THE SYNTHESIS OF BETA ALUMINA FROM ALUMINIUM HYDROXIDE AND OXYHYDROXIDE PRECURSORS

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ABSTRACT

Two aluminium oxyhydroxides, boehmite and pseudoboehmite, and two aluminium hydroxides, bayerite and gibbsite, have been investigated as precursors for the synthesis of the solid electrolyte, beta alumina. Reaction pathways and products have been characterized by thermal analysis and powder X-ray diffraction. A solid state reaction model for the formation of β''-Al_2O_3 is proposed.

MATERIALS INDEX: beta alumina, aluminium, hydroxides, oxyhydroxides

Introduction

Beta alumina is a two-dimensional sodium-ion conductor which acts as the solid electrolyte in high temperature sodium/sulphur cells [1] and in sodium/metal chloride cells

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[2,3]. The two main subgroups of beta alumina are ß-Al_2O_3 and ß"-Al_2O_3 which differ in stoichiometry and in the stacking sequence of the oxygen ions across the conduction plane. Because of its higher conductivity, ß"-Al_2O_3 is the preferred phase for battery applications.

The synthesis of ß"-Al_2O_3 is conventionally carried out by the solid state reaction of α-Al_2O_3 with Na_2O and a small amount of Li_2O and/or MgO stabilizer. In addition to the conventional solid state reaction route to ß"-Al_2O_3, alternative routes have been reported. For example, ß"-Al_2O_3 has been synthesized by alkoxide hydrolysis [4-6], sol-gel processing [7,8] and co-precipitation techniques [9,10]. The ternary phase diagram for the system Na_2O-Li_2O-Al_2O_3 at 1500°C has been reported [11,12] and shows that single-phase ß"-Al_2O_3 exists over a range of compositions. According to Duncan [11] the centre of this region has the molar composition 84% Al_2O_3, 13% Na_2O and 3% Li_2O.

The synthesis of ß"-Al_2O_3 from an α-Al_2O_3 precursor has the disadvantage that a two-phase mixture of ß-Al_2O_3 and ß"-Al_2O_3 is formed by the reconstructive transformation of the hexagonal-close-packed oxygen lattice of α-Al_2O_3 to the cubic-close-packed stacking sequence of the oxygen ions in the spinel blocks in beta alumina. In order to maximize the formation of the ß"-Al_2O_3 phase several techniques can be employed. These include a post-sinter anneal [13], a two-peak firing schedule [14], the so-called Zeta process [15] and seeding with pre-reacted ß"-Al_2O_3 [13]. When other chemical precursors are used, the beta alumina product often contains an oxygen stacking fault disorder which results in a reduced Na^+-ion conductivity.

Several routes by which beta alumina materials are formed from α-Al_2O_3 and from other precursors have been reported. For example, Bugden and Duncan [16] have demonstrated that the solid state reaction of α-Al_2O_3, Na_2O and Li_2O produces a $NaAlO_2$ intermediate phase at 800°C; at 1200°C the reaction product is typically 60% ß-Al_2O_3 and 40% ß"-Al_2O_3.

A crystallization route to ß-Al_2O_3 by alkoxide hydrolysis has been reported by Hodge [17]. An intermediate sodium-rich mullite-like phase, m-Al_2O_3, was observed at about 600°C. At 1200°C the product was a pure ß-Al_2O_3 phase.

An intergrown ß/ß"-Al_2O_3 product synthesized from disordered transition aluminas has been reported by Morgan [5] and Poulieff and co-workers [18]. This intergrown product is characterized by an oxygen stacking fault disorder, which is evident from the combination of sharp and diffuse peaks in its powder X-ray diffraction pattern. Two different models have been proposed to explain this phenomenon. Morgan [5] and Poulieff and co-workers [18] suggest that this intergrowth is formed when the beta alumina product inherits the stacking fault disorder of the transition alumina. Hodge [17] proposes that the disordered transition alumina precursor acts as a substrate for the epitaxial nucleation of both ß- and ß"-Al_2O_3. De Jonge [19] has reported that the intergrown product remains unaffected by heat-treatment below the melting point of the material.

Duncan et al. [20] have reported the synthesis of beta aluminas from commercially available aluminium hydroxides. In particular, they showed that single phase ß"-Al_2O_3 is formed at temperatures as low as 1200°C if the aluminium oxide is either boehmite or bayerite.

This paper describes the solid state synthesis of beta alumina products from four high purity, synthetic aluminium oxyhydroxides and hydroxides, namely boehmite, pseudoboehmite, bayerite and gibbsite. On the basis of thermal analysis of the reaction products at different temperatures, a generalized model for the formation of beta alumina, and in particular ß"-Al_2O_3, is proposed.

Experimental Methods

Beta alumina was synthesized by the solid state reaction of Na_2CO_3 and Li_2CO_3 with the following aluminium oxyhydroxides and hydroxides (hereafter simply referred to as hydroxy aluminas):

(a)   Oxyhydroxides
            Boehmite (AlOOH)
            Pseudoboehmite (AllOOH.xH$_2$O)

(b)   Hydroxides
            Bayerite (Al(OH)$_3$)
            Gibbsite (Al(OH)$_3$)

The synthesis was carried out in two stages. Firstly, the hydroxy aluminas were prepared individually from a common aluminium alkoxide parent material; in the second stage the hydroxy aluminas were mixed with Na_2CO_3 and Li_2CO_3 and reacted at elevated temperatures.

