 (1) ($\times 2$)		
Al(3)—O(3)	1.856 (1) ($\times 1$)		
Al(3)—O(2)	1.953 (1) ($\times 1$)		
Al(4)—O(4)	1.766 (1) ($\times 3$)	1.751	1.754
Al(4)—O(5)	1.705 (3) ($\times 1$)		

* Shortest contact.

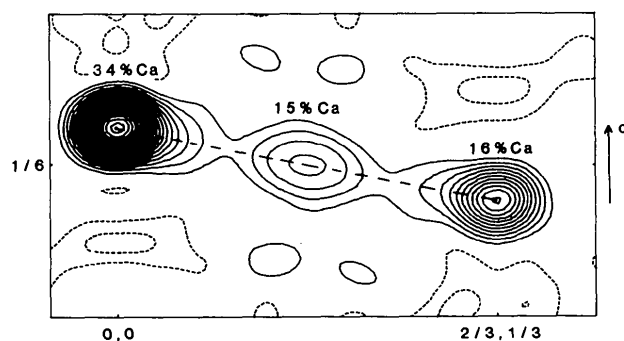


Fig. 2. ρ map in the vertical ($2x, x, z$) plane through the conduction path in Ca^{2+} β' -alumina; calculated as for Fig. 1 (contour interval: $1.5 e \text{ \AA}^{-3}$).

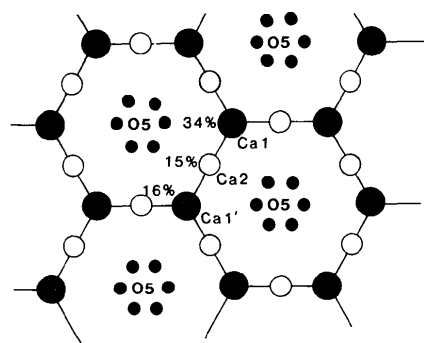


Fig. 3. Schematic representation of the Ca^{2+} -ion distribution in the conducting layer of Ca^{2+} β' -alumina. The percentage occupations refined within the $R\bar{3}m$ space group are indicated.

The Ca²⁺ distribution

The Ca²⁺ ions occupy the hexagonal toroid-like pathways in the planes between the spinel blocks. These planes are otherwise only occupied by the supporting column oxygen O(5), which is here found to be disordered over six 18(*h*) sites around the 3(*b*) position at ($\frac{1}{3}, \frac{2}{3}, \frac{1}{6}$). The conduction planes lie at $z = \frac{1}{6}, \frac{1}{2}$ and $\frac{5}{6}$ in the unit cell, although the conduction pathways (Fig. 3) can be described more exactly as undulating from 0.30 Å above the planes at one 6(*c*) site (an *up* site), *via* the 9(*d*) symmetry centre at $z = \frac{1}{6}$, to 0.30 Å below the plane at an adjacent 6(*c*) site (a *down* site).

As in the case of Ba²⁺ β''-alumina (Thomas, Aldén, McIntyre & Farrington, 1984), indirect evidence for the occurrence of short-range order in the Ca²⁺ ion distribution is found in the preference for the non-centrosymmetric space group *R3m*; the refined site occupations are given in Fig. 3 and Table 1. That no significantly observed $-h + k + l \neq 3n$ reflections appeared in a preliminary low-statistics data set suggests that any further lowering of the average local symmetry is negligible. The time- and space-average of the Ca²⁺-ion distribution, assuming the validity of the $a \times a \times c$ hexagonal cell, is plotted in Figs. 1 and 2. The disordering of the O(5) column oxygen is also seen. This disorder is presumably coupled to the short-range order in the Ca²⁺ ions; we note that O(5) is displaced towards the 6(*c*) sites of the Ca²⁺ ions.

It is relevant to consider more carefully the implications of the Ca²⁺ short-range order. Clearly, the crystal as a whole will contain just as many Ca²⁺ ions in *up* as in *down* positions. Only at short range does the occupation of (say) a 6(*c*) *up*-site (Fig. 3) influence site occupations in its immediate vicinity, *e.g.* by eliminating the possibility for occupation of the three nearest-neighbour 9(*d*) sites and lowering the occupations of the nearest 6(*c*) *down* sites. In more general terms, we can say that site occupations are highly correlated at short range and become statistically decorrelated with respect to a given occupied site as we move away from that site. The notion emerges of local regions (domains) in which the ions follow one mode of occupation (say, *up*), 'decorrelating' into *down* domains, before returning to *up*, *etc.* (see also van Gool & Bottelberghs, 1973). The shift of an ion from a *down* to an *up* site will represent a local shift in domain boundary, and introduce the suggestive picture of fast ion transport as the cooperative movement of statistical domain boundaries. As discussed in detail by Thomas, Aldén, McIntyre & Farrington (1984) for Ba²⁺ β''-alumina, the fact that we actually *observe* evidence of short-range order must imply that the diffraction correlation length is less than or, at least, the same order of magnitude as the

site-occupation correlation length. Considering the ratio of site occupations for adjacent 6(*c*) sites (symmetry equivalent with respect to the spinel skeleton), this ratio will tend to be lower for longer diffraction correlation lengths and shorter site-occupation correlation lengths. The refined value (here ~2.0) will at least set a lower limit for the true ratio between the occupancies of adjacent 6(*c*) sites.

Comparison of this ratio for Ca²⁺ β''-alumina (~2.0) with the value of ~3.5 obtained earlier for Ba²⁺ β''-alumina suggests that the diffraction correlation length is longer and/or the site-occupation correlation length shorter for the Ca²⁺ case. The latter condition would seem reasonable, partly in view of the smaller Ca²⁺ radius, and partly since the occupation of a mid-oxygen site will tend to have the effect of converting an *up* domain to a *down* domain and *vice versa*.

Two parameters thus emerge as possibly significant in characterizing the ion distribution in the structure: (i) The refined occupation ratio for adjacent 6(*c*) sites, which gives information about the size of the statistical domains. (ii) The occupation of the 9(*d*) mid-oxygen sites, which can be related to the occurrence of domain boundaries and to the ease of passage of ions from one 6(*c*) site to the next; mid-oxygen occupation may hinder ion mobility.

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