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Structural Aspects of the $Na^+ \rightarrow Cd^{2+}$ Ion-Exchange Process in Na^+ β-Alumina

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Abstract

The crystal structure and ionic distributions in the conduction plane of the system $Na_{1\cdot22-y}Cd_{y/2}Al_{11}O_{17\cdot11}$, Na^+/Cd^{2+} β-alumina, have been determined by single-crystal X-ray diffraction (Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å) for the four compositions $y = 0{\cdot}00$, 0·22, 0·45 and 1·22 at 295 K. All crystals have the hexagonal space group $P6_3/mmc$, $Z = 2$. Crystal data for two of the compositions: for $y = 0{\cdot}00$, $M_r = 598{\cdot}6$, $a = 5{\cdot}5929\ (4)$, $c = 22{\cdot}526\ (4)$ Å, $V = 610{\cdot}22\ (1)$ Å^3, $D_x = 3{\cdot}26$ Mg m^{-3}, $\mu_o = 1{\cdot}03$, $\mu_c = 1{\cdot}03$ mm^{-1}, $F(000) = 586{\cdot}6$, final $R(F) = 0{\cdot}0187$, $wR(F^2) = 0{\cdot}0436$ for 2306 observations; for $y = 1{\cdot}22$, $M_r = 639{\cdot}1$, $a = 5{\cdot}5869\ (4)$, $c = 22{\cdot}370\ (4)$ Å, $V = 604{\cdot}71\ (1)$ Å^3, $D_x = 3{\cdot}51$ Mg m^{-3}, $\mu_o = 2{\cdot}11$, $\mu_c = 2{\cdot}06$ mm^{-1}, $F(000) = 618{\cdot}1$, final $R(F) = 0{\cdot}0289$, $wR(F^2) = 0{\cdot}0651$ for 909 reflections. The Na^+ ions occupy the $z = \frac{1}{4}$ and $\frac{3}{4}$ conduction planes at predominantly one 2(*d*) site [Beevers–Ross (BR) site] and one 6(*h*) site (*A* site) ($P6_3/mmc$ notation) in the crude ratio 3:2. The Cd^{2+} ions first replace Na^+ ions at the *A* site as they take up a different 6(*h*) site (*B* site). When all *A*-site Na^+ ions have been replaced, Cd^{2+} ions continue to occupy *B* sites as they replace the remaining BR-site Na^+ ions. Somewhere between $y = 0{\cdot}45$ and $y = 1{\cdot}22$ there is a distinct qualitative shift in the relative Cd-site occupations. At full replacement (Cd^{2+} β-alumina), the Cd electron density is extended over a large part of the conduction pathways and is best described with four different Cd^{2+}-ion sites. Most of the Cd^{2+} ions occupy a 6(*h*) site (*C* site). The remainder are found in three less frequented sites: one 12(*k*) and two 12(*j*) sites (*D*, *E* and *F*, respectively). The positive charge excess in the conduction plane is stabilized by Roth–Reidinger defects, each comprising two interstitial Al atoms, one on either side of the conduction plane (at $z \sim 0{\cdot}175$ and $\sim 0{\cdot}325$), in combination with an extra O atom at a 6(*h*) mid-oxygen site. This defect exists on average once in every nine unit-cell layers (4·5 unit cells). The implications of the crystallographic results and the importance of the Roth–Reidinger defect for Na^+-ion mobility are discussed.

Introduction

The non-stoichiometric ionic conductor Na^+ β-alumina, $Na_{1+x}Al_{11}O_{17\cdot11}$, $x \simeq 0{\cdot}22$, space group $P6_3/mmc$, was shown to have an Na^+-ion conductivity at room temperature comparable to that of aqueous NaCl (0·1 *M*) (Yao & Kummer, 1967). The discovery immediately provoked considerable industrial interest in the material, particularly as a solid electrolyte in energy storage devices. It was also demonstrated that the Na^+ ions could be exchanged for other monovalent and a few divalent ions. In the 20 years that have elapsed since the discovery, much basic research effort has gone into exchanging Na^+ ions for other monovalent ions as an artifice for probing the Na^+-ion diffusion mechanism. Yao & Kummer's attempts to exchange divalent ions showed that their diffusion rates are very slow. Interest in the divalent isomorphs has been reawakened more recently, however, by the realization that partial exchange of divalent ions into the β-alumina host can perhaps serve to extend our basic understanding of ionic conduction mechanisms.

β-Alumina is always non-stoichiometric. Synthesis of the stoichiometric (or rather near-stoichiometric) compound may be possible, but would necessitate the use of special synthetic techniques (Tofield, 1982, and references therein). Moreover, the resulting material could be expected to be a poor ionic conductor since, as postulated by Whittingham & Huggins (1971), it is the excess Na^+ ions that are responsible for the high conductivity. This excess is charge compensated for by extra oxygen ions [O(6)] [at the mid-oxygen (mO) site] in combination with two displaced interstitial Al^{3+} ions (Roth–Reidinger defect).

It is clear that this Roth–Reidinger defect (Roth, Reidinger & LaPlaca, 1976; Reidinger, 1979) must

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play a vital rôle in influencing the mobility of the Na^+ ions. We focus on the detailed structural aspects of this influence, using an approach first suggested by Sutter, Cratty, Saltzberg & Farrington (1983) whereby Cd^{2+} ions replace Na^+ ions to produce a range of crystals with different vacancy densities corresponding to the approximate formula $Na_{1\cdot22-y}Cd_{y/2}Al_{11}O_{17\cdot11}$. Ca^{2+} ions are the only divalent ions known to exchange readily into Na^+ β-alumina. It is anticipated that we can probe the conduction mechanism(s) with respect to excess Na^+-ion concentration and vacancy concentration. The Na^+/Cd^{2+} β-alumina system is ideal for this purpose if we can assume that the Cd^{2+} ions are effectively trapped in the structure at temperatures below 700 K, and that the ionic mobility can be attributed solely to the Na^+ ions. In the earlier work of Sutter *et al.* (1983), a range of Na^+/Cd^{2+} β-alumina single-crystal compositions were prepared, and the diffusion constants and ionic conductivities measured. The conductivity was observed to increase slightly for low Cd^{2+} replacement, and then decrease abruptly when 36–40% of the Na^+ ions had been replaced. The activation energy displayed a corresponding behaviour (Sutter *et al.*, 1983). The four compositions studied in this series of single-crystal X-ray investigations have been chosen to focus specifically on this behaviour: namely 0·0, 17·4, 36·5 and 99·6% Na^+-ion substitution, *i.e.* $y = 0\cdot00$, 0·22, 0·45 and 1·22, respectively, in the formula $Na_{1\cdot22-y}Cd_{y/2}Al_{11}O_{17\cdot11}$. One composition (80% Na^+-ion substitution, $y = 1\cdot00$) has already been studied by X-ray diffraction (Catti, Cazzanelli, Ivaldi & Mariotto, 1987). Their results will be commented upon in our discussion.