Synthesis of Hydroxy Aluminas

High purity hydroxy aluminas were synthesized from aluminium tri-isopropoxide (Alfa products, 99.999% purity). This material reacts vigorously with water and, under different reaction conditions, produces hydroxy aluminas with a variety of structures. The hydroxy aluminas investigated in this work were prepared by methods reported by Yoldas [21].

Pseudoboehmite was synthesized by reacting 200ml of a 0.5M stock solution of aluminium tri-isopropoxide in isopropanol, preheated to 80°C, with 300ml of preheated, deionized water in a static mixer. The suspension was stirred in a jacketed vessel at 80°C for two hours to ensure complete reaction. The suspension was aged at 20°C for 24 hours after which it was centrifuged and dried at 120°C in a vacuum oven.

Bayerite was synthesized in a similar way to pseudoboehmite except that the stock solutions were pre-cooled to 5°C before reaction in a static mixer. The resulting suspension was stirred in a jacketed vessel at 5°C for 6 hours before aging the solution for 60 hours at 20°C. The material was centrifuged and dried at 120°C in a vacuum oven.

Gibbsite was synthesized by reacting 200ml of a 0.5M stock solution of aluminium tri-isopropoxide in isopropanol with 300ml of a 1.25×10^{-3}M NaOH solution in a static mixer at room temperature. The suspension was stirred for two hours, aged for 60 hours at 20°C and centrifuged; the product was washed in distilled water three times before drying at 120°C in a vacuum oven.

Boehmite was synthesized by subjecting a pseudoboehmite suspension to autoclaving for 24 hours at 200°C at a saturated steam pressure of approximately 15 bar. The resulting suspension was centrifuged and dried at 120°C in a vacuum oven.

Samples of the hydroxy aluminas were stored under ambient conditions. Each hydroxy alumina was characterized by differential thermal analysis (DTA) and powder X-ray diffraction (XRD) techniques. DTA traces were generated on a Du Pont 1090 thermal analyser with a heating rate of 5°C per minute. Compacted α-Al_2O_3 powder was used as the reference material. XRD patterns were obtained on an automated Rigaku diffractometer using CuKα radiation monochromated by a curved graphite single crystal. Silicon powder was used as an internal standard.

Solid State Reactions

Beta alumina samples were synthesised by the solid state reaction of each of the four hydroxy alumina precursors with Na_2CO_3 (BDH Analar grade) and Li_2CO_3 (Merck Analytical grade). Each sample had the ß"-Al_2O_3 composition, namely, 84% Al_2O_3, 13% Na_2O and 3% Li_2O. A slurry containing approximately 75g of hydroxy alumina, Na_2CO_3 and Li_2CO_3 in 100ml of distilled water was attritor-milled for two hours. The slurry was rapidly cooled by injection into liquid nitrogen and freeze-dried under vacuum (0.06 mbar). The resulting powders were compacted uniaxially into cylindrical discs at 20MPa and encapsulated in platinum foil to prevent loss of Na_2O and Li_2O during reaction. Samples were reacted in a Super Kanthal furnace for 24 hours at temperatures ranging from 600°C. The heating and cooling rate was 5°C per minute.

Results and Discussion

The XRD patterns of the four hydroxy alumina precursor materials used in this investigation are given in Fig. 1(a-d). Boehmite, bayerite and gibbsite are highly ordered, crystalline phases (Fig. 1a, c, d). In contrast, pseudoboehmite has a diffuse pattern, with peaks corresponding to those of boehmite (Fig. 1b).

The dehydroxylation behaviour of hydroxy aluminas such as boehmite, pseudoboehmite, bayerite and gibbsite has been reported extensively [22-26]. In general, heat-treatment of these materials produces α-Al_2O_3 at 1200°C. The formation of α-Al_2O_3 occurs via a series of poorly crystalline and metastable transition alumina phases which include γ-, η, δ-, θ-, κ- and χ-Al_2O_3. Reaction sequences of various hydroxy aluminas to α-Al_2O_3 as reported by Stumpf [27] are summarized in Fig. 2. Krischner [28] has categorized the dehydroxylation products of these materials according to the oxygen stacking sequence in the transition aluminas. Boehmite and bayerite both form defect spinel structures with a cubic-close-packed ABCABC... oxygen stacking sequence. Diaspore converts directly to the hexagonal-close-packed stacking sequence ABABAB... of α-Al_2O_3. Gibbsite, when dehydroxylated, produces an alumina with an ABACABAC... stacking sequence which has both cubic-close-packed and hexagonal-close-packed character. Pseudoboehmite, which itself is a poorly crystalline aluminium oxyhydroxide produces a highly faulted, virtually amorphous, transition alumina with an irregular oxygen stacking sequence.

The following results demonstrate that when Li_2CO_3 and Na_2CO_3 are reacted with the hydroxy aluminas to form beta alumina, the oxygen stacking sequence of the transition alumina plays a vital role in controlling the formation of a single-phase ß"-Al_2O_3 product. (Note: For convenience, throughout the rest of this paper, the term γ-Al_2O_3 is used to refer to all transition aluminas with a cubic-close-packed oxygen network).

