JOURNAL OF SOLID STATE CHEMISTRY 43, 227–236 (1982)

The Preparation and Physical Properties of Indium β-Alumina Single Crystals

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Received November 24, 1980; in final form November 10, 1981

This study reports the preparation of single crystals of indium β-alumina, the characterization of the structure, and the thermal stability. The crystal structure of indium β-alumina was determined from three-dimensional X-ray data. The compound has a hexagonal structure with space group $P6_3/mmc$ and lattice constants $a = 5.599$ Å, $c = 22.901$ Å, with an empirical formula $In_{2.47}Al_{22}O_{34}$.

Introduction

β-Alumina has the empirical formula $Na_2O \cdot 11Al_2O_3$ and the possibility of ion exchange was first reported by Toropov and Stukalova (*1, 2*), who concluded that Ca^{2+}, Sr^{2+}, and Ba^{2+} β-alumina could be formed by immersion of β-alumina in an appropriate molten salt. Yao and Kummer (*3*) further investigated the ion-exchange properties and were able to form several different ion-substituted β-aluminas from sodium β-alumina by immersion in molten salts. With some β-aluminas the chemical equilibrium favored the salt of the element and little exchange occurred, but this problem was usually overcome by exchange from a substituted β-alumina such as silver β-alumina. Using this technique, Yao and Kummer (*3*) were able to prepare Ag^+, Tl^+, K^+, and Rb^+ β-aluminas by direct exchange with Na β-alumina and Li^+ and In^+ β-aluminas could be obtained by exchange with Ag β-alumina. It was also observed that some exchange was possible with certain divalent ions (such as Pb^{2+}, Sr^{2+}, Ca^{2+}, Zn^{2+}, Fe^{2+}, Mn^{2+}), although in all cases exchange occurred slowly and was not complete. Other workers have indicated that it is possible to prepare NO^+ (*4*), Ca^+ (*5*), H_3O^+ (*6*), H^+ (*7*), Cu^+ (*8, 9*), and Zn^{2+} (*10*) β-aluminas. Whittingham *et al.* (*8*) prepared ion-exchanged β-aluminas by the use of an electrochemical cell, with β-alumina as the electrolyte and molten salt electrodes. With regard to In β-alumina, Yao and Kummer (*3*) observed that no measurable exchange occurred when 1-mm crystals of Monofrax H sodium β-alumina were immersed in molten InI at 673 K. They were, however, able to obtain complete substitution of Ag^+ β-alumina by treatment with In metal containing a small amount of mercury.

The crystal structure of sodium β-alumina is well defined and has a hexagonal layer structure with lattice constants $a = 5.594$ and $c = 22.53$ Å. The sodium atoms are situated exclusively in planes 11.27 Å apart and perpendicular to the c axis as

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0022-4596/82/090227-10$02.00/0

shown in Fig. 1. Between these planes containing the sodium ions are four close-packed oxygen layers, also perpendicular to the axis, with appropriate aluminum ions in both octahedral and tetrahedral interstices, the oxygen atoms being arranged cubically. Beevers and Ross (*11*) postulated two positions for the sodium atoms, at $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{4}$ and at 0, 0, $\frac{1}{4}$. These are known as the Beevers and Ross (BR) and anti-Beevers and Ross (aBR) sites, respectively. They considered the first site to be the most probable. Peters *et al.* (*12*) found these to be an excess of sodium oxide relative to the ideal formula which corresponds to 2.58 Na atoms per unit cell instead of the ideal value of 2. They found the normal BR position to be only about 75% occupied at room temperature, the sodium atoms being displaced slightly from the BR position, giving a very broad, triangular distribution of electron density in the conduction plane. No sodium ions were found at the aBR site, the remaining Na^+ being centered near positions which are halfway between the oxygen atoms in the conduction plane (sometimes referred to as the mid-oxygen or mOx sites with coordinates $\frac{1}{6}$, $\frac{5}{6}$, $\frac{1}{4}$). Later, Roth (*16*) estimated some occupation of the aBR site at room temperature.

