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Thermal expansion behaviour of sodium-beta-alumina

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The thermal expansion of sodium β- and β''-alumina in the *a* and *c* directions has been determined by high temperature X-ray diffractometry using polycrystalline samples. The measured values show that internal stresses as a result of anisotropy in the thermal expansion of the two phases should have little adverse effect on the application of beta-alumina in electrochemical devices.

1. Introduction

Sodium-beta-alumina has attracted considerable attention in recent years on account of its high sodium-ion conductivity and negligible electronic conductivity [1, 2]. This has lead to a variety of potential applications in electrochemical devices, particularly the sodium–sulphur cell [3, 4]. For many applications beta-alumina ceramics consist of two phases; β-alumina, hexagonal ($P6_3/mmc$) [5, 6] and β''-alumina, rhombohedral ($R\bar{3}m$) [7, 8]. Both materials have a basic structural unit consisting of four close-packed oxygen layers with aluminium ions in the interstices; these units are frequently referred to as "spinel blocks". The spinel blocks are held together by bridging Al–O–Al bonds so forming loosely packed planes in which the sodium ions reside and are relatively free to migrate in an electric field. The perfect basal cleavage of beta-alumina can be related to the presence of these conduction planes. Small doping additions of Li and Mg, substituting for Al, tend to stabilize the β''-structure and enhance the overall ionic conductivity.

Examination by transmission electron microscopy shows that both β- and β''-alumina can co-exist within single grains [9, 10]. Fracture of beta-alumina under conditions of electrolysis is associated with the formation and penetration of metallic sodium into pre-existing cracks [11–13]. In this context, it is clearly important to know accurately the thermal expansion coefficients of both phases in different crystallographic directions as there could be microcracking within grains as well as at grain boundaries if there is significant mismatch in the expansion coefficients and this, in turn, could contribute to the failure of the ceramic electrolyte in a cell. Only two determinations of the thermal expansion of the cell parameters of sodium-beta-alumina have been reported in the literature and no work has been carried out on materials containing both phases. The mean thermal coefficients of β-alumina, determined by interferometry on large single crystals, give values of $7.5 \times 10^{-6}\,K^{-1}$ in the *a* direction and $5.9 \times 10^{-6}\,K^{-1}$ in the *c* direction between 573 and 973 K [14, 15]. The thermal expansion coefficients of β''-alumina, determined by X-ray diffractometry, are $7.8 \times 10^{-6}\,K^{-1}$ in the *a* direction and $7.3 \times 10^{-6}\,K^{-1}$ in the *c* direction between 673 and 1173 K [16].

In the present work, the thermal expansion of both β- and β''-alumina has been determined in a material containing both phases of a type used in sodium–sulphur cells and conclusions are drawn from the results as to the durability of materials of this type under conditions of electrolysis.

2. Experimental methods

2.1. Sample preparation

Beta-alumina samples were prepared in the form of thin-walled tubes using high purity starting materials in the form of finely ground α-Al_2O_3,

$NaAlO_2$ and small additions of MgO and Li_2CO_3. The overall composition was $Na_2O{\cdot}6.5\,Al_2O_3$ with less than 2% by weight of dopant. The starting materials were vibro-energy milled together using α-Al_2O_3 cylinders as grinding media to produce a homogeneous powder that was then consolidated into green shapes by isostatic pressing at 275 MN m^{-2}. These samples were then fired in a pass-through zone-sintering furnace with a peak temperature of 1975 K and a short hot zone at a speed of ~ 50 mm min^{-1}. The atmosphere in the hot zone was effectively saturated with sodium oxide vapour and the rapid, buffered firing cycle minimized sodium oxide loss by evaporation. This ensured that the final composition was close to that of the starting material powder and this was confirmed both by X-ray fluorescence and neutron activation analyses. The material was finally annealed at 1575 K and cooled at ~ 150 K h^{-1} to minimize quenched-in stresses.

2.2. Microstructural examination

Samples were prepared for examination by optical microscopy by polishing to a 1 μm diamond finish and etching in boiling H_3PO_4 for 30 min. For transmission electron microscopy, samples were first pre-ground and then ion-beam thinned before examination at 80 kV.