Reactions of Hydroxy Aluminas with Li_2CO_3 and Na_2CO_3

1.   Boehmite + Li_2CO_3 + Na_2CO_3

The development of a single phase ß"-Al_2O_3 product from boehmite, Li_2CO_3 and Na_2CO_3 is shown in Fig. 3a. For comparison, the phase development of the two-phase ß-Al_2O_3 + ß"-Al_2O_3 product that is formed from an α-Al_2O_3 precursor (via a distinct $NaAlO_2$ intermediate phase) is shown in Fig. 3b. The presence of the hydrated sodium aluminate, ρ-$Na_2O.Al_2O_3.6H_2O$, in the XRD patterns of Fig. 3b can be explained by the highly hygroscopic nature of $NaAlO_2$ [29] and the fact that the reacted samples were stored in containers under normal atmospheric conditions prior to X-ray data collection.
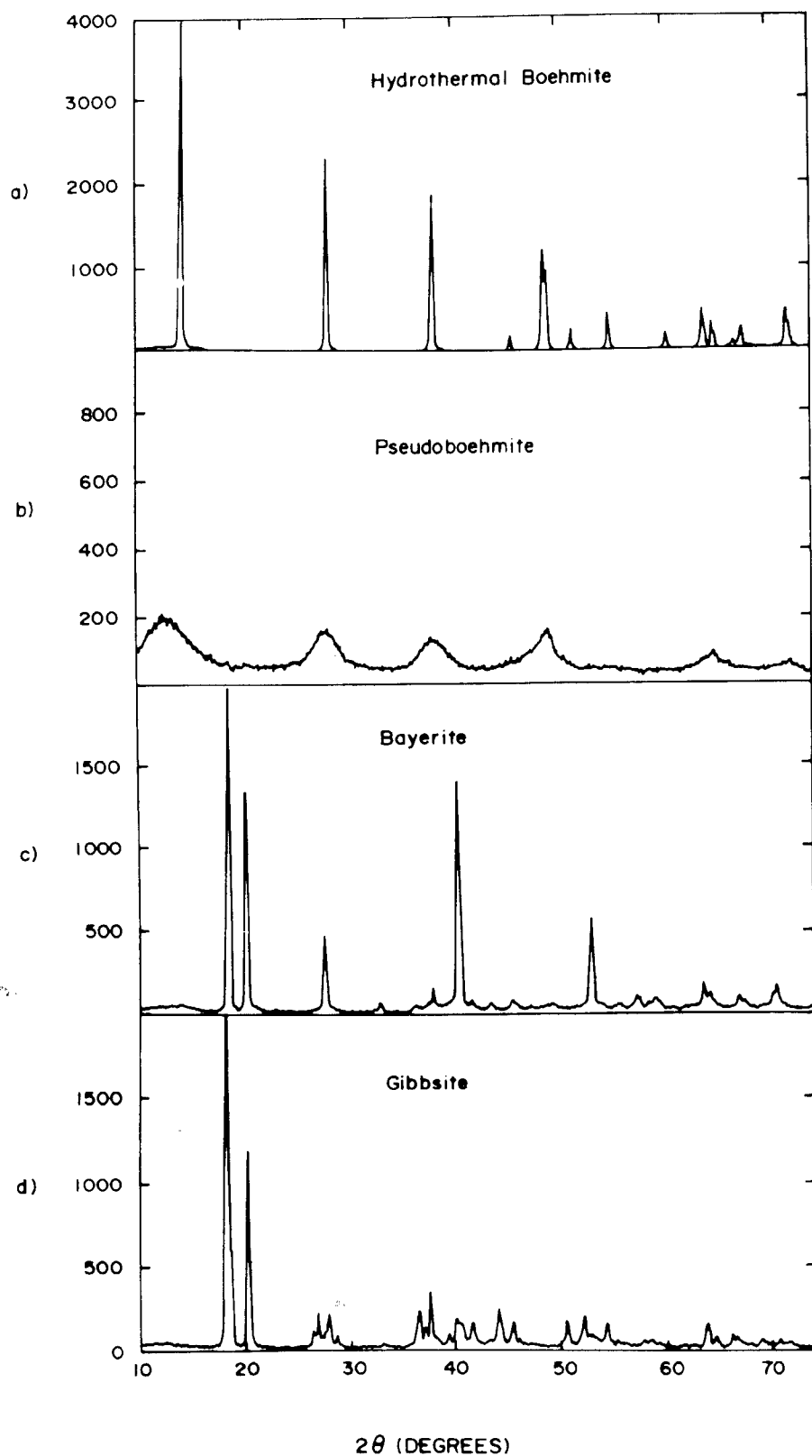
FIG. 1

Powder X-ray diffraction patterns of the four different hydroxy aluminas used
in the synthesis of beta alumina.