The Na^+/Cd^{2+} β-alumina system has recently been studied by several other techniques, *e.g.* Raman (Hattori, Kurokawa & Mitsuishi, 1983; Mariotto & Farrington, 1986; Catti *et al.*, 1987) and NMR spectroscopy (Carduner, 1984; Carduner & White, 1987). The interpretation of these results has been handicapped, however, by a lack of detailed structural information. The present work is an attempt to rectify the situation.

Experimental

Single crystals of Na^+/Cd^{2+} β-alumina were prepared with the above-mentioned compositions by Sutter *et al.*, as described in their paper of 1983. Cd^{2+} ions were exchanged into the Na^+ β-alumina crystals in a $CdCl_2$ melt at 925 K. The degree of exchange was monitored using a ^{22}Na radiotracer and checked by careful weight measurements. The crystals were then annealed for 12 h at 1025 K to produce compositional homogeneity. Small crystals were cut from the larger parent crystals and used for the single-crystal X-ray diffraction studies.

Table 1. *Some experimental parameters relating to the data collections and refinements of* $Na_{1\cdot22-y}Cd_{y/2}Al_{11}O_{17\cdot11}$, $y = 0\cdot0$, 0·22, 0·45 *and* 1·22

	$y = 0\cdot00$	$y = 0\cdot22$	$y = 0\cdot45$	$y = 1\cdot22$
$F(000)$	586·6	592·3	598·3	618·1
Cell parameters (Å) a	5·5929 (4)	5·5921 (9)	5·5906 (3)	5·5869 (4)
c	22·526 (4)	22·526 (7)	22·519 (3)	22·370 (4)
Cell volume (Å^3)	610·22	610·05	609·53	604·71
No. of reflections for cell determination	25	25	28	25
2θ range (°)	22–45	26–28	26–50	29–50
D_x (Mg m^{-3})	3·26	3·30	3·34	3·51
Max./min. crystal dimensions (mm)	0·22/0·13	0·22/0·04	0·22/0·10	0·24/0·03
μ_o (mm^{-1})	1·03	1·18	1·36	2·11
μ_c (mm^{-1})	1·03	1·17	1·39	2·06
Transmission factors	0·83–0·88	0·84–0·89	0·71–0·86	0·74–0·93
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	1·09	1·08	1·08	1·08
h, k, l range h	0–10	0–10	0–10	0–10
k	0–10	0–10	0–10	0–10
l	0–48	0–48	0–48	0–48
No. of standard reflections	5	5	5	5
No. of observed reflections	2446	2422	2437	2008
No. of reflections used in refinement $[F_o^2 > 2\sigma(F^2)]$	2036	1011	1004	928
No. of unique reflections	1285	1284	1282	1178
$R_{int} = \sum \lvert I_o - \bar{I}_o \rvert / \sum I_o$	0·023	0·028	0·030	0·030
No. of parameters refined	46	46	46	64
Max./min. peak in final difference map (e Å^{-3})	0·72/−1·06	1·32/−0·81	1·07/−1·15	0·98/−0·72
$R(F_o)$ $[F_o^2 < 2\sigma(F^2)$ excluded]	0·0187	0·0242	0·0324	0·0289
$R(F^2)$ $[F_o^2 < 2\sigma(F^2)$ excluded]	0·0240	0·0398	0·0562	0·0578
S	2·623	1·606	1·984	1·936
Max. Δ/σ	0·1	0·1	0·1	0·1
wR $[F_o^2 < 2\sigma(F^2)$ excluded]	0·0436	0·0598	0·0734	0·0651

The general procedure and relevant parameters for the data collections are summarized in Table 1. Intensities were measured at 295 K with an automatic Nonius CAD-4 diffractometer controlled by a PDP8/A computer. Integrated intensities were measured using an $\omega/2\theta$ step scan (96 steps). Each intensity was measured three times at 0·5° intervals in ψ as a check on multiple reflections. Mo $K\bar{\alpha}$ radiation ($\lambda = 0\cdot71073$ Å). Intensity data were corrected for background (Lehmann & Larsen, 1974). Five standard reflections were used to scale intensities and standard deviations (McCandlish, Stout & Andrews, 1975). Lp and absorption corrections were applied (Table 1). Linear absorption coefficients were measured experimentally for all four crystals and the values were used in the absorption corrections which employed explicit descriptions of crystal shape and dimensions. Systematic absences indicated the possible space groups $P6_3/mmc$ and $P6_3mc$. $P6_3/mmc$ was used throughout, although a special test for $P6_3mc$ is described in the discussion. All results were refined using the full-matrix least-squares program *DUPALS* (Lundgren, 1982). The function minimized was $\sum w(\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2$, where $w^{-1} = \sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (kF_o^2)^2$, k is an empirical constant (see Table 1). Reflections with F_o^2 less than $2\sigma(F_o^2)$ were removed from all four refinements. Isotropic extinction refined for all compositions. The number of reflections used in each case is given in Table 1. The coherent scattering amplitudes and anomalous-dispersion terms used for Al^{3+}, O^{2-}, Na^+ and Cd^{2+} were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Refinements

The refinements and subsequent Fourier calculations for the Na^+ β-alumina case are described elsewhere (Edström, Thomas & Farrington, 1991). Essentially, Na^+ ions have been refined in two sites: a Beevers–Ross (BR) site with ~60% of the Na^+ ions and an *A* site with ~40% of the total 1·22 Na^+ ions in one conduction layer (Figs. 2*a* and 2*e*). The BR-site Na^+ ion) was described with second- and third-rank thermal parameters (β_{ij}'s and γ_{ijk}'s). The *A*-site ion was only refined with β_{ij}'s (Table 2).* The other three refinement sequences have been based on the Na^+ β-alumina structure with the following exceptions:

(i) For $y = 0{\cdot}22$, the parameters from $y = 0{\cdot}00$ were used in the first refinement. The difference Fourier synthesis showed a new electron density peak along the conduction pathway, which was assigned to Cd^{2+} ions; see Figs. 2(*b*) and 2(*f*) in which the Cd^{2+} site [a 6(*h*) site] is denoted by *B*. The Na^+ ions were again found at BR and *A* sites. The electron density maps showed that only the *A* site had decreased in occupation, the electron density in the BR site was unaffected by the introduction of Cd^{2+} ions. The positions for both Na^+ ions were constrained to be the same as in $y = 0{\cdot}00$. Anisotropic temperature factors for the Na^+ ion in the BR site were refined (β_{ij}'s and γ_{ijk}'s) (Table 2). The temperature factors for the *A*-site Na^+ ion were constrained to the same values as in the $y = 0{\cdot}00$ case. The temperature factors for the Cd^{2+} ion were also refined but the positions constrained to those refined for $y = 0{\cdot}45$. The Cd^{2+} occupation was constrained to be consistent with the experimentally determined composition. This model fails, however, to describe satisfactorily the form of the average electron density for the BR-site Na^+ ions in the *z* direction (see Fig. 2*f*).

(ii) The first crude picture of the conduction plane for $y = 0{\cdot}45$ was obtained in the same way as for $y = 0{\cdot}22$. The same *B* site for the Cd^{2+} ions was observed. Also in this case, only the *A*-site Na^+ ions were seen to disappear and the BR-site Na^+ ions were unaffected (Figs. 2*c* and 2*g*). The position of the Cd^{2+} ion (*B*) was refined but the occupation kept fixed to its experimentally determined value. The anisotropic displacement parameters were refined, except for the small amount of Na(2) at the *A* site which was fixed at the $y = 0{\cdot}00$ value. The observed Fourier observation maps indicate some electron density at the 2(*b*) site [anti-Beevers–Ross (aBr) site] (Figs. 2*c* and 2*g*). The refined model succeeds in describing this feature without actually placing ions at this site (see later). This model could not describe the electron density at the BR site completely satisfactorily.

(iii) In the $y = 1{\cdot}22$ case, the Cd^{2+} ions were found in an extended region in the conduction pathways, see Figs. 2(*d*) and 2(*h*). The maximum in the electron density was found at a *C* site, close to the mO site. To be able to describe all of the electron density, a model was refined using four different Cd^{2+} positions: *C*, *D*, *E* and *F* sites. The *D* site was refined at a position shifted out of the plane in the *z* direction (to $z \sim 0{\cdot}26$) (Fig. 2*h*). The *E* and *F* sites were refined at 12(*j*) sites closer to the BR site (Fig. 2*d*). A test to refine the content in the BR site gave a negative result. Anisotropic temperature factors were refined for the ions in the *C* and *D* sites; both β_{ij} and γ_{ijk} tensors were refined for the *C* site, only β_{ij}'s for the *D* site. The resulting two sites, *E* and *F*, were refined with isotropic temperature factors. Note, however, that these four refined Cd^{2+} positions should not be interpreted in terms of ions actually occupying these sites. They simply represent the best way of describing an extended Cd^{2+} distribution. The total Cd^{2+} content was also constrained to the total experimentally determined Cd^{2+} content. The column-oxygen O(5) was refined as a split atom in three equivalent 6(*h*) sites (Fig. 2*d*).

In all cases, the interstitial Al atoms [Al(5)] in the Frenkel defect could be readily located in our Fourier maps, while the presence of the extra O atom was more difficult to establish. Although it has been

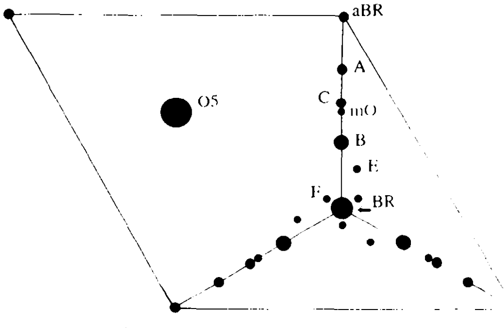

Fig. 1. A schematic representation of the different sites (see text) available for Na^+- and Cd^{2+}-ion occupation in the conduction plane of β-alumina; mO is the so-called mid-oxygen site.

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* Lists of structure factors, anisotropic thermal parameters and refinement details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54079 (88 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