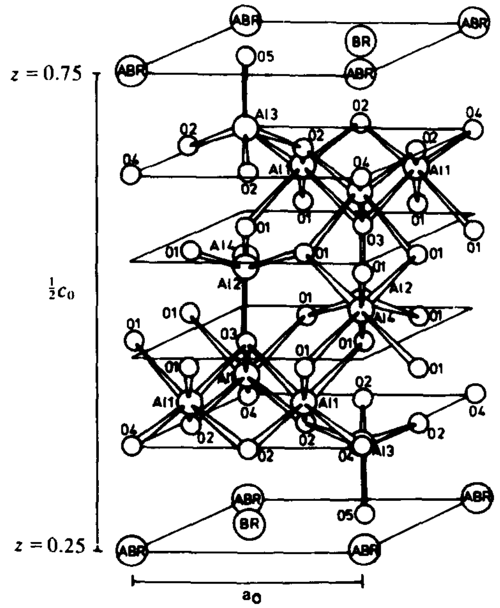

FIG. 1. Crystal structure of sodium β-alumina. Taken from Tofield and Farrington (*13*).

The excess sodium ion concentration above that required for the ideal crystal structure necessitates some kind of countercharge. Peters *et al.* (*12*) suggested that the countercharge is produced by aluminum ion vacancies distributed over the 12-fold Al ion sites that fall just below the close-packed oxygen planes which are next to the Na ions. However, Roth (*16*), in a detailed analysis of silver β-alumina, did not detect aluminum vacancies and proposed that charge compensation is achieved by the incorporation of extra oxygen ions in the conduction plane.

Lattice parameter determination of a number of substituted β-aluminas (*3, 5–10*) indicates that while the *a* lattice parameter remains relatively constant, the *c* parameter is very dependent on the type of ion present. This is due to a dependence of the conduction plane on the conducting ion; the larger the ion, the greater the expansion of the *c* axis. Exceptions are Li^+ and H^+, which produce expansions of the *c* axis on conversion from Na β-alumina although Li^+ and H^+ are smaller ions. This is due to the fact that the Li^+ and H^+ ions do not lie in the conduction planes but above or below them (*7, 13, 14*).

Structure analysis of several substituted β-aluminas indicates that the spinel blocks remain relatively unchanged upon transformation (*13–18*). There are, however, substantial differences in the conduction plane regarding the position of ion sites and occupancy.

Experimental Procedure

Single-crystal sodium β-alumina was cleaved from a Monofrax H refractory brick purchased from the Carborundum Company of Falconer, New York. Chemical analysis showed this to have a composition of 93.91 wt% Al_2O_3, 5.59 wt% Na_2O, 0.18 wt% SiO_2, 0.08 wt% Fe_2O_3, 0.1 wt% CaO, 0.05 wt% MgO, and 0.03 wt% TiO_2.

Indium metal of 99.999% purity was supplied by Cambridge Analysing Instruments. All other chemicals were of AnalaR grade.

As it was not possible to prepare indium β-alumina single crystals directly from sodium β-alumina, it was first necessary to synthesize silver β-alumina. Monofrax H single crystals were soaked in molten silver nitrate with silver wire at a temperature of 503 K. After immersion for 24 hr, the crystals were removed and washed briefly in distilled water in order to remove any surplus salt and then weighed to assess the degree of conversion. This process was repeated until no further weight increase was observed—usually three soakings were sufficient. Exchange to indium β-alumina was performed in a sealed Pyrex tube with iodine and excess indium metal present for 72 hr at 773 K. Indium(I) iodide formed *in situ* and, at the end of the experiment, the sealed tube was cooled to 453 K, removed from the furnace, carefully broken, and excess molten metal and salt were poured away. The crystals were washed in distilled water and dried, and their density was measured to ascertain the degree of conversion. The density was measured using Clerici's solution (aqueous thallium formate/thallium malonate), which had a density of approximately 4000 kg m^{-3}. About 100 mg of material was added to the solution and water was added until the median crystals were suspended in the liquid. The liquid was centrifuged after each addition of water in order to homogenize the solution and the density was measured from the upthrust of a bobbin suspended in the solution.