Dehydroxylation of boehmite destroys its highly crystalline character and after heat-treatment at 600°C, produces a poorly crystalline γ-Al_2O_3 phase which has a defect spinel structure. At this stage the XRD pattern shows no evidence of any reaction of the Li^+ or Na^+ ions with the alumina phase. Heat-treatment of the reaction mixture through 1000°C, 1200°C to 1600°C clearly shows the development and increasing crystallinity of a single phase ß"-Al_2O_3 product. The development of the [4 0 0] spinel peak of the transition alumina, γ-Al_2O_3, into the equivalent sharp, strongly defined [0 2 10] peak of ß"-Al_2O_3 demonstrates the retention of a constant oxygen network during ß"-Al_2O_3 formation. It is of particular significance that during this reaction no $NaAlO_2$, α-Al_2O_3 or ß-Al_2O_3 intermediate products were formed. The reaction route directly to ß"-Al_2O_3 from boehmite therefore contrasts strongly with the route from α-Al_2O_3.

DTA traces of boehmite and of the boehmite, Li_2CO_3 and Na_2CO_3 mixture are shown in Figs. 4a and b, respectively. The two endothermic peaks at 90°C and 540°C in Fig. 4b, which also characterize the DTA trace of pure boehmite are attributed to the loss of surface and crystalline water, respectively. Two additional endothermic peaks at 300°C and 400°C (Fig. 4b) can be attributed to thermal events associated with the decomposition of Li_2CO_3 and Na_2CO_3.

The DTA trace of pure boehmite (Fig. 4a) shows a transformation of the transition alumina to α-Al_2O_3 at 1200°C. In the DTA trace of the reaction mixture (Fig. 4b) no significant thermal events were observed between 600°C and 1200°C. This result is consistent with the XRD data and confirms that the oxygen sublattice of the γ-Al_2O_3 intermediate phase does not undergo a major reconstructive transformation, for example to α-Al_2O_3 or to an intermediate $NaAlO_2$ phase, prior to ß"-Al_2O_3 formation.

2.   Bayerite + Li_2CO_3 + Na_2CO_3

The development of single phase ß"-Al_2O_3 from bayerite, Li_2CO_3 and Na_2CO_3 is illustrated in Fig. 3c. Bayerite transforms during dehydroxylation to a poorly crystalline γ-like transition alumina. The phase development of ß"-Al_2O_3 from bayerite is similar to that from boehmite.

3.   Pseudoboehmite + Li_2CO_3 + Na_2CO_3

The development of a ß/ß"-Al_2O_3 intergrown product from a mixture of pseudoboehmite, Li_2CO_3 and Na_2CO_3 is illustrated in Fig. 3d. The transition alumina formed after heat-treatment at 600°C is virtually amorphous. After heating the mixture to 1000°C, the XRD pattern is characterized by both sharp and broad peaks. The sharp peaks were found to be common to both the ß- and ß"-Al_2O_3 phases, whereas the broad overlapping peaks occurred in regions where unique ß- and ß"-Al_2O_3 peaks are normally located. This is indicative of the formation of an intergrown ß/ß"-Al_2O_3 product. The diffuse peaks remain in the XRD pattern even after reaction to 1600°C.

4.   Gibbsite + Li_2CO_3 + Na_2CO_3

The phase development of beta alumina from gibbsite is shown in Fig. 3e. Dehydration of gibbsite at 600°C results in a virtually amorphous transition alumina; at 1600°C, the product is a combination of an intergrown ß/ß"-Al_2O_3 phase (like that derived from pseudoboehmite) and ß"-Al_2O_3. This is evident from the low relative intensity of the characteristic ß"-Al_2O_3 peaks at ~34.6°2θ and 46°2θ (when compared to the single phase
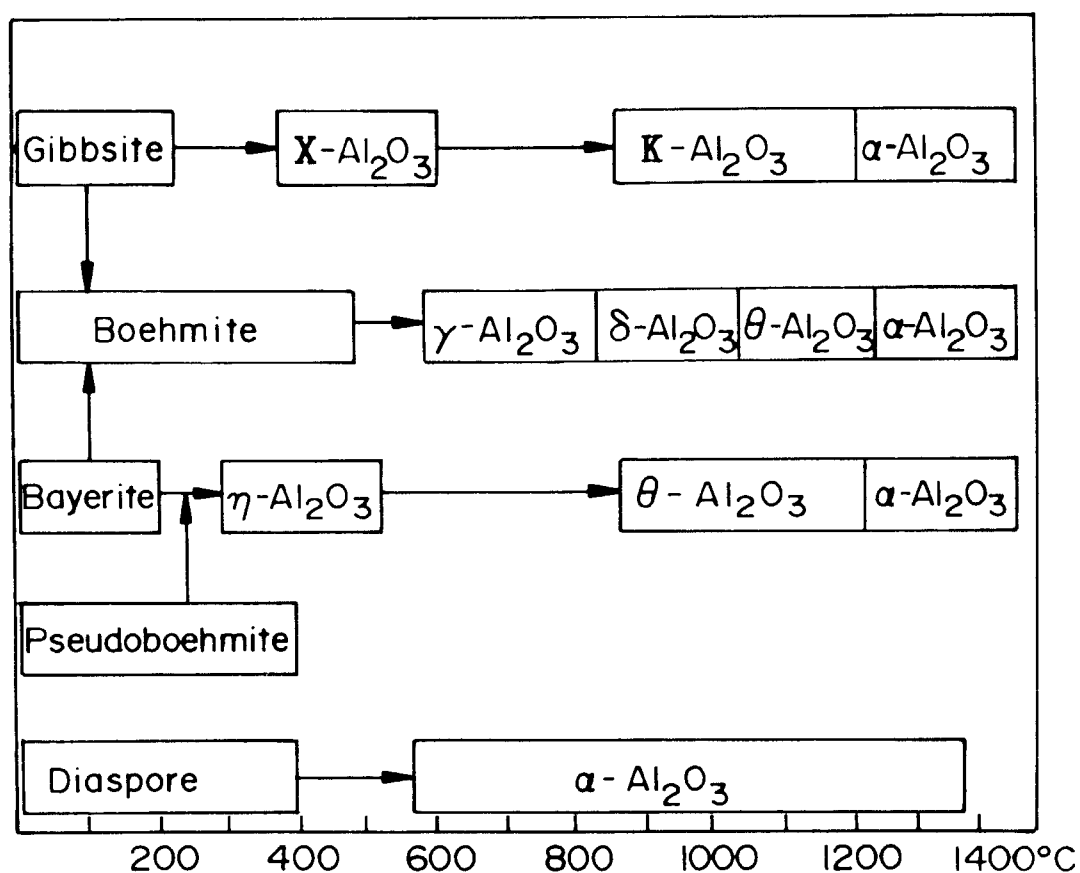
FIG. 2