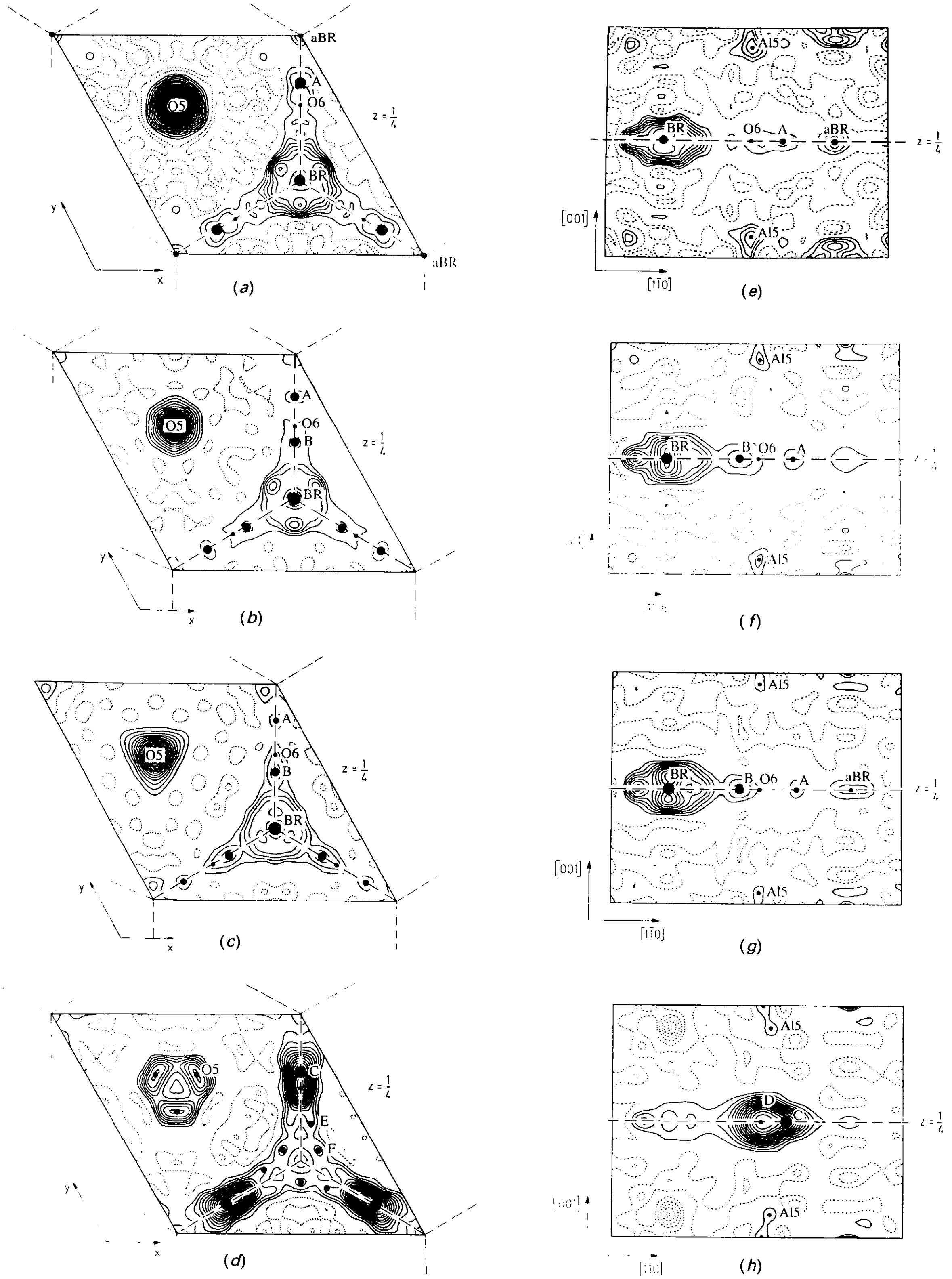

Fig. 2. F_o syntheses for $Na_{1\cdot22-y}Cd_{y/2}Al_{11}O_{17\cdot11}$ with y = 0·00, 0·21, 0·45 and 1·22. (*a*)–(*d*) The conduction plane at $z = \frac{1}{4}$, (*e*)–(*h*) the (x, y, z) plane perpendicular to the conduction plane for the respective compositions. Contour intervals for y = 0·00 are 0·7 e Å^{-3}; otherwise they are 1·0 e Å^{-3}. Zero contours are omitted.

Table 2. *Atomic positional parameters* ($\times 10^5$) *in* $Na_{1\cdot22-y}Cd_{y/2}Al_{11}O_{17\cdot11}$

Equivalent isotropic displacement parameters for the spinel block [expressed as mean-square amplitudes, $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}) \times 10^3$] and anisotropic displacement parameters ($\beta_{ij} \times 10^4$) for Na^+ and Cd^{2+} ions and the O(5) atom. For each atom the four rows refer to compositions y = 0·00, 0·22, 0·45 and 1·22, respectively.

	Site	Fractional occupation	x	y	z	β_{11} or U_{eq} (Å^2)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na(1)	2(d)	0·723	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	1229 (16)	β_{11}	14·9 (4)	$\beta_{11}/2$	0	0
		0·723				1304 (30)		15·8 (9)			
		0·723				1656 (31)		24·2 (10)			
		—	—	—	—	—	—	—	—	—	—
Na(2)	6(h)	0·166	89702 (130)	$-x$	$\frac{1}{4}$	1338 (34)	β_{11}	3·9 (4)	−400 (48)	0	0
		0·095	89702			1338		3·9	−400		
		0·017	89702			1338		3·9	−400		
		—		—		—	—	—	—	—	—
Cd(B)	6(h)	—	—		—	—	—	—	—	—	—
		0·035	78763	$-x$	$\frac{1}{4}$	1593 (106)	β_{11}	12·3 (15)	−684 (108)	0	0
		0·074	78763 (200)			4932 (158)		9·7 (4)	−4245 (168)		
			—	—	—	—	—		—		—
Cd(C)	6(h)	—	—			—	—	—		—	—
		—	—	—	—	—	—	—	—	—	—
			—	—	—		—		—		—
		0·129 (14)	86044 (355)	$-x$	$\frac{1}{4}$	735 (33)	β_{11}	8·4 (7)	−206 (33)	0	0
Cd(D)	12(k)	—	—	—	—	—		—	—		—
		—		—	—	—	—	—	—	—	—
			—	—		—	—	—	—	—	—
		0·023 (1)	83617 (114)	x	26124 (40)	235 (21)	β_{11}	4·4 (5)	−8 (1)	4·8 (18)	−4·8 (18)
Cd(E)	12(j)		—			—					
		—	—	—	—	—					
		—	—	—	—	—					
		0·011 (2)	73583 (243)	33195 (379)	$\frac{1}{4}$	3·2					
Cd(F)	12(j)	—		—	—						
			—	—	—	—					
		—	—	—	—						
		0·004 (2)	79815 (340)	29258 (541)	$\frac{1}{4}$	10·6					
O(5)	2(c)		$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	660 (6)	β_{11}	0·93 (10)	$\beta_{11}/2$	0	0
						501 (9)		1·6 (2)			
						468 (12)		2·2 (3)			
	6(h)		277736 (41)	$-x$		492 (21)		1·7 (3)	106 (9)	0	0
Al(1)	12(k)	0·963	−16798 (1)	$2x$	10610 (1)	4·9					
			−16771 (2)		10643 (1)	4·8					
			−16765 (3)		10661 (1)	4·6					
			−16795 (3)		10711 (1)	5·5					
Al(2)	4(f)		$\frac{1}{3}$	$\frac{2}{3}$	2482 (1)	3·8					
					2479 (2)	3·9					
					2475 (2)	3·7					
					2501 (2)	4·1					
Al(3)	4(f)		$\frac{1}{3}$	$\frac{2}{3}$	17576 (1)	6·1					
					17564 (1)	6·1					
					17577 (2)	6·0					
					17632 (2)	7·5					
Al(4)	2(a)	100·0	0	0	0	4·3					
						4·4					
						4·0					
						4·4					
O(1)	12(k)		15712 (2)	$2x$	4998 (1)	5·1					
			15730 (5)		4999 (2)	4·9					
			15728 (6)		4983 (3)	4·9					
			15714 (6)		5028 (3)	5·3					
O(2)	12(k)		50305 (2)	$-x$	14633 (1)	5·0					
			50311 (5)		14640 (2)	5·9					
			50314 (7)		14646 (3)	5·8					
			50234 (6)		14684 (3)	7·1					
O(3)	4(f)		$\frac{2}{3}$	$\frac{1}{3}$	5525 (2)	5·2					
					5545 (4)	5·1					
					5539 (4)	4·8					
					5578 (4)	5·5					
O(4)	4(e)		0	0	14219 (2)	4·7					
					14223 (4)	4·8					
					14212 (5)	4·5					
					14368 (4)	4·9					
Al(5)	12(k)	0·037	−16045 (5)	$2x$	17523 (13)	4·9					
			−16365 (60)		17496 (27)	4·8					
			16333 (70)		17345 (50)	4·6					
			−16019 (44)		17540 (31)	5·5					
O(6)	6(h)	0·037	$\frac{5}{6}$	$\frac{1}{6}$	$\frac{1}{4}$	3·0					
			$\frac{5}{6}$	$\frac{1}{6}$	$\frac{1}{4}$	3·0					
			$\frac{5}{6}$	$\frac{1}{6}$	$\frac{1}{4}$	3·0					
			$\frac{5}{6}$	$\frac{1}{6}$	$\frac{1}{4}$	3·0					