The degree of transformation to indium β-alumina was measured directly from the density changes obtained during the transformation. The structure of indium β-alumina at 298 K was determined from intensity data obtained from a four-circle diffractometer. The single crystals were partially crushed in an agate mortar to obtain crystals in the range 0.05–1 mm. Crystals were examined under a Zeiss Universal microscope (using transmitted light and a polarizer) for defects and potentially suitable crystals were mounted on silica glass fibers using Araldite epoxy resin. Oscillation X-ray photographs, which were greatly overexposed in order to reveal any secondary spots due to crystal defects, were taken of potentially suitable crystals using a Pye Unicam Oscillation camera. An optically clean crystal which was a parallelopiped of dimensions 0.5 × 0.2 × 0.05 mm, was selected that showed no evidence of spot splitting on the oscillation photographs.

A Stoe AED computer-controlled four-circle diffractometer was used for the determination of unit cell dimensions and intensities. An oscillation photograph was used to obtain the approximate position of 20 peaks. These were then located using a scintillation counter as the detector and an approximate unit cell and orientation matrix were obtained. A preliminary data set consisting of a further 50 peaks was obtained in order to refine the cell constants and orientation matrix, Mo$K\alpha$ radiation being used throughout. A graphite single crystal was used as a monochromator, attenuators being automatically inserted when the count rate exceeded 80,000 counts/second.

A final data set consisting of 1893 measured reflections was then obtained. Two strong peaks (025 and 110) were measured after every 50 reflections to check for systematic drift. Background was determined from 15-sec counts on both sides of each peak, 120 steps of 0.01° in omega of $\frac{1}{2}$ sec each being made.

Absorption corrections were made by measuring azimuthal reflections at increments of 10° in 2θ for nine different peaks.

The 1893 measured reflections produced 446 unique reflections of which 69 were rejected for the purposes of least-squares refinement by the condition that the structure factor be greater than three times the standard deviation. The remaining 377 structure factors were analyzed using the SHELX-76 program of G. M. Sheldrick (Chemical Laboratory, University of Cambridge) on the Cambridge University IBM 370/165 computer.

Initially the atomic parameters of Peters *et al.* (*12*) were used with suitable isotropic temperature factors for each atom. Indium atoms were placed at both the BR and aBR positions and the occupancy of each site was allowed to vary. After six cycles of full-matrix least-squares refinement an R value of 0.24 was obtained, where R, the residual, $=\Sigma||F_0|-|F_c||/|F_0|$. It became apparent that the position of the indium atoms could not be described simply in terms of occupancy at the BR and aBR positions and a three-dimensional Patterson synthesis was carried out in order to locate the missing atom positions. At this stage in the refinement a damping factor was added to the matrix. A further six cycles of refinement resulted in an R value of 0.14. At this stage anisotropic temperatures were added and a final R value of 0.04 was obtained after a further six cycles of refinement.

In order to measure the thermal stability of indium β-alumina, the method of Little and Fray (*9*) was followed. Samples of 0.8 g of indium β-alumina material prepared from Monofrax H were placed in recrystallized alumina furnace boats and heated in air at different temperatures for a period of 1 hr. After removal from the furnace, the specimens were weighed, 10 wt% silicon powder was added as a standard, and the mixture was ground to a fine powder in an agate mortar. X-Ray analysis was performed using a Phillips PW1050 vertical diffractometer. A $\frac{1}{30}°$ slit was used because of the low θ values measured. The degree of breakdown was calculated from the relative intensities of the 002 and 004 peaks of the heated specimens against the silicon standard 002 peak.

Results

Ion Exchange

Only about 2% exchange was observed when sodium β-alumina Monofrax H crystals were soaked in molten indium iodide containing excess indium. However, prior conversion to silver β-alumina enabled conversion to occur with two soakings of 72 hr at 673 K, each with greater than 90% conversion after the first immersion. Density measurements of ion-exchanged crystals indicated that complete ion exchange occurred, the crystals having a dark bronze color with a somewhat metallic appearance, although small crystals were translucent. This may indicate the presence of multiple oxidation states of the indium atoms, possibly a mixture of In^+ and In^{2+}.

It was also possible to produce indium β-alumina single crystals by the method of Yao and Kummer (*3*) in which crystals of silver β-alumina were soaked in molten indium metal to which a small amount of mercury had been added to aid wettability. This method did not appear to produce such a rapid rate of conversion although quantitative measurements were not made.

Using heavy liquids, the density of indium β-alumina single crystals was found to be 3810 ± 20 kg m^{-3} at 293 K.