The dehydroxylation sequences of several hydroxy aluminas (from [27]).
Note that reaction conditions which favour the bayerite to boehmite and gibbsite
to boehmite reactions include high pressure, fast heating rates and large
particle size.

ß"-Al_2O_3 products from boehmite or bayerite, shown in Figs. 3a and 3c, respectively) which are superposed on the broad peaks characteristic of an intergrown ß/ß"-Al_2O_3 phase.

The DTA traces of bayerite, pseudoboehmite and gibbsite, when heated in the presence of Li_2CO_3 and Na_2CO_3 showed the same characteristics of the boehmite, Li_2CO_3 and Na_2CO_3 reaction mixture, and will therefore not be described in detail. In general, all three traces contained endothermic events between 90°C and 500°C which could be attributed to surface and bulk dehydration of the hydroxy aluminas and to Li_2CO_3 and Na_2CO_3 decomposition. The outstanding feature of the boehmite, bayerite and gibbsite traces, was the absence of the exothermic peak at 1200°C which normally defines the transformation of the transition alumina to α-Al_2O_3 in the absence of Li_2CO_3 and Na_2CO_3.
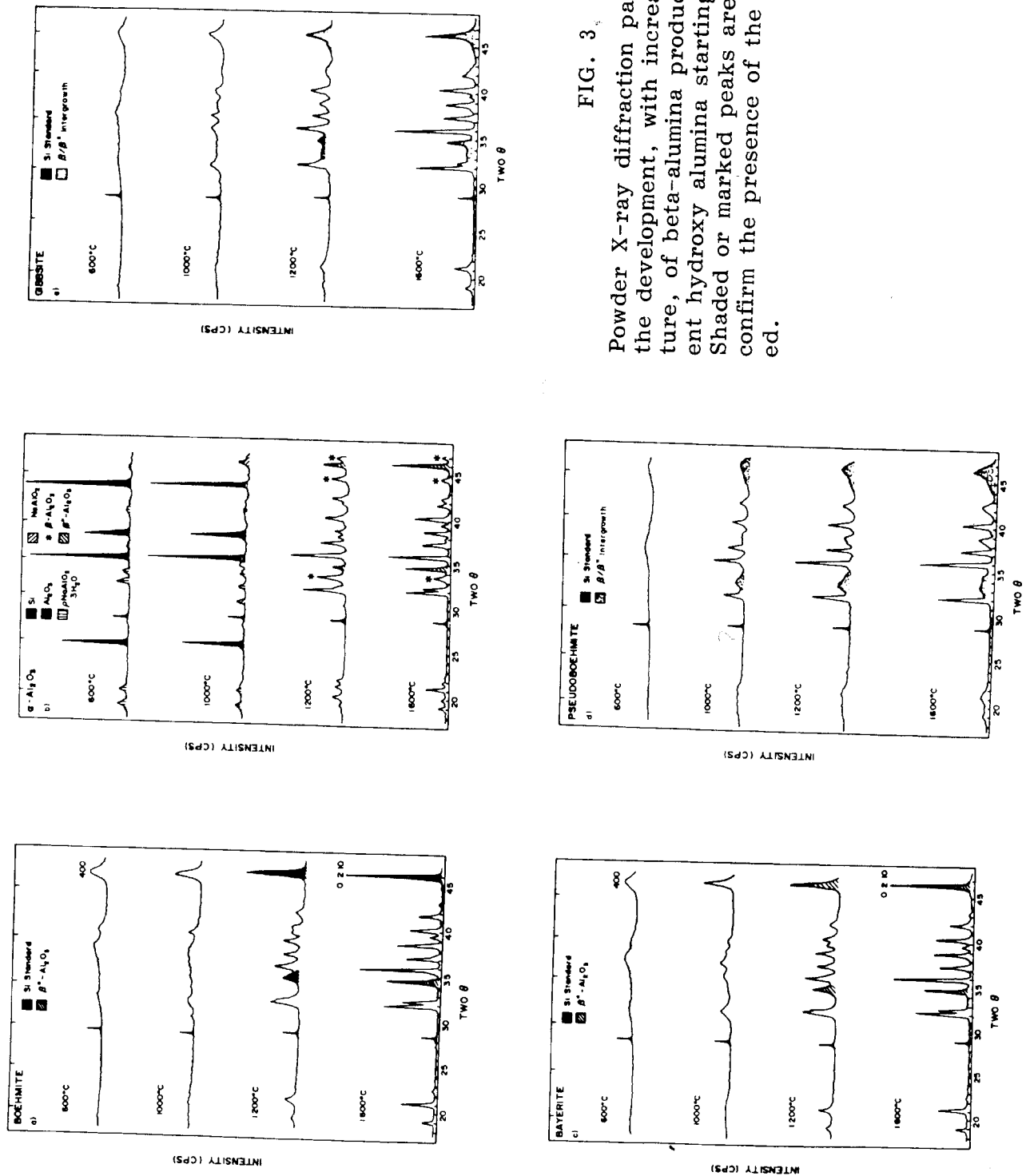
FIG. 3.