detected earlier in a neutron study (Reidinger, 1979), it is unrealistic to expect to observe its contribution among the total electron distribution in the conduction plane in an X-ray diffraction experiment. In our refinements, interstitial O atoms, O(6), are kept fixed at mO positions. A test was made to refine the occupations of the Al(1) and Al(5) atoms. In all cases involving Cd^{2+} ions, the occupation of the Al(5) site was seen to decrease. The occupations in the Al(1) and Al(5) sites were therefore fixed to correspond to our picture of the Roth–Reidinger defect, two Al(5) atoms per O(6) atom. Refined positional parameters and occupations for all four structures are given in Table 2.

The results of an earlier reported structural study (Catti *et al.*, 1987) of the $y = 1{\cdot}00$ case may be summarized as follows. The O(5) ion is disordered, as in the $y = 1{\cdot}22$ case. The Cd^{2+} ions occupy sites similar to the Cd(C) site in $y = 1{\cdot}22$ but are displaced to a disordered position ~0·17 Å from the conduction plane. The remaining Na^+ ions occupy the same site as the Na(1) ions in our $y = 0{\cdot}00$, 0·21 and 0·45 cases. This result agrees well with our picture, except that we see no displacement of Cd^{2+} out of the conduction plane (Figs. 2*d* and 2*h*).

Results and discussion

Description of the structure

The structure comprises Al atoms octahedrally and tetrahedrally coordinated by O atoms to form spinel layers separated in the *c* direction by Al(3)—O(5)—Al(3) bridging bonds. The spinel-block structure of Na$^+$ β-alumina (Peters, Bettman, Moore & Glick, 1971) is retained in all its essential features in the mixed Na$^+$/Cd^{2+} β-alumina structures, see also Edström, Thomas & Farrington (1988, 1991). The *c* axis shortens when Na$^+$ ions are exchanged for Cd^{2+} ions [22·534 (4), 22·526 (7), 22·519 (9) and 22·371 (4) Å for y = 0·00, 0·22, 0·45 and 1·22, respectively]. The conduction planes contain the column-oxygen O(5) (at $z = \frac{1}{4}$ and $\frac{3}{4}$) along with Na$^+$ and/or Cd^{2+} ions and extra O(6) ions in (on average) every nine unit-cell layers (Fig. 1). The Na$^+$ ions are distributed along edge-linked hexagonal pathways around the O(5) ions (see Edström *et al.*, 1991) with the O(5) atom occupying a 2(*c*) site. The extra oxygens O(6) occupy 6(*h*) (mO) sites at the centre of the conduction-plane pathways and are bonded to the spinel block through interstitial Al ions at $z \simeq 0·175$ and $z \simeq 0·325$. These Al ions [Al(5)] have become displaced from the Al(1) site, such that the occupation of Al(1) is diminished by an amount corresponding to the Al(5) occupation (a Frenkel defect). This Roth–Reidinger defect compensates for the Na$^+$ and Cd^{2+} excess in the conduction planes.

The Na$^+$ *distribution in* Na$^+$ *β-alumina*

The distribution of electron density along the conduction pathways involves a maximum at the 2(*d*) (BR) site and a smaller maximum at the refined *A* site [6(*h*)] (see Figs. 2*a* and 2*e*). The Na$^+$-ion distribution in Na$^+$ β-alumina has been discussed at length in Edström *et al.* (1991). We shall here focus our attention on the mixed ion system.

The Na$^+$/Cd^{2+} *distribution*

When 17·4% of the Na$^+$ ions have been replaced by Cd^{2+} ions (y = 0·22) a new site (*B*) appears near the mO site in the conduction plane (Figs. 2*b* and 2*f*). As further Cd^{2+} ions are exchanged into the structure, the electron density at this *B* site increases (Figs. 2*c* and 2*g*). In the almost fully exchanged case, a Cd^{2+} electron density maximum is found nearer to the mO site (*C*), and some are found near the BR site (sites *E* and *F* in Fig. 2*d*). These results suggest that, at low Na$^+$-ion replacement, Cd^{2+} ions move to the *B* site to replace Na$^+$ ions at the *A* site. This situation is maintained until more than 36·5% (y = 0·45) of the Na$^+$ ions have been replaced. The Na$^+$ ions at the BR sites then begin to be exchanged for Cd^{2+} ions. In the almost fully exchanged case, ~85% of the Cd^{2+} ions occupy *C* and *D* sites and ~15% *E* and *F* sites. The column-oxygen O(5) also becomes disordered over three 6(*h*) positions; the effect of this is also seen in a shortening of the *c* axis by 0·16 Å with respect to the Na$^+$ β-alumina value. Although no splitting of the O(5) position is resolved in the other three structures, some degree of disorder is suggested by the unusually high anisotropic thermal displacement parameters refined for O(5) (Table 2). The distance from the Cd(*B*) ion to O(5) is 2·830 (10) Å, and from Cd(*C*) to O(5) is 2·324 (18) Å. The Na(2)—O(5) distance is 2·864 (6) Å (Table 3).