The structure analysis of single-crystal indium β-alumina confirmed that the structure was hexagonal with a space group $P6_3/mmc$. Measurement of two strong peaks, (025) and (110), during the course of the final data set collection showed that there was a nonsystematic drift with standard deviations of the peaks of 0.8 and 1.1%, respectively. A total of 1893 peaks were measured, which were subsequently reduced to

TABLE I

Final Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^4$) for Indium β-Alumina

Atom	I	II	III	IV	x	z	β_{11}	β_{22}	β_{33}	β_{13}
In(BR)	2	*d*	6*m*2	1.176 (91)	6667 (0)	2500 (0)	259 (27)	β_{11}	276 (24)	0
In(BR′)	6	*h*	*mm*	0.655 (91)	6949 (26)	2500 (0)	297 (41)	298 (49)	235 (45)	0
In(aBR)	2	*b*	6*m*2	0.290 (29)	0 (0)	2500 (0)	354 (60)	β_{11}	27 (33)	0
In(aBR′)	6	*h*	*mm*	0.346 (34)	9324 (33)	2500 (0)	808 (43)	1294 (67)	211 (46)	0
Al(1)	12	*k*	*m*	12	8321 (2)	1046 (1)	63 (9)	41 (7)	58 (7)	3 (10)
Al(2)	4	*f*	3*m*	4	3333 (0)	0245 (1)	32 (8)	β_{11}	6 (12)	0
Al(3)	4	*f*	3*m*	4	3333 (0)	1750 (1)	60 (8)	β_{11}	21 (12)	0
Al(4)	2	*a*	3*m*	2	0 (0)	0 (0)	61 (12)	β_{11}	1 (15)	0
O(1)	12	*k*	*m*	12	1572 (5)	0491 (2)	22 (14)	45 (15)	41 (15)	0 (23)
O(2)	12	*k*	*m*	12	4978 (6)	1448 (2)	41 (10)	65 (12)	62 (15)	3 (14)
O(3)	4	*f*	3*m*	4	6667 (0)	0546 (3)	45 (18)	β_{11}	46 (27)	0
O(4)	4	*e*	3*m*	4	0 (0)	1393 (3)	51 (17)	β_{11}	50 (26)	0
O(5)	2	*c*	6*m*2	2	3333 (0)	2500 (0)	322 (45)	β_{11}	19 (38)	0

Note. I = Number of positions, II = Wyckoff notation, III = point symmetry, and IV = number of atoms per unit cell. Estimated standard deviations of the rightmost digits are shown in parentheses. The y fraction is related to the x fraction by the equation $y = 2x$. Thermal parameters are in the form $\exp(-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2kl\beta_{23} + 2hl\beta_{13} + 2hk\beta_{12}))$. $\beta_{12} = \frac{1}{2}\beta_{22}$; $\beta_{23} = 2\beta_{13}$.

446 independent reflections of which 69 were rejected for the purposes of refinement. A final value of the residual, R, of 0.04 was obtained and the final atomic parameters are shown in Table I.[1]

Attempts were made to locate counterion defects by varying the occupancies of Al and O atoms but there was no improvement in the R value when refinement of these parameters was attempted. An electron density map of the plane $z = 0.25$ was calculated and is shown in Fig. 2. The interval between the continuous contours is 5.78 $e/\text{Å}^3$, whereas the dotted contours are shown at 0 and at intervals of 28.9 $e/\text{Å}^3$.

Final occupational parameters obtained for indium atoms give 2.47 atoms per unit cell, the main occupancy being at the Beevers and Ross (BR) position, although it was found that the structure could best be

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[1] See NAPS document No. 03928 for 1 page of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only, for each NAPS Accession Number. Institutions and organizations may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are \$5.00. Microfiche are \$3.00. Outside of the U.S. and Canada, postage is \$3.00 for a photocopy or \$1.50 for a fiche.