2.3. X-ray diffractometry

Samples for thermal expansion measurements were ground to ~ 5 μm and run on a Philips PW 1050 diffractometer with a heating stage operated in vacuum [17, 18]. The sample holder was a platinum plate which had been calibrated against silicon at 298 K taking the silicon cell edge as 0.543 065 nm, The thermocouples on the heating stage were calibrated against the melting point of tin (505 K), the inversion temperature of cryolite (836 K), and the melting point of silver (1234 K). At the melting point of silver the thermal gradient across the platinum was <3 K and the error in temperature measurement was ± 5 K over the full temperature range. The diffraction peaks from the platinum plate served as an internal standard, using published expansion data [19]. After the heating experiments the platinum plate was recalibrated with silicon and showed close agreement with initial values. The X-ray wavelengths used were 0.154 178 nm for Cu$K\alpha$ and 0.154 051 nm for Cu$K\alpha^1$. Cell parameters and their standard errors were computed, by least squares refinement, from the d values of the 0 1 2, 0 1 3, 1 1 0, 0 1 7, 0 2 2, 0 2 5, 0 2 6, 0 2 7, 1 2 7, 0 2 11, 0 3 6, and 2 2 0 diffraction peaks for β-alumina and the 0 1 2, 1 0 4, 1 1 0, 1 0 10, 0 1 11, 0 2 4, 0 2 7, 1 2 11, and 2 2 0 peaks for β''-alumina.

In a first sample, final cooling from elevated temperatures was carried out in air and all room-temperature X-ray measurements were also made in air. Initial elevated temperature experiments, under vacuum, were carried out at 200 K intervals to 1273 K; the sample was then re-heated to obtain data at intermediate temperatures. The effects of hydration of this sample in the room temperature experiments, and the incipient alteration of the sample at 1273 K, were subsequently recognized and further experiments were carried out. A second sample was X-rayed in air before heating, and under vacuum and in air after heating to 373 and 763 K. A third sample was pre-heated to 688 K, cooled under vacuum and X-rayed at room temperature under vacuum. This sample was then reheated to obtain data at other temperatures to 1178 K and was then once more cooled and X-rayed at room temperature under vacuum. The third sample was finally held at 1273 K for 2 h before X-raying and was then cooled and X-rayed at room temperature under vacuum. The order of data collection on the three samples is identified in Tables I and II and Table I also gives details of the thermal history of all samples X-rayed at room temperature.

3. Results

3.1. Microstructure

The material had a duplex microstructure with a small amount of secondary grain growth (<2% by volume of grains ~ 50 μm) in a fine-grained matrix (0.5 to 2.0 μm). The matrix grain size was substantially smaller than the particle size used for X-ray diffractometer measurements (~ 5 μm). Individual grains were composed of discrete regions of β- and β''-alumina, typically 20 nm wide (Fig. 1). The approximate relative proportions of the two phases determined from the intensities of selected diffraction peaks are 40% β- and 60% β''-alumina. The sintered density (3240 kg m^{-3}) was ~99% the theoretical density (3275 kg m^{-3}).

3.2. Thermal expansion measurements

The cell parameters for all three samples studied are given in Tables I and II. The experiments on the first sample (data collection nos. 2–12 Table II)

TABLE I Room-temperature cell parameters (293 K)

Sample	Order of data collection	Thermal history	a (nm)	c (nm)	V (nm^3)	Peak width (°2θ) at half-height		Ratio a/b for β'' (1 0 10) (see Fig. 2)	Comments
						β (0 1 7)	β'' (0 1 11)		
1 β-	1	Before heating	0.561 21 (12)	2.228 7 (12)	0.607 92 (29)	0.28	0.28	3.0	As-ground; X-rayed in air
β''			0.561 04 (08)	3.352 8 (17)	0.913 97 (43)				
β-	7	After 1273 K	0.561 10 (17)	2.230 1 (17)	0.608 04 (40)	0.35	0.35	1.8	24 h after heating, X-rayed in air
β''			0.560 93 (09)	3.355 0 (23)	0.914 20 (54)				
β-	13	After all experiments	0.561 09 (17)	2.230 9 (17)	0.608 24 (40)	0.33	0.40	1.8	24 h after heating; X-rayed in air
β''-			0.560 95 (07)	3.363 0 (25)	0.916 43 (67)				
2 β-	14	Before heating	0.561 06 (11)	2.229 4 (11)	0.607 76 (26)	0.29	0.29	3.2	As-ground: X-rayed in air
β''-			0.561 01 (07)	3.352 0 (15)	0.913 65 (37)				
β-	17	After 763 K	0.561 22 (10)	2.228 4 (10)	0.607 85 (23)	0.28	0.24	5.8	16 h after heating; X-rayed *in vacuo*
β''-			0.561 17 (04)	3.350 5 (09)	0.913 75 (22)				
β-	18	After 763 K	0.561 29 (08)	2.230 3 (08)	0.608 50 (19)	0.30	0.34	1.4	48 h after heating; X-rayed in air
β''-			0.561 20 (06)	3.354 0 (13)	0.914 82 (33)				
3 β-	20	After 688 K	0.561 13 (08)	2.228 9 (08)	0.607 78 (19)	0.25	0.21	7.0	Ground, pre-heated to 688 K, X-rayed *in vacuo* 1.5 h after heating
β''-			0.561 05 (07)	3.348 5 (15)	0.912 79 (36)				
β-	24	After 1178 K	0.561 19 (12)	2.229 4 (12)	0.608 05 (28)	0.24	0.21	9.3	2 h after heating, X-rayed *in vacuo*
β''-			0.561 10 (04)	3.348 8 (08)	0.913 05 (21)				
β-	26	After 1273 K	0.561 09 (19)	2.229 8 (19)	0.607 94 (44)	0.32	0.26	5.5	2 h after heating; X-rayed *in vacuo*
β''-			0.560 87 (08)	3.355 5 (14)	0.914 12 (35)				