Table 3. *Some interatomic distances* (Å) *for* Na$_{1·22-y}$Cd$_{y/2}$Al$_{11}$O$_{17·11}$, y = 0·00, 0·22, 0·45 *and* 1·22 *with* $P6_3/mmc$ *notation*

		y = 0·00	y = 0·21	y = 0·45	y = 1·22
Na(1)—O(2)	(×6)	2·822 (1)	2·821 (1)	2·820 (1)	
Na(1)—O(5)	(×3)	3·229 (1)	3·229 (1)	3·228 (1)	
Na(2)—O(6)	(×1)	2·283 (6)	2·283	2·282	
Na(2)—O(4)	(×2)	2·626 (2)	2·624 (1)	2·626 (1)	
Na(2)—O(5)	(×2)	2·864 (6)	2·863 (1)	2·863 (1)	
Na(2)—O(6)	(×1)	3·345 (6)	3·345	3·344	
Cd(*B*)—O(6)	(×1)		2·423	2·410 (9)	
Cd(*B*)—O(2)	(×2)		2·733 (1)	2·729 (5)	
Cd(*B*)—O(5)	(×2)		2·831 (1)	2·832 (9)	
Cd(*B*)—O(6)	(×1)		3·187	3·199 (9)	
Cd(*C*)—O(6)	(×1)				2·570 (17)
Cd(*C*)—O(4)	(×2)				2·735 (9)
Cd(*C*)—O(2)	(×4)				2·896 (17)
Cd(*C*)—O(5)	(×2)				2·907 (17)
Cd(*C*)—O(6)	(×1)				3·023 (17)
Al(1)—O(4)	(×1)	1·819 (1)	1·814 (1)	1·810 (1)	1·820 (1)
Al(1)—O(2)	(×2)	1·833 (1)	1·831 (1)	1·829 (1)	1·826 (1)
Al(1)—O(3)	(×1)	1·969 (1)	1·973 (1)	1·976 (1)	1·970 (1)
Al(1)—O(1)	(×2)	2·021 (1)	2·025 (1)	2·029 (1)	2·024 (1)
Al(2)—O(1)	(×3)	1·799 (1)	1·797 (1)	1·796 (1)	1·796 (1)
Al(2)—O(3)	(×1)	1·804 (1)	1·808 (1)	1·804 (1)	1·807 (1)
Al(3)—O(5)	(×1)	1·672 (1)	1·675 (1)	1·672 (1)	1·735 (1)
Al(3)—O(2)	(×3)	1·773 (1)	1·771 (1)	1·772 (1)	1·763 (1)
Al(4)—O(1)	(×6)	1·893 (1)	1·895 (1)	1·892 (1)	1·891 (1)
Al(5)—O(6)	(×1)	1·685 (3)	1·691 (6)	1·724 (10)	1·670 (7)
Al(5)—O(4)	(×1)	1·723 (1)	1·748 (3)	1·732 (5)	1·705 (5)
Al(5)—O(2)	(×2)	1·757 (1)	1·738 (3)	1·726 (4)	1·755 (3)

The conductivity mechanism

The critical point in the earlier discussion of the conductivity mechanism in Na$^+$ β-alumina was whether the Na$^+$ ions found at so-called interstitial sites in the conduction plane are responsible for the high ionic mobility and should be the first to become replaced by Cd^{2+} ions (Sutter *et al.*, 1983). In this context, the diffraction result presented here can be interpreted as follows. The Na$^+$ ions at the *A* sites (the 'interstitial' Na$^+$ ions in the earlier discussion) are the first to be replaced. When these sites are empty, the Na$^+$ ions at the BR sites are replaced. The real structural picture is more complex, however, if we take into account the presence and the influence of the compensating O(6) atoms. Discussions of the influence of O(6) on the Na$^+$-ion arrangement are many (Roth *et al.*, 1976; Reidinger, 1979; Wang, 1980; Wolf, 1979; Walker & Catlow, 1982; Carduner & White, 1987, Zendejas & Thomas, 1990; Edström *et al.*, 1991). Our diffraction results support a picture in which Na$^+$ ions will take up four *A* sites around an O(6) atom (Fig. 3*a*). The shortest *A* site to O(6) distance is 2·283 (6) Å, slightly longer than a Na$^+$—O distance in Na$_2$O (~2·16 Å). The next nearest *A* site is 3·345 (6) Å away from

O(6). At low temperatures, the O(6) atom is thus surrounded by two types of Na^+-ion pairs. The question then arises as to whether it is some or all of these Na^+ ions that are involved in the conduction process (Wolf, 1979), or whether conduction, in fact, involves the ions outside this region.

The exchange of Cd^{2+} ions into Na^+ β-alumina is performed at 975 K. At this relatively high temperature, the overall mobility of the ions is large. We should bear this in mind when interpreting the room-temperature results to rationalize processes which have occurred at higher temperatures. The present study shows that the Cd^{2+} ions occupy one specific site (*B* site) in the conduction plane. The *B* site to O(6) distance of 2·528 (13) Å suggests a Cd^{2+}—O(6) interaction; the Cd^{2+}—O distance of ~2·36 Å in CdO supports this idea. Since one Cd^{2+} ion appears to replace an Na^+ pair in the structure, we can speculate that the Na^+-ion pair with the longer Na^+—O(6) distance [3·390 (8) Å] (Fig. 3*a*) will thus be the first to be replaced by one Cd^{2+} ion on the side of O(6), where the *B* site to O(6) distance is shortest (Fig. 3*b*). It could be that the shortest Na^+—O(6) bond lengthens (relaxes) in response to the strong attraction between Cd^{2+} and O(6). This factor can also contribute to the higher conductivity reported when small amounts of Na^+ are replaced by Cd^{2+} ions (Sutter *et al.*, 1983); the Cd^{2+} ion may be seen as 'screening' the O(6) ion. When all such pairs are removed, the remaining Na^+ ions will presumably continue to be replaced pairwise. These can be either a pair involving one BR-site ion and one *A*-site ion, or two *A*-site ions (Fig. 3*b*). Both possibilities give ultimately the same result; in the former case, a vacancy is created at another BR site for the *A*-site Na^+ ion to relax into. This is the same situation as would follow the replacement of two *A*-site ions; a low-conductivity quasi-stoichiometric compound in which the Na^+ ions only occupy BR sites. As more Cd^{2+} ions replace BR-site Na^+ ions, the conductivity continues to be low. This is, again, experimental evidence discounting a vacancy mechanism for rapid ion mobility in Na^+ β-alumina. Returning to the question of the rôle of O(6) in the conduction mechanism of the unexchanged Na^+ β-alumina, it is tempting to suggest that, even here, local Na^+ binding to O(6) hinders the mobility of the associated Na^+ ions and that the mobility is restricted to those Na^+ ions more distant from O(6). This is indeed the picture which emerges from recent molecular-dynamics simulations (Zendejas & Thomas, 1990). It is not possible, however, to extract unambiguous confirmation of these ideas directly from our diffraction results; the overlap problem introduces too severe a handicap. On the other hand, we stress that the diffraction results in no way invalidate these ideas. Molecular-dynamics simulation of the mixed-ion system is underway to gain greater insights into the structural arrangements of Na^+ and Cd^{2+} ions around the O(6) atom.