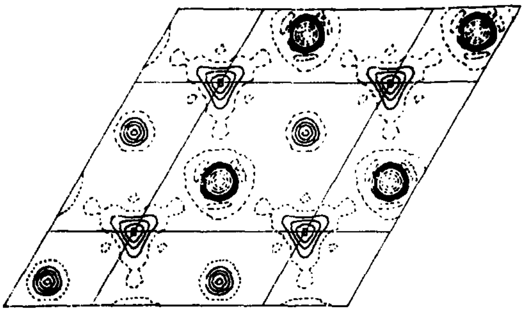

FIG. 2. Electron density map of the conduction plane in indium β-alumina ($z = \frac{1}{4}$) from $x = -\frac{1}{2}$ to $+\frac{1}{2}$. Continuous contours at 5.78 $e/\text{Å}^3$. Dotted contours at intervals of 28.9 $e/\text{Å}^3$.

described by occupancy at the BR position with some occupancy near this position at 0.6949, 0.3899, 0.25. There is a small occupancy of the anti-Beevers Ross position with the electron density distributed triangularly around that location, this being due to the main occupancy occurring at 0.9324, 0.8648, 0.25 and equivalent positions. The cell volume of 621.7 Å^3 would indicate a calculated density for the material of 3800 kg m^{-3} which is in excellent agreement with the measured value of 3810 kg m^{-3}.

The degree of thermal breakdown was calculated from X-ray intensity data for both the 002 and 004 reflections and is shown in Figs. 3 and 4. Error bars show the standard deviation estimated from X-ray data.

The same trend is observed for both reflections with complete decomposition about 1450 K and relative stability below 900 K.

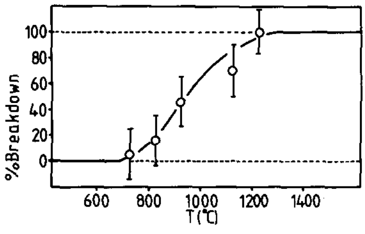

FIG. 3. Thermal stability of indium β-alumina; from 002 reflections.

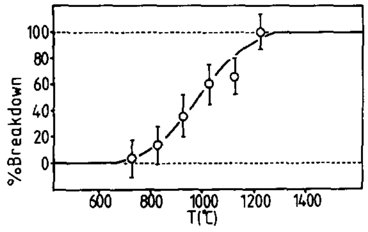

FIG. 4. Thermal stability of indium β-alumina; from 004 reflections.

Discussion of Results

Yao and Kummer (*3*) reported the possibility of ion exchange in producing single-crystal indium β-alumina from sodium β-alumina, but were unable to detect any measurable degree of exchange when crystals were soaked in indium(I) iodide. The present work is broadly in agreement with this, but a small degree of conversion was observed (2%) when sodium β-alumina crystals were soaked in indium iodide and this molten salt was found to be suitable for complete conversion from silver β-alumina. The degree of conversion was measured by the density of the crystals and, in the case of indium β-alumina, this was 3810 kg m^{-3}, which would indicate an empirical formula of $\text{In}_x\text{Al}_{22}\text{O}_{34}$, $x = 2.51 \pm 0.10$, although the exact formula depends on the type of counterions that are present. The excess of the conducting ion is 26 ± 5%, which corresponds closely to the value of 29% found by Peters *et al.* (*12*). It would thus appear that complete exchange had occurred although the residual sodium and silver concentrations were not estimated.

The indium β-alumina structure consists of the alternate stacking of the conduction layer of the indium ion and the spinel block, composed of the oxygen and aluminum atoms, along the *c* axis indefinitely. Two successive spinel blocks are covalently bonded by the corner-sharing $\text{O}_3\text{Al–O–AlO}_3$ tetrahedra along the *c* axis, and the common oxygen of the $\text{O}_3\text{Al–O–AlO}_3$ spacer column is located on the conduction plane, which is a mirror plane of the space group $P6_3/mmc$. The space necessary for the movement of the indium ion is maintained by the column.

In the spinel block the oxygen atoms are in an approximate cubic-packing arrangement with aluminum atoms located in octahedral and tetrahedral interstices. The aluminum atoms assume the same set of positions as the combined sets of positions of magnesium and aluminum in $MgAl_2O_4$ spinel. The positions of Al and O atoms in the spinel block of indium β-alumina differ only slightly from those reported for sodium β-alumina (*12*).