Note: Numbers in brackets are one standard error in the last two places for cell parameters.

TABLE II Elevated-temperature cell parameters

Sample no. (order of data collection)	T (K)	β-alumina a (nm)	c (nm)	V (nm^3)	β''-alumina a (nm)	c (nm)	V (nm^3)
1 (8)	373	0.561 40 (15)	2.231 6 (17)	0.609 11 (40)	0.561 21 (07)	3.356 0 (13)	0.915 40 (27)
1 (2)*	473	0.561 68 (09)	2.232 2 (09)	0.609 89 (22)	0.561 54 (06)	3.353 0 (12)	0.915 66 (29)
1 (9)	573	0.562 11 (15)	2.235 1 (15)	0.611 59 (36)	0.561 92 (08)	3.360 6 (17)	0.918 96 (38)
1 (3)*	673	0.562 65 (11)	2.235 3 (11)	0.612 83 (28)	0.562 34 (04)	3.357 3 (10)	0.920 07 (24)
1 (10)	773	0.563 02 (13)	2.238 6 (14)	0.614 55 (35)	0.562 83 (05)	3.364 4 (11)	0.922 99 (25)
1 (4)*	888	0.563 77 (07)	2.239 5 (08)	0.616 41 (19)	0.563 65 (05)	3.361 9 (10)	0.924 98 (24)
1 (11)	973	0.564 11 (15)	2.241 3 (17)	0.617 68 (42)	0.563 82 (10)	3.369 2 (20)	0.927 55 (48)
1 (5)*	1073	0.564 66 (09)	2.244 0 (10)	0.619 61 (25)	0.564 59 (07)	3.369 2 (15)	0.930 09 (34)
1 (12)	1173	0.565 02 (16)	2.247 0 (16)	0.621 25 (38)	0.564 88 (08)	3.376 4 (18)	0.933 02 (41)
1 (6)	1273	0.565 52 (15)	2.247 9 (15)	0.622 58 (36)	0.565 33 (08)	3.376 4 (16)	0.934 53 (39)
2 (17)*	293	0.561 22 (10)	2.228 4 (10)	0.607 85 (23)	0.561 17 (04)	3.350 5 (09)	0.913 75 (22)
2 (15)*	373	0.561 35 (09)	2.230 9 (09)	0.608 79 (22)	0.561 24 (03)	3.350 3 (07)	0.913 93 (17)
2 (16)*	763	0.563 11 (09)	2.236 3 (09)	0.614 09 (23)	0.563 01 (02)	3.359 3 (05)	0.922 16 (12)
3 (20)*	293	0.561 13 (08)	2.228 9 (08)	0.607 78 (19)	0.561 05 (07)	3.348 5 (15)	0.912 79 (36)
3 (21)*	578	0.562 28 (08)	2.233 2 (08)	0.611 45 (20)	0.562 19 (06)	3.354 6 (12)	0.918 20 (29)
3 (19)*	688	0.562 78 (08)	2.234 8 (08)	0.612 98 (19)	0.562 66 (05)	3.356 3 (11)	0.920 20 (28)
3 (22)*	973	0.564 01 (07)	2.240 9 (07)	0.617 36 (16)	0.564 01 (04)	3.364 2 (08)	0.926 80 (19)
3 (23)*	1178	0.565 06 (08)	2.244 9 (08)	0.620 76 (20)	0.565 05 (06)	3.369 2 (12)	0.931 60 (32)
3 (25)	1273	0.565 32 (14)	2.247 0 (14)	0.621 89 (35)	0.565 24 (05)	3.377 4 (10)	0.934 50 (25)

Notes: (1) Data marked with an asterisk (*) were used to calculate thermal expansion coefficients. (2) Numbers in brackets are one standard error in the last two places for cell parameters.