Powder X-ray diffraction patterns showing the development, with increasing temperature, of beta-alumina products from different hydroxy alumina starting materials. Shaded or marked peaks are those used to confirm the presence of the phases indicated.
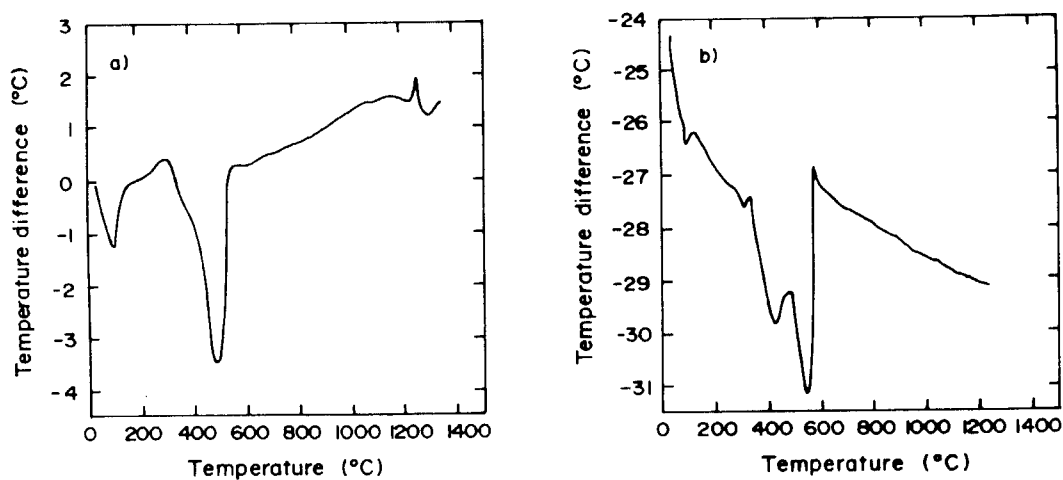
FIG. 4

DTA traces of (a) pure boehmite and (b) a boehmite, Li_2CO_3 and Na_2CO_3 mixture.

However, DTA traces of the pseudoboehmite reaction mixture consistently contained a weak exothermic event at 1200°C. This event was attributed to the transformation of local, highly concentrated regions of hexagonal-close-packed stacking to α-Al_2O_3. These regions are likely to be found in a highly faulted transition alumina.

Beta Alumina Formation from Boehmite or Bayerite

In contrast to the distinct two-phase mixture of ß-Al_2O_3 and ß"-Al_2O_3 which results from the reaction of α-Al_2O_3 with Li_2CO_3 and Na_2CO_3, it is clear from this work that a single phase ß"-Al_2O_3 product can be prepared from boehmite and bayerite and that an intergrown ß/ß"-Al_2O_3 product is formed from gibbsite and pseudoboehmite.

The structure of ß"-Al_2O_3 is composed of layers of cubic-close-packed oxygen ions with three-quarters of the oxygen ions missing in every fifth layer [30]. The Na^+ ions reside in the oxygen-deficient layers (the conduction planes); the oxygen ions in the conduction plane maintain the cubic-close-packing and link the remaining 4-layer "spinel" blocks in which the Al^{3+} ions and stabilizing Li^+ ions occupy tetrahedral and octahedral sites normally occupied by the cations in the mineral spinel, $MgAl_2O_4$. By contrast, the conduction plane in ß-Al_2O_3 is a mirror plane. As a result, an element of hexagonal-close-packing of the oxygen ions is present across the conduction plane thus disrupting the cubic-close-packing sequence of the structure. It is interesting to note that not only do the transition aluminas derived from boehmite and bayerite have defect spinel structures [31], but ß"-Al_2O_3 itself has essentially the stoichiometry of an ideal spinel M_3O_4 (M = cation) [32]. Phase diagram studies [11,32] have shown that a range of ß"-Al_2O_3 compositions form on the pseudo-ternary section "$NaAl_5O_8$"-$LiAl_5O_8$-$MgAl_2O_4$, i.e. with a spinel-like stoichiometry.