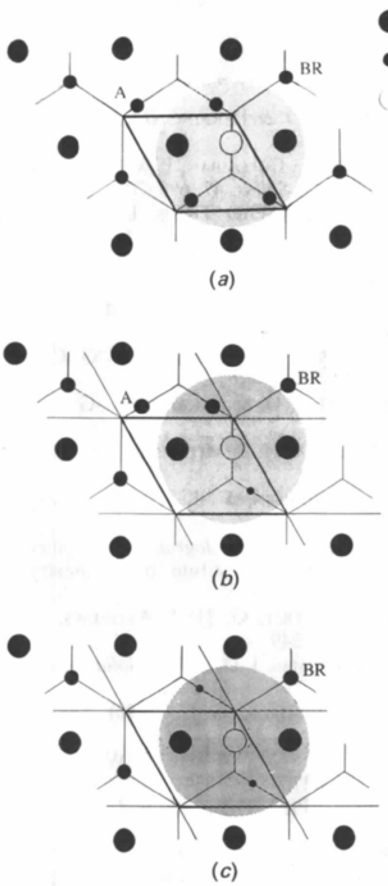

Fig. 3. Sphere of greatest influence around O(6), the charge-compensating O atom, for (*a*) Na^+ β-alumina, (*b*) a situation where two Na^+ ions have been replaced by one Cd^{2+} ion ($y \simeq$ 0·18), (*c*) a situation where four Na^+ ions have been replaced by two Cd^{2+} ions ($y \simeq 0{\cdot}36$).

A consensus emerges from all efforts made to study the Na^+ β-alumina system; high ionic conductivity in Na^+ β-alumina is directly attributable to the excess Na^+ ions. Complications arise from the conflicting rôles of the O(6) atom in the Roth–Reidinger defect; it is needed both to compensate for the extra Na^+ ions and yet it is also serves to block the Na^+-conduction pathways and to trap a fraction of the Na^+ population.

Short-range order in Cd^{2+} *β-alumina*

In closing, let us focus on a somewhat more general structural phenomenon: local correlation in the ionic distribution. The general assumption that Bragg diffraction data arise from the structural average over the entire crystal breaks down if some short-range ordering feature is present with a correlation length comparable to or greater than the coherence length of the diffraction process. Thomas and coworkers (Aldén, Thomas & Farrington, 1981; McIntyre & Thomas, 1983; Thomas, Aldén, McIntyre & Farrington, 1984) have shown that such a situation is present in divalent β″-aluminas, where additional information about short-range ordering could be obtained by lowering the effective space-group symmetry from centrosymmetric $R\bar{3}m$ to non-centrosymmetric $R3m$ for the divalent ions in the centrosymmetric β″-alumina host. The question thus arises as to whether a similar treatment can be applied to advantage for the ionic distributions in the present β-alumina system. The situation can be examined in the fully exchanged Cd^{2+} β-alumina case by removing the mirror symmetry for the Cd^{2+} ions in the conduction plane and for the interstitial Al atoms, Al(5) (effective space group $P6_3mc$); the symmetry of the spinel block is otherwise retained ($P6_3/mmc$). The Cd^{2+} ions were shifted systematically away from the conduction plane prior to refinement. However, after only a few cycles, they had returned to their in-plane positions at $z = 0{\cdot}25$ and $z = 0{\cdot}75$ suggesting no significant tendency towards short-range ordering. Catti *et al.* (1987) have, in fact, reported a displacement of the Cd^{2+} ions ~0·17 Å out of the mirror plane for 80% Na^+ replacement by Cd^{2+}. Boilot, Lee, Colomban, Collin & Comès (1986) have also studied nominally Cd^{2+} β-alumina, but with a much higher Cd^{2+} content ($Cd_{0{\cdot}83}$), where the excess Cd^{2+} ions are compensated by Mg^{2+} ions in the spinel block (general formula for the parent compound $Na_{1+y}Mg_yAl_{11-y}O_{17}$). They have used X-ray diffuse scattering to study this same compound. Short-range order characterized by a short correlation length ($\xi < 10$ Å) was found and no superlattice reflections were observed. The different compositions and compensating mechanism in these two cases make it difficult to assess the relevance of the differences in the observed ionic distributions. On the other hand, a correlation length as short as 10 Å may not be detected by our refinement test. We observe the average of an effectively randomized distribution.

Summary

This study has provided the structural basis for a better understanding of the conduction mechanism in Na^+ β-alumina. Earlier β-alumina literature has clearly tended to overstate the role of the special positions in the conduction plane. Typically, discussions of how ions at so-called mO sites are involved in the conduction mechanism are fallacious to the extent that no such sites are indeed occupied systematically. The real situation is more complex: it is a distribution of ions with its maximum clearly displaced from the mO position.

We have shown that, although certain methodological difficulties exist in the diffraction treatment of non-stoichiometric mobile-ion systems, some significant information can be extracted from our data concerning the nature of local ionic arrangements. It is clear, however, that supporting techniques are needed. In this connection, we have therefore turned recently to molecular-dynamics simulation as an alternative approach to this problem, whereby we can extend our perspectives beyond the space- and time-averaged picture of crystallographic unit-cell content obtained from a diffraction experiment.

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References

Aldén, M., Thomas, J. O. & Farrington, G. (1981). *Solid State Ionics*, **5**, 205.

Boilot, J. P., Lee, M. R., Colomban, P., Collin, G. & Comès, R. (1986). *J. Phys. Chem. Solids*, **47**, 693–706.

Carduner, K. R. (1984). PhD Thesis, Univ. of Pennsylvania, USA.

Carduner, K. R. & White, D. (1987). *Solid State Ionics*, **25**, 93–97.