gave reliable, internally consistent data for the a cell parameters of both phases, but the c cell parameters, especially for β''-alumina, were less satisfactory. This is due to two related effects. Firstly, significant increases occurred in the room-temperature c parameters after heating or exposure to air; this is well shown for determinations 1 and 13 (Table I) on β''-alumina. Secondly, the c parameters for both phases at 1273 K (no. 6, Table II) were larger than expected on the basis of a linear extrapolation from data obtained at lower temperatures in the same series of experiments (nos. 2 to 5, Table II); the c parameter at 1273 K for β-alumina was ~0.001 nm too large while that for β''-alumina was ~0.05 nm too large. In addition, the c parameters determined subsequently on the same sample at elevated temperatures (nos. 8 to 12 Table II) were displaced to higher values relative to the c parameters determined for the earlier heating experiments (nos. 2 to 5, Table II).

Experiments carried out on samples 2 and 3 allowed the above two effects to be distinguished and the causes identified. Sample 2 when freshly

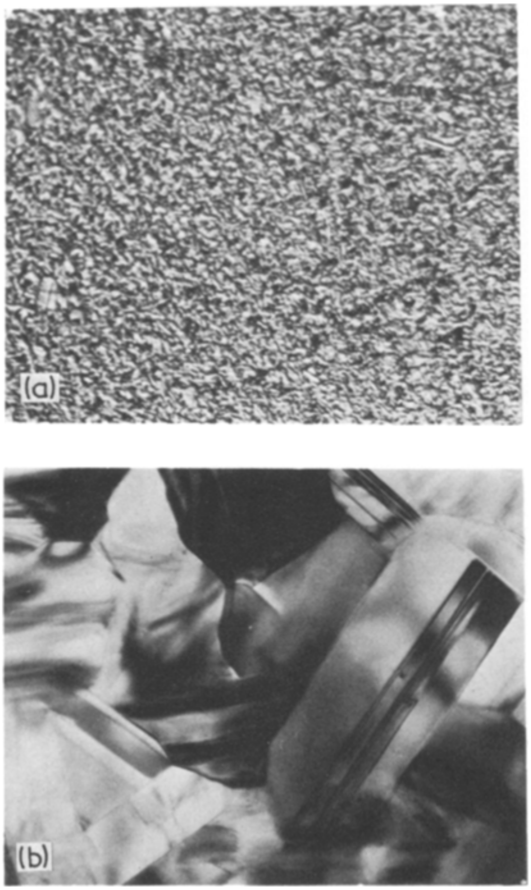

Figure 1 Microstructure of beta-alumina showing: (a) a fine-grained matrix with a few large grains (× 850); and (b) details of the structure of the matrix as revealed by transmission electron microscopy (× 13 000).

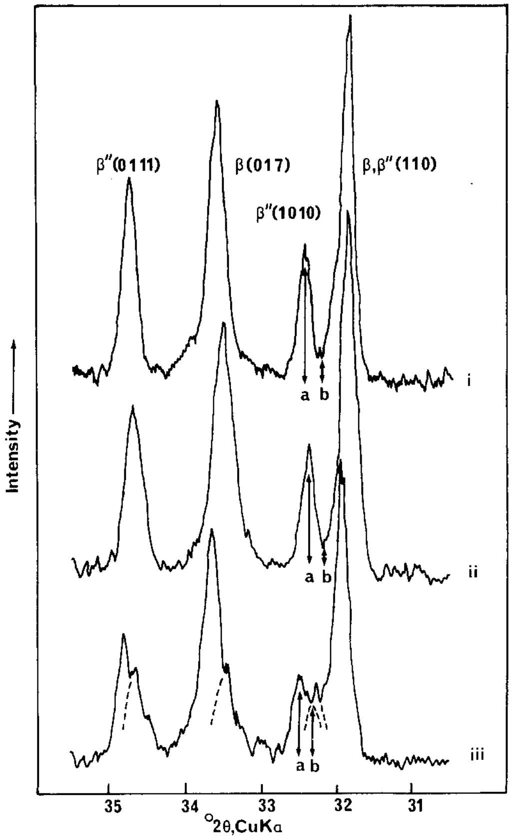

Figure 2 X-ray diffraction traces of beta-alumina: (i) sample 3, room temperature after 688 K, cooled and X-rayed under vacuum (no. 20, Table I). Note that the peaks are sharp and well resolved for both phases. (ii) sample 3, room temperature after 1273 K, cooled and X-rayed under vacuum (no. 26, Table I). Note that the peaks are slightly broadened. (iii) Sample 2, room temperature, left open to air for 48 h after heating to 736 K, X-rayed in air (no. 18, Table I). Note the broad and poorly resolved peaks. The ratio (a/b) (Table I) is used as a measure of the resolution of the β'' (1 0 10) peak from the $\beta + \beta''$-(1 1 0) peak.