In the formation of single-phase ß"-Al_2O_3 from boehmite and bayerite, there are two major structural aspects that deserve mention:

1. Both boehmite and bayerite have highly crystalline and ordered structures. When dehydrated, they form transition aluminas which can be described as defect spinel phases $Al_{8/3}\square_{1/3}O_4$ which are characterized predominantly by a <u>regular</u> cubic-close-packed oxygen ion array.

2. The contribution of oxygen ions from Li_2O and Na_2O to the overall oxygen content in the ß"-Al_2O_3 structure (5.97%) coincides, within 1.5%, with the fraction of oxygen in the conduction plane (5.88%).

Therefore, in the formation of ß"-Al_2O_3 from a regular cubic-close-packed transition alumina, it is possible to visualize a solid state reaction, whereby the oxygen ions from the Li_2O and Na_2O components are inserted between the close-packed layers to provide the bridging oxygens of the ß"-Al_2O_3 structure (Fig. 5).

For reasons of stoichiometry, the oxygen contribution from Li_2O and Na_2O must be accommodated between every 4th and 5th layer of the transition alumina structure. Note that this mechanism must invoke a shear of the "spinel blocks" that originate from the γ-Al_2O_3 structure to maintain the overall cubic-close-packed stacking of oxygens in the ß"-Al_2O_3 product.

The introduction of the bridging oxygens into the transition alumina imparts an overall negative charge to the γ-Al_2O_3 structure, thereby permitting the diffusion of Li^+ ions into the defect spinel blocks until all the cation sites of the spinel block are occupied. Indeed, it has been shown that Li^+ ions can migrate readily through the face-shared tetrahedral (8a) - octahedral (16c) - tetrahedral (8a)... network of a spinel structure even at room temperature, for example, as in the spinel $Li_{8a}[Mn_2]_{16d}O_4$, which has prototypic symmetry Fd3m [33]. The Na^+ ions are too large to diffuse through the spinel blocks and therefore remain in the conduction plane. These observations emphasize the critical stabilizing role played by the Li^+ ions, particularly in "pinning" the cubic-close-packed oxygen ion array during ß"-Al_2O_3 formation. It should be noted that a metastable, single phase ß"-Al_2O_3 product can be obtained from a $Na_2O.xAl_2O_3$ binary system, for example, when a commercially available boehmite is used [20,34]. However, the ß"-Al_2O_3 phase tends to transform to ß-Al_2O_3 with prolonged heat-treatment above 1400°C [11].

Wilson has shown by transmission electron microscopy that boehmite, fired in air at 400°C produces a fine, lamellar porous microstructure [35]. The pore spacing was reported to be typically 35-40 Å, the pore width ~8 Å, and there was evidence of cross-linking between adjacent pores. It is thus possible that these pores could become at least partially occupied by Li_2O and Na_2O prior to ß"-Al_2O_3 formation. The reported regularity of orientation and spacing of the pores are important factors that would account for the homogeneity and single-phase character of the final ß"-Al_2O_3 product.

Intergrown ß/ß"-Al_2O_3 Formation from Gibbsite or Pseudoboehmite

It has been reported that gibbsite, when heated, produces a poorly crystalline transition alumina with a high stacking fault density [28]; the stacking sequence of the oxygen layers, which in general, is ABACABAC... contains both hexagonal-close-packed (α-Al_2O_3) and cubic-close-packed (γ-Al_2O_3) character, unlike the stacking sequence in transition aluminas derived from boehmite and bayerite which are predominantly cubic-close-packed. Dehydroxylation of pseudoboehmite, like gibbsite, produces a highly-faulted transition alumina.