Catti, M., Cazzanelli, E., Ivaldi, G. & Mariotto, G. (1987). *Phys. Rev. B*, **36**, 9451–9460.

Edström, K., Thomas, J. O. & Farrington, G. C. (1988). *Solid State Ionics*, **28–30**, 363–368.

Edström, K., Thomas, J. O. & Farrington, G. C. (1991). *Acta Cryst.* **B47**, 210–216.

Hattori, T., Kurokawa, H. & Mitsuishi, A. (1983). *Solid State Ionics*, **9–10**, 215–220.

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* **A30**, 580–584.

Lundgren, J.-O. (1982). *Crystallographic Computer Programs*. Report UUIC-B13-04-05. Institute of Chemistry, Univ. of Uppsala, Sweden.

McCandlish, L. E., Stout, G. H. & Andrews, L. C. (1975). *Acta Cryst.* **A31**, 245–249.

McIntyre, G. J. & Thomas, J. O. (1983). *Solid State Ionics*, **9–10**, 195–198.

Mariotto, G. & Farrington, G. C. (1986). *Solid State Ionics*, **18–19**, 619–623.

Peters, C. R., Bettman, M., Moore, J. W. & Glick, M. D. (1971). *Acta Cryst.* **B27**, 1826–1834.

Reidinger, F. (1979). PhD Thesis, State Univ. of New York, Albany, USA.

Roth, W. L. Reidinger, F. & LaPlaca, S. (1976). *Superionic Conductors*, edited by G. D. Mahan & W. L. Roth, pp. 223–241. New York: Plenum Press.

Sutter, P. H., Cratty, L., Saltzberg, M. & Farrington, G. C. (1983). *Solid State Ionics*, **9–10**, 295–298.

Thomas, J. O., Aldén, M., McIntyre, G. J. & Farrington, G. C. (1984). *Acta Cryst.* **B40**, 208–213.

Tofield, B. C. (1982). *Intercalation Chemistry*, edited by A. J. Jacobson & M. S. Whittingham, pp. 181–227. New York: Academic Press.

Walker, J. R. & Catlow, C. R. A. (1982). *J. Phys. C*, **15**, 6151–6161.

Wang, J. C. (1980). *J. Chem. Phys.* **73**, 5786–5795.

Whittingham, M. S. & Huggins, R. A. (1971). *J. Electrochem. Soc.* **118**, 1–6.

Wolf, D. (1979). *J. Phys. Chem. Solids*, **40**, 757–773.

Yao, Y. F. & Kummer, J. T. (1967). *J. Inorg. Nucl. Chem.* **29**, 2453–2474.

Zendejas, M. A. & Thomas, J. O. (1990). *Phys. Scr.* In the press.

Acta Cryst. (1991). B**47**, 643–650

A Single-Crystal X-ray Diffraction Study of the Ion Exchange of Cd^{2+} into Ag^{+} β-Alumina

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Abstract

Conventional single-crystal X-ray diffraction (Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å) at 295 K has been used to study the ionic distribution of five compositions of the mixed-cation system Ag^{+}/Cd^{2+} β-alumina, $Ag_{1\cdot22-y}Cd_{y/2}Al_{11}O_{17\cdot11}$, $y = 0{\cdot}00$, 0·10, 0·41, 0·99 and 1·11. $M_r = 702{\cdot}1$, 697·1, 680·7, 651·1 and 644·8, $F(000) = 674{\cdot}4$, 670·0, 655·4, 629·0 and 623·4. The compounds are made by the controlled ion exchange of Cd^{2+} ions into Ag^{+} β-alumina from a $CdCl_2$ melt at 873 K. The structure comprises a hexagonal framework of spinel-type blocks of aluminium oxide separating two-dimensional conduction planes with a spacing of ~ 11 Å. All atoms in the spinel framework follow the centrosymmetric hexagonal space group $P6_3/mmc$, $Z = 2$, with cell dimensions $a = 5{\cdot}5914\,(3)$, 5·6032 (2), 5·5959 (2), 5·5896 (5) and 5·5900 (7) Å and $c = 22{\cdot}430\,(4)$, 22·504 (3), 22·458 (1), 22·434 (8) and 22·396 (6) Å for $y = 0{\cdot}00$, 0·10, 0·41, 0·99 and 1·11, respectively. Final $wR(F_o^2)$ values are 0·0796, 0·0693, 0·0698, 0·0874 and 0·0853, respectively. In Ag^{+} β-alumina, the Ag^{+} ions occupy three different 6(*h*) sites: one near the 2(*d*) site, Ag(1); one close to the 2(*b*) site, Ag(3); and a third site, Ag(2), between these two sites, close to Ag(1). The occupations are 41, 33 and 26% for Ag(1), Ag(2) and Ag(3), respectively. The Cd^{2+} ions enter a new 6(*h*) site, not previously occupied by Ag^{+} ions. At low replacement (~ 8%), the Ag(1)-site occupation is unchanged. By the time ~ 34% of the Ag^{+} ions have been replaced, three Ag^{+} sites are replaced with almost equal amounts by Cd^{2+} ions. When 81 and 91% of the Ag^{+} ions have been replaced, Ag(1) is the only site still containing Ag^{+} ions. The implications of these results are discussed with reference to the general aspects of ion exchange in β-alumina.

Introduction

The Na^{+} β-alumina structure offers a unique opportunity for studying the behaviour of mixed cations with different radii and valence because different monovalent cation types can be accommodated into the same structural host (Yao & Kummer, 1967). The structure comprises loosely packed conduction layers which interleave rigid spinel blocks. More recently, Na^{+} β-alumina has been exploited as a host for probing the structural and chemical properties of mixed-cation systems, typically, the non-additive behaviour of ionic conductivity of mixed-alkali systems which is a phenomenon commonly referred to as the mixed alkali effect, *e.g.* Na^{+}–K^{+} and Na^{+}–Ag^{+} β-alumina (Bruce, Howie & Ingram, 1986) and Na^{+}–Li^{+} β-alumina (Tofield & Farrington, 1979).

In contrast, divalent ions are found to be reluctant to exchange into β-alumina and the resulting compounds are poor ionic conductors (unlike the situation in the related compound β''-alumina, which accepts a diversity of divalent ions). It has been found that Cd^{2+} is the only divalent cation type which can exchange totally into β-alumina and that this process can serve as a valuable structural probe

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