ground and X-rayed in air (no. 14, Table I) gave almost identical cell parameters, for both phases, to those determined for sample 1 under the same conditions (no. 1, Table I). The smallest values observed for the room-temperature *c* parameters of both phases were found for sample 2 after heating to 763 K and sample 3 after heating to 688 and 1178 K (nos. 17, 20 and 24, Table I). These last three determinations were made under vacuum after cooling under vacuum from the elevated temperatures. Sample 2 after exposure to air showed increases in the *c* parameters for both phases. The variability in the room-temperature *c* parameters can be correlated with changes in the appearance of peaks in the X-ray diffraction patterns. After exposure to air certain peaks show pronounced broadening with shoulders, and even partially resolved peaks, developing on the low 2θ sides of the original peaks. These effects are well characterized by measuring the peak width at half-height for the β-(0 1 7) and β''-(0 1 11) peaks and the resolution of the β''-(1 0 10) peak from the adjacent $\beta + \beta''$-(1 1 0) reflection; the latter relationship is quantified by measuring the arbitrarily defined ratio (a/b) (see Fig. 2 and Table I). Higher values for the peak-widths at half-height and lower values for the ratio (a/b) correlate with higher *c* parameters (Table I). Heating sample 2 in small increments ($\sim$ 10 K) showed that the peak widths started to decrease, and the ratio (a/b) to increase, at temperatures as low as $\sim$330 K and little further change occured above $\sim$525 K. This temperature range coincides with the range over which the bulk of adsorbed water is lost from finely powdered sodium-beta-alumina [20]. Thus it seems that the cause of the effects described above is hydration of the sample on exposure to air.

Thermogravimetric measurements, of a coarser fraction of the sample that had been exposed to air, showed weight losses up to $\sim$425 K but differential thermal analysis showed an endothermic peak at 490 K. Examination by infra-red spectrophotometry showed absorption bands characteristic of adsorbed water and of fairly tightly bound molecules of water. Absorption bands due to bound water diminished significantly after heating the sample to 1273 K for 1 h. No absorption bands characteristic of hydronium ion (or hydroxide) were evident. These results suggest that water molecules enter the conduction plane of beta-alumina and expand the cell in the *c* direction. The resolved peaks and shoulders on the low 2θ side of the β-(0 1 7) and β''-(0 1 11) peaks (Fig. 2iii) can be used to estimate *c* parameters for the hydrous phases of $\sim$2.256 nm for β- and $\sim$3.386 nm for β''-alumina. These values are equivalent to $\sim$ 1% expansion relative to the parameters for the anhydrous phases. The infra-red data and the fact that the hydration process can be reversed by heating above $\sim$600 K and cooling under vacuum indicates that hydronium-beta-alumina [21] is not formed. Similar effects of increased *c* parameters due to uptake of water have been reported for β''-alumina [16] and potassium ferrite which has the beta-alumina structure [22].