If a negative charge is induced into γ-Al_2O_3, as it is by the bridging oxygens in ß"-Al_2O_3, Li^+-ion diffusion into the defect spinel structure is both energetically and sterically
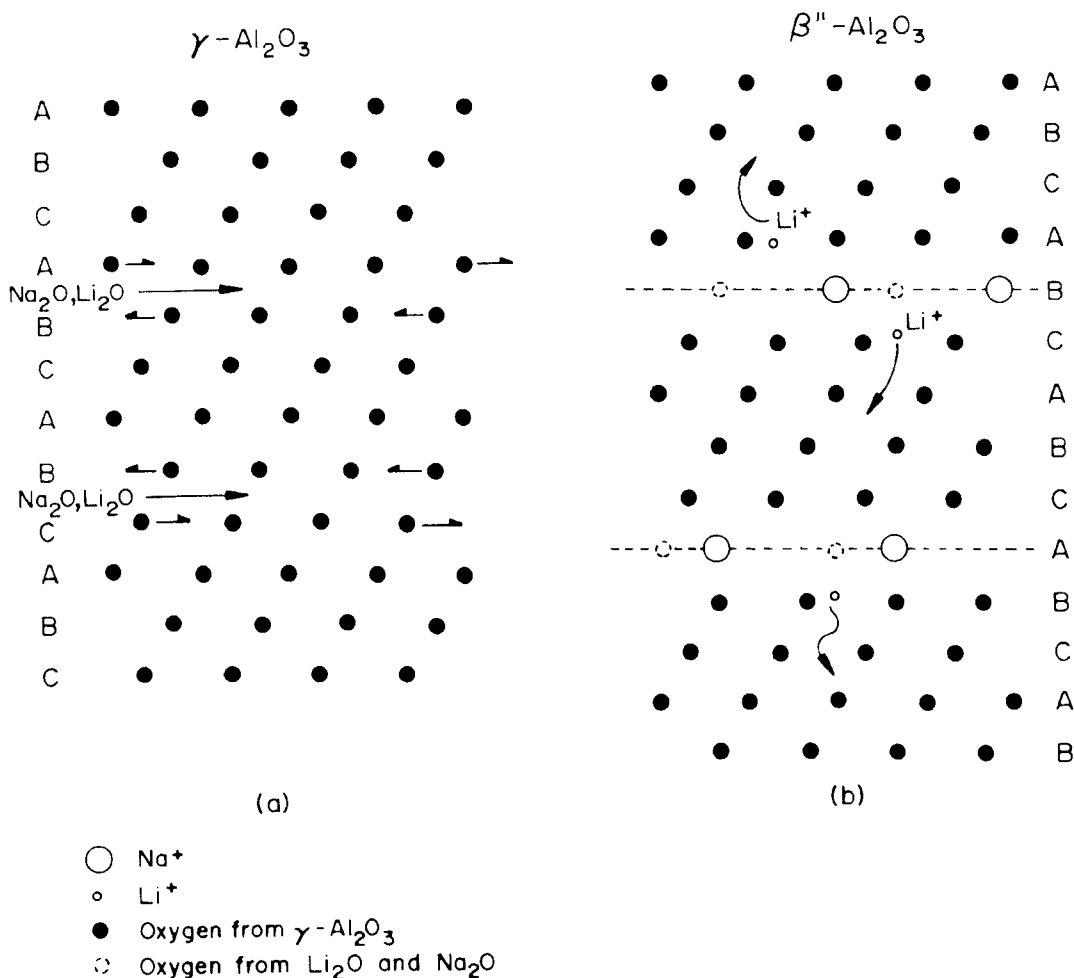
FIG. 5

Schematic illustration of the proposed mechanism for the conversion of the oxygen lattice of (a) γ-Al_2O_3 to (b) β''-Al_2O_3 (b). The oxygen ions from Li_2O and Na_2O are inserted between the close-packed layers of γ-Al_2O_3 to form the bridging oxygens in β''-Al_2O_3.

possible. If the Al^{3+} ions occupy all the octahedral B-sites of an $A[B_2]O_4$ spinel structure, and if the remaining Al^{3+} ions and vacancies are distributed over the tetrahedral A-sites, Li^+ ions can still percolate through a three-dimensional network of face-sharing A-tetrahedra and interstitial octahedra. [Note that the tetrahedra and octahedra of this network share edges, not faces, with the occupied B-octahedra. Note also that if all the vacancies are on tetrahedral sites and all the Al^{3+} ions distributed over octahedral sites, a defect rock salt structure results, which contains alternative pathways of face-sharing tetrahedra and octahedra for the Li^+ ions. The possibility that such a defect rock salt structure exists as an intermediate phase in the dehydration of boehmite has already been proposed [35,36]].

By contrast, in the α-Al_2O_3 structure in which the Al^{3+} ions are ordered on two-thirds of the octahdral sites, every tetrahedron in the structure shares two faces with neighbouring Al^{3+}-octahedra. Li^+-ion diffusion through a network of face-sharing interstitial tetrahedra and octahedra in such a hexagonal-close-packed oxygen-ion array is therefore restricted for steric reasons by the short, energetically unfavourable Li^+_{tet}-Al^{3+}_{oct} distances. Li^+ ions cannot therefore be expected to become evenly distributed throughout negatively charged transition aluminas with hexagonal-close-packed character. Regions of hexagonal-close-packed stacking in a transition alumina are therefore expected to be associated with regions of low lithium content, and domains of ß-Al_2O_3 within a ß"-Al_2O_3 matrix are likely to result, thereby giving rise to a final intergrown ß/ß"-Al_2O_3 product.

Conclusions

It has been demonstrated that single phase ß"-Al_2O_3 can be synthesized from γ-like transition aluminas. These transition aluminas, which can be derived from the hydroxy aluminas boehmite and bayerite, are characterized by a regular cubic-close-packed oxygen-ion array. A solid state reaction model by which the oxygen ions from Li_2O and Na_2O are incorporated into the γ-Al_2O_3 structure to form the bridging oxygens in the conduction plane of ß"-Al_2O_3 has been proposed. The Li^+ ions play a critical role in stabilizing the overall cubic-close-packed oxygen framework of this solid electrolyte. By contrast, the hydroxy aluminas pseudoboehmite and gibbsite that form transition aluminas with an irregular oxygen-ion stacking sequence, produce intergrown ß-Al_2O_3 and ß"-Al_2O_3 products. The formation of the intergrown product is attributed to the inability of the Li^+ ions to diffuse uniformly through a negatively charged alumina framework that has both hexagonal-close-packed and cubic-close-packed character.

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