Differences in structure between the various β-aluminas are due almost entirely to variations within the conduction plane. Consequently there is a considerable variation in the conduction layer width and *c* lattice parameter due to the type of conduction atom. The conduction layer width may be most conveniently measured by consideration of the O(2)–*M*(BR)–O(2)′ and O(4)–*M*(aBR)–O(4) distances parallel to the *c* axis. The spinel block layer widths may also be described by oxygen–oxygen distances along the *c* axis. Values calculated for indium β-alumina are shown in Table II, together with values for a number of other β-aluminas. There is a considerable variation in the O(2)–*M*(BR)–O(2)′ and O(4)–*M*(aBR)–O(4)′ perpendicular distances with ion type. While there is a positive variation of these distances with ion the relationship is by no means clear and the conduction layer is considerably larger than expected from the In^+ ionic radius. Measurement of spinel block layers using the O(3)–Al(1)–O(2), O(1)–Al(1)–O(2), O(3)–Al(2)–O(1), and O(1)–Al(4)–O(1) distances shows there to be practically no variation in the spinel block width between the different β-aluminas, the only appreciable difference being the O(1)–Al(1)–O(2) distance. However, the variation is minor and there does not appear to be any correlation with the ionic radius.

The bond lengths and angles for spinel block tetrahedra and octahedra for indium β-alumina are shown in Table III. There is no significant variation of the bond lengths and angles of indium β-alumina to those found in other β-aluminas.

The electron density map of the conduction plane, $z = \frac{1}{4}$, is shown in Fig. 2. It shows the BR position to be fairly circularly distributed. The structure refinement, how-

TABLE II

PERPENDICULAR DISTANCES ALONG THE *c* AXIS BETWEEN OXYGEN ATOMS OF DIFFERENT LAYERS

Mobile ion	In^+	Na^+	K^+	Ag^+	Rb^+	Tl^+
Ionic radii of the mobile ion (Å)	1.32	0.97	1.33	1.26	1.47	1.47
Lattice constants (Å)						
a	5.599	5.594	5.591	5.595	5.600	5.608
c	22.90	22.53	22.71	22.49	22.87	22.96
	Perpendicular distances along the *c* axis (Å)					
O(2)–*M*(BR)–O(2)′	4.82	4.65	4.72	4.63	4.84	4.84
O(4)–*M*(aBR)–O(4)′	5.07	4.84	4.92	4.82	5.00	5.05
O(3)–Al(1)–O(2)	2.07	2.06	2.06	2.06	2.06	2.06
O(1)–Al(1)–O(2)	2.19	2.18	2.19	2.17	2.17	2.20
O(3)–Al(2)–O(1)″	2.37	2.38	2.37	2.37	2.37	2.38
O(1)–Al(4)–O(1)″	2.25	2.26	2.25	2.26	2.26	2.25
Reference	—	(*12*)	(*18*)	(*16*)	(*15*)	(*17*)

TABLE III

BOND LENGTHS AND ANGLES FOR INDIUM β-ALUMINA

Coordination	No. of bonds	Bond length (Å)
Octahedral		
Al(1)–O(1)	2	2.027
Al(1)–O(2)	2	1.827
Al(1)–O(3)	1	1.971
Al(1)–O(4)	1	1.812
Al(4)–O(1)	6	1.894
Tetrahedral		
Al(2)–O(1)	3	1.799
Al(2)–O(3)	1	1.812
Al(3)–O(2)	3	1.779
Al(3)–O(5)	1	1.718
Coordination	Bond angle (°)	
Octahedral		
O(1)–Al(1)–O(2)	90.7	
O(1)–Al(1)–O(3)	89.1	
O(1)–Al(1)–O(4)	83.7	
O(2)–Al(1)–O(3)	86.7	
O(1)–Al(4)–O(1)′	88.4	
O(1)–Al(4)–O(1)″	91.6	
Tetrahedral		
O(1)–Al(2)–O(1)′	110.7	
O(1)–Al(2)–O(3)	108.3	
O(2)–Al(3)–O(2)′	107.2	
O(2)–Al(3)–O(5)	112.9	

ever, required two distinct atom positions, at $x = 0.6667$ and 0.6949. This dual occupancy is also a feature of Tl and Rb β-aluminas. The aBR position likewise shows such a splitting of the atom position with occupancy at $x = 0$ and 0.9324. The aBR' position is thus further from the central position than in the case of the BR position and this is reflected in the electron distribution map, which shows a very triangular distribution on this site, a common feature of all the β-aluminas. The conduction paths in a conduction layer form a hexagonal net with the O(5) atom at the center and the side of each hexagon containing BR–BR′–aBR′–aBR.