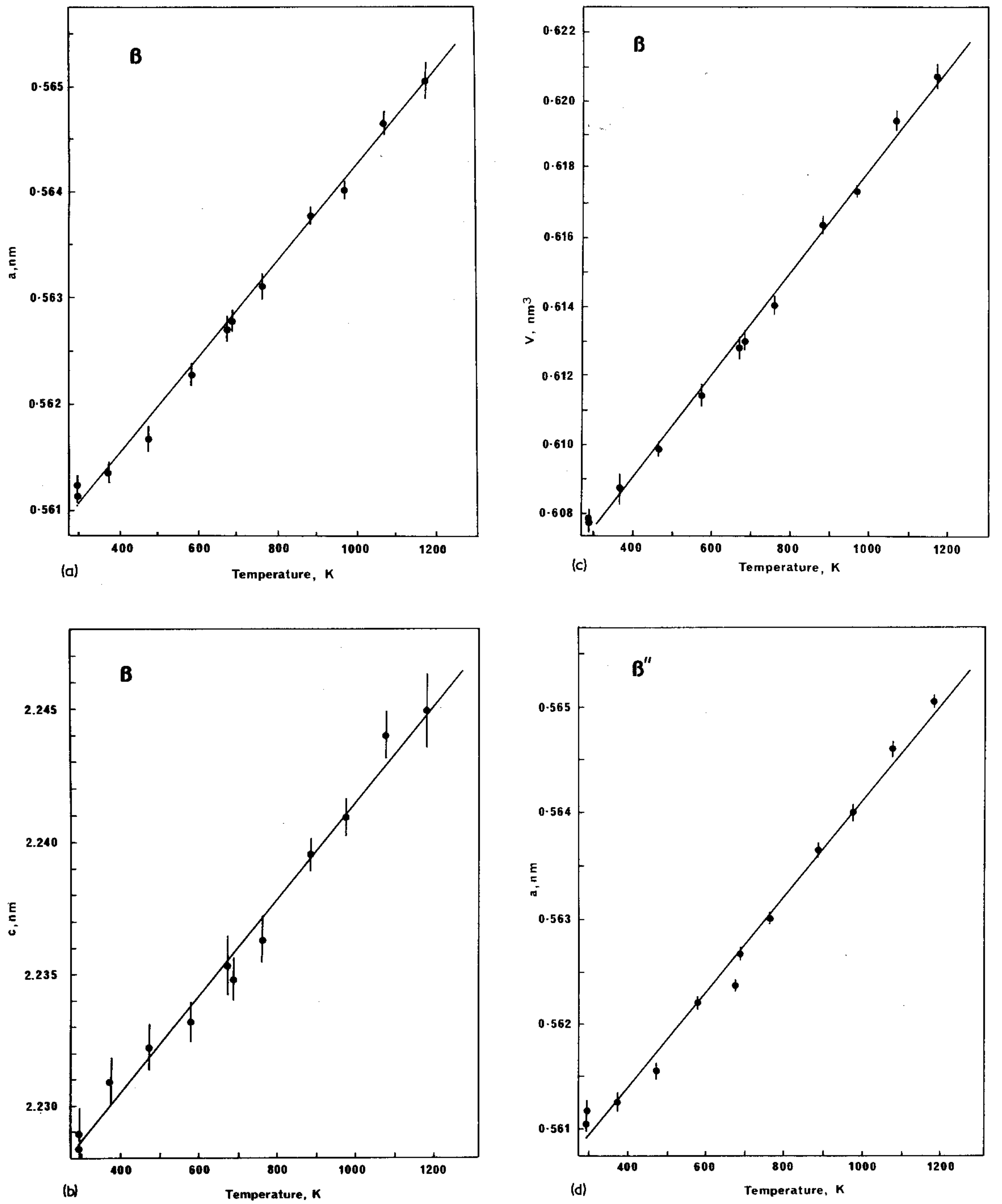

Figure 3 Variation of a, c and V cell parameters of β- and β'-alumina with temperature. Data plotted are marked with asterisks in Table II. The error bars are for one standard error. The lines were computed by least squares.

It is important to distinguish the effects of hydration from the effect of irreversible change that occurs during heating to 1273 K. Sample 3 was held at 1273 K for 2 h before being X-rayed and showed similar high c parameters to those determined on sample 1 at the same temperature (cf. nos. 6 and 25, Table II). Sample 3 was cooled to room temperature under vacuum and, when X-rayed, showed broadened peaks (Table I, Fig. 2ii) and increased c parameters, especially for β''-alumina, relative to the values for the anhydrous, unaltered phases (Table II). Sample 3

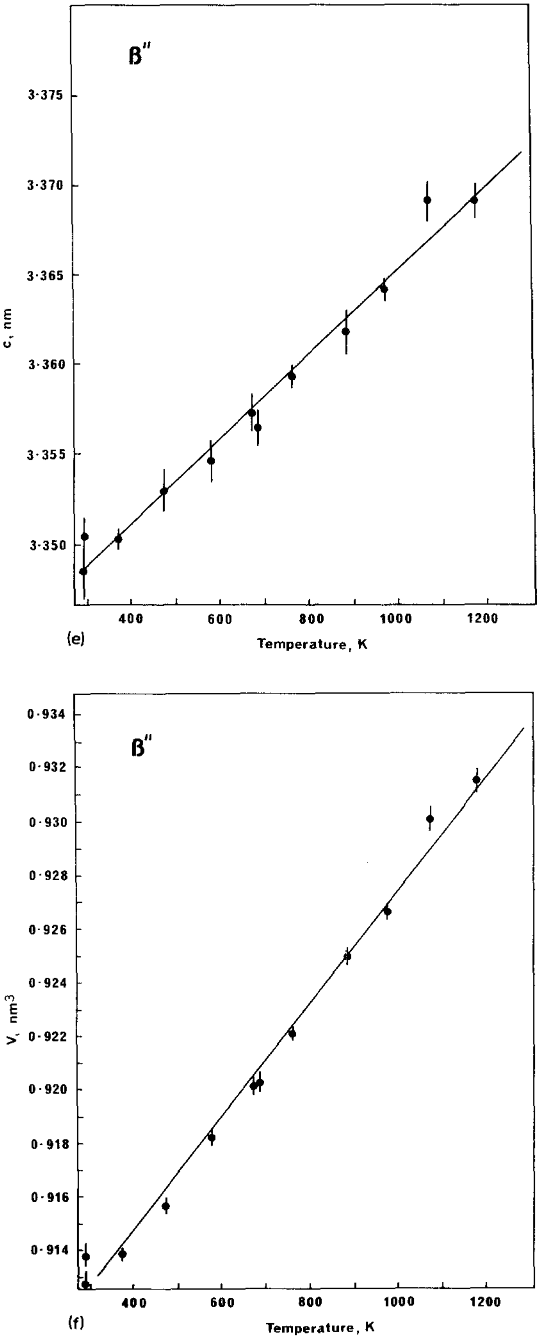

Figure 3 continued.

showed no such changes after it had been heated to 1178 K. No peaks for corundum (α-alumina) were observed. This effect is probably due to evaporation of sodium from the sample when it was heated to 1273 K in the vacuum of the furnace. The fact that the vapour pressure of Na above β-alumina at 1273 K is 0.27 N m^{-2} whereas at 1178 K it is only 0.09 N m^{-2} [1] presumably accounts for the lack of alteration at 1178 K. Sodium loss has been shown, by direct observation of lattice fringes in the electron microscope [10], to lead to collapse of the spinel blocks; this would cause an overall contraction of the *c* parameter. This transformation involves shear of the lattice and is unlikely to occur until substantial loss of Na has occurred. However, small Na losses from the conduction plane will probably increase the electrostatic repulsion between the spinel blocks and should result in expansion of the *c* parameter. The fact that this effect is most pronounced in β''-alumina reflects the different volatilities of Na in the two phases.

Because of the two effects discussed above we have chosen to characterize the thermal expansion of our beta-alumina sample using data collected up to a maximum temperature of 1178 K, on samples which had never been heated above this temperature under vacuum, and taking care to ensure that the sample was under vacuum at all times. The values used to calculate the thermal expansion coefficients are marked with asterisks in Table II and are plotted in Fig. 3. The lines drawn through the points in Fig. 3 were calculated by least squares and the statistical data and mean linear thermal expansion coefficients between 293 and 1178 K are given in Table III. A weighted mean for the expansion of the cell volume may be calculated knowing the relative proportions of the β- and β''-phases and, to a good approximation, the linear expansion coefficient of the material is one-third of this value at $7.9 \pm 0.3 \times 10^{-6}$ K^{-1}. This is in good agreement with a value of $7.5 \pm 0.5 \times 10^{-6}$ K^{-1} determined by direct dilatometer measurements over the temperature range 473 to 873 K [23]. The dilatometer measurements deviated from linearity below 473 K, probably as a result of mechanical hysteresis in the equipment although it is possible that there was a small effect due to hydration.

The thermal expansion data for sample 1 after it had been altered by heating at 1273 K give almost identical mean thermal expansion coefficients (293 to 1173 K) to those of the unaltered sample: β-alumina, *a* 8.02 (24), *c* 8.31 (37), V 24.55 (65); β''-alumina, *a* 8.05 (67), *c* 6.95 (42), V 23.21 (88) (all values $\times 10^{-6}$).

TABLE III Linear regression data* for beta-alumina thermal expansion

Phase	Parameter	x_0 (nm)	$\gamma \times 10^{-5}$	r	S.E. (nm)	$\alpha \times 10^{-6}\ K^{-1}$
β-alumina	a	0.560 95	0.450 (11)†	0.997	0.000 11	8.01 (21)†
	c	2.228 2	1.84 (07)	0.993	0.006 7	8.25 (34)
	V (nm^3)	0.607 17	0.014 84 (34)	0.997	0.000 33	24.44 (62)
β''-alumina	a	0.560 82	0.456 (16)	0.994	0.000 16	8.13 (32)
	c	3.348 2	2.34 (11)	0.988	0.001 12	6.98 (38)
	V (nm^3)	0.912 01	0.021 35 (66)	0.995	0.000 65	23.40 (80)

*Data fitted to $x = x_0 + \gamma T$ where T is temperature; x_0 is parameter at 273K. S.E. = standard error of the estimate: r = multiple correlation coefficient; α = mean linear expansion coefficient between 293 and 1178 K.