The percentage conduction ion distribution calculated from the occupational parameters for indium β-alumina and a number of other β-aluminas are shown in Fig. 5. Due to the proximity of the BR and BR′ sites in Tl, Rb, and In β-aluminas these are shown together.

The material shows almost complete occupancy of the BR site, this being 92% (taking the BR and Br′ sites together); the aBR site (including aBR′) is 32% full.

In many respects, however, indium β-alumina resembles the behavior of Tl and Rb β-aluminas in showing a high BR occupancy (>70% of total occupancy) with a widely distributed aBR site. In contrast, Na, Ag, and K β-aluminas have a lower BR occupancy (50–60% of total occupancy) with the remaining electron distribution at the mid-oxygen position ($x = \frac{1}{8}$ (in the case of Na and K β-aluminas) or at the aBR site (Ag β-alumina). Indium β-alumina does show a positive electron density at the mid-oxygen position, without an atom being assigned there. This is a situation similar to that described for Rb β-alumina (*17*), where the position was considered a mobile

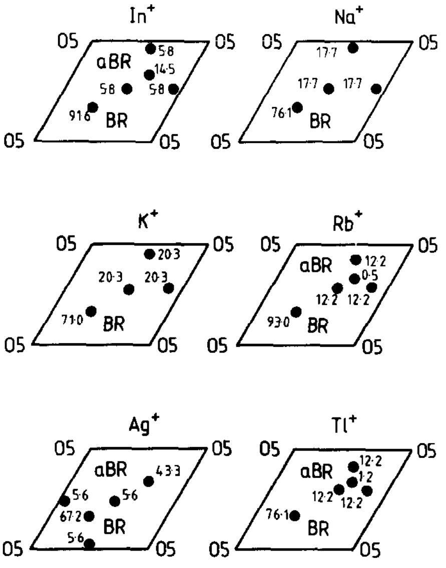

FIG. 5. Percentage distribution of conduction ions over sites for a number of β-aluminas.

ion site. It is possible that this position plays a role in the ionic conduction of indium β-alumina.

The extremely large anisotropic temperature factors for atoms in the conduction planes observed in other β-aluminas were also found in indium β-alumina. The calculated density of 3800 kg m^{-3} is in excellent agreement with the measured density of 3810 kg m^{-3}.

This study indicates that indium β-alumina would readily decompose above about 1000 K although complete decomposition did not occur in a 1-hr heating period until 1500 K was reached. It is unclear whether indium β-alumina is truly stable at any temperature. However, it is likely that the material is suitable for use as an electrolyte at temperatures below about 900 K. The electrical properties of this material are discussed elsewhere (*19*).

This shows the material to be considerably less stable than copper β-alumina. Little and Fray, (*9*) in a similar study, found this material to be reasonably stable to about 1500 K. The thermal stability of gallium β-alumina was investigated by Radzilowski (*5*), who found it stable in air to at least 800 K.

Conclusions

This study has shown that it is possible to prepare indium β-alumina from silver β-alumina by immersion in indium halides and by electrochemically using molten salt/metal electrodes; from density measurements it appears that both techniques gave 100% conversion.

The thermal stability of indium β-alumina was measured and it showed the material to be potentially suitable as an electrolyte at temperatures up to around 900 K.

Finally, the structure of indium β-alumina was determined using X-ray analysis. This showed that while there was little difference in the structure of the aluminum/oxygen spinel block and that found in other β-aluminas there were substantial differences in the conduction plane. Indium β-alumina is hexagonal, with the space group $P6_3/mmc$, and has cell constants $a = 5.599$, $c = 22.901$ Å.

In common with other β-aluminas indium was found to have triangularly distributed conduction ion sites with extremely large anisotropic temperature factors. In general, however, the structure was found to be most similar to that found for thallium β-alumina. Determination of indium atom occupancy gave an empirical formula of $In_{2.47}Al_{22}O_{34}$.

Acknowledgments

The authors are grateful to the Science Research Council for financial support and to Cambridge Analysing Instruments for support through the CASE scheme.

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