† Values in parentheses are one standard error in the last place(s). The errors in the expansion coefficients are calculated from one S.E.

4. Discussion

4.1. Thermal expansion characteristics of beta-aluminas

The mean thermal expansion coefficients determined here for β''-alumina show close agreement (i.e. within experimental error) with the published data for the β''-phase [16]. However, there are substantial differences between our data for β-alumina and the earlier values [15]. The main difference is that our value for the expansion coefficient along c is greater than that along a; the reverse is true for the earlier determination. However, it is possible that the interferometer measurements carried out on large single crystals (greatest dimension 1 cm) suffered from the sluggish expansion of the macro-specimen and hydration might also have been a problem.

The expansions of β- and β''-alumina in our sample along a are almost identical (Table III). This is not unexpected as the expansion in this direction will be controlled by that of the spinel blocks and our data compare favourably with an expansion coefficient for spinel ($MgAl_2O_4$) of $8.5 \pm 0.1 \times 10^{-6}\ K^{-1}$ between 293 and 1173 K [17]. The overall expansion along c depends on the relative expansion coefficient of the spinel blocks and the conduction plane regions [22]. Our data for β-alumina suggest that the expansion rates of these two components are very similar (note that the expansion of the β-phase is almost isotropic). However, for β''-alumina the expansion along a is greater than that along c and the implication is that the expansion of the conduction plane region is less than that within the spinel blocks. Thermal expansion data for beta-aluminas (our data and [22]) show that the expansion coefficients along a and c are never greatly dissimilar but there is no general relationship regarding which coefficient is the greater. It has been shown [24] that the expansion coefficient of mica parallel to the sheet structure is about half of that perpendicular to the sheets (i.e. along c). The basal cleavage planes of micas contain K and the high expansion rate parallel to c has been attributed to the substantial expansion of the K–O bonds holding the mica sheets together. The fact that beta-aluminas do not show such high expansion rates along c relative to those along a indicates that the spinel blocks are tightly held together by the Al–O–Al bridges.

4.2. Significance of expansion data to the application of beta-alumina

The close matching of the expansion of the a parameters of β- and β''-alumina is consistent with lattice matching of the two phases on the basal plane within single grains over the temperature range studied. The difference in c parameters is significant and would lead to a stress σ at a grain boundary given approximately by:

$$\sigma = E\Delta\alpha\Delta T,$$

where E is the elastic modulus ($2.1 \times 10^{11}\ N\,m^{-2}$), $\Delta\alpha$ is the difference in expansion coefficient, and ΔT is the temperature difference between the onset of plasticity (~ 1475 K) and the operating temperature of a device (say 575 K for a sodium–sulphur cell). The maximum resultant stress is $\pm 140\ MN\,m^{-2}$ which is comparable with the macroscopic tensile strength but since stresses of this magnitude will only occur in extremely small volumes, the material will be able to tolerate much higher local stresses without cracking. In a similar manner, taking the weighted mean of the expansions in the c direction ($7.5 \pm 0.4 \times 10^{-6}\ K^{-1}$) and comparing this with the expansion in the a direction ($8.1 \pm 0.3 \times 10^{-6}\ K^{-1}$) gives a maximum stress of $\sim 120\ MN\,m^{-2}$ between unfavourably oriented grains. Stresses of this magnitude can be readily tolerated in a fine-grained material and it is unlikely that this contributes to the failure of beta-alumina in sodium–sulphur cells and other electrochemical devices. Coarse-grained materials will, however, tend to be less durable than fine-grained materials produced by rapid sintering techniques because of their reduced resistance to thermally induced cracks as well as their lower overall strength.

5. Conclusions

The thermal expansion of β- and β''-alumina in a polycrystalline sample of beta-alumina has been measured by high temperature X-ray diffractometry taking care to avoid complications due to hydration at low temperatures and sodium loss at high temperatures. The values are (293 to 1178 K):

$$\beta \quad a\ 8.0 \pm 0.2 \times 10^{-6}\ \mathrm{K}^{-1}$$

$$c\ 8.1 \pm 0.3 \times 10^{-6}\ \mathrm{K}^{-1}$$

$$\beta'' \quad a\ 8.1 \pm 0.3 \times 10^{-6}\ \mathrm{K}^{-1}$$

$$c\ 7.0 \pm 0.4 \times 10^{-6}\ \mathrm{K}^{-1}.$$

Taking a weighted mean of the expansions of the two phases shows that internal stresses as a result of variations in the thermal expansions are unlikely to cause cracking and contribute to the failure of the material in electrochemical cells. The linear expansion derived from these measurements is in close agreement with values obtained by dilatometric techniques.

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