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Direct Synthesis of Binary K−*β*- and K−*β*″-Alumina. 1. Phase Relations and Influence of Precursor Chemistry

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This paper explores the formation of phase-pure K−*β*- and K−*β*″-alumina during direct synthesis in the $K_2O-Al_2O_3$ quasi-binary, at temperatures between 800 and 1700 °C. The effect that is investigated is the structural influence of alumina precursors on *β*-alumina formation, and the identical effect on the thermal stability of the formed *β*-alumina products. At temperatures below 1400 °C, alumina raw materials that form transition aluminas with cubic-close-packed oxygen ion sublattices (γ), similar to the spinel blocks of the *β*-alumina family of compounds, lead to the direct formation of the *β*″-alumina phase. Precursors with a hexagonal-close-packed oxygen ion array (α) form *β*-alumina. At temperatures above 1400 °C, defects originating from the disordered transition aluminas destabilize K−*β*″-alumina, and lead to its subsequent transformation into K−*β*-alumina. Single-phased K−*β*″-alumina based on crystalline boehmite was found to be stable in air at 1400 °C for up to 24 h. Single-phased K−*β*-alumina was found exclusively with corundum, gibbsite, and pseudoboehmite, at temperatures above 1400 °C. Under these experimental conditions, the samples are not held in thermodynamic equilibrium.

I. Introduction

β-Aluminas belong to the five common structures of aluminate compounds found in nature. Besides *β*-alumina these structures are perovskite, tridymite (or "stuffed silica"), spinel, and garnet.[1] However, *β*-aluminas have one unique characteristic that makes them scientifically and technologically important: due to the intercalation of alkali ions their crystal structure (Figure 1) is characterized by defects localized in two-dimensional "conduction planes" flanking spinel-like building blocks.[2−4] Due to the existence of these conduction planes, *β*-aluminas are excellent solid ionic conductors at relatively low temperatures (<500 °C).

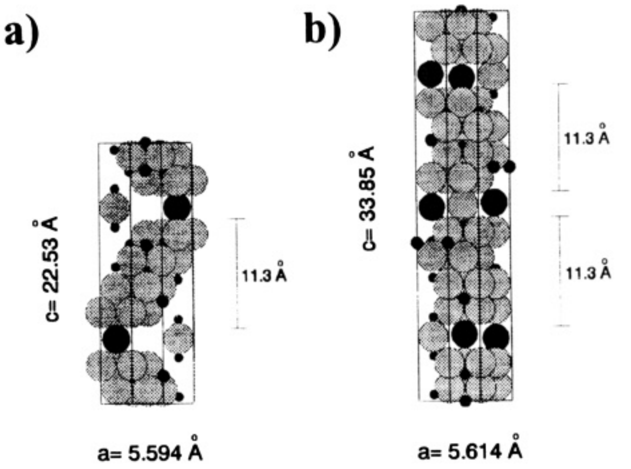

Figure 1. Unit cells of (a) *β*-alumina, space group $P6_3/mmc$, and (b) *β*″-alumina, space group $R\bar{3}m$, projected along the *c*-axis, with typical dimensions and indication of the spinel blocks. Gray spheres represent oxygen ions, large black spheres alkali ions, and small black spheres aluminum ions.

Over the past few decades, battery technology has been the prime driving force behind the development of *β*-alumina materials. The initial goal was to cut back exhaust emissions in the transportation sector and to decrease economic dependency on liquid fuels, using suitable energy-storage battery systems.[5] In 1967, Weber and Kummer of the Ford Motor Co. introduced the Na/S battery, incorporating Na−*β*-alumina as solid electrolyte, separating liquid metallic sodium and sodium polysulfide electrodes.[6,7] This battery type was developed for use in electric vehicles but has since been found to be much more suited for stationary energy-storage stations in connection to power plants.[4] In 1992, a 50 kW/400 kWh Na/S battery cell was installed at TEPCO's Kawasaki site.[8] A second application of *β*-alumina in the energy-field is the sodium heat-engine (also called thermoelectric converter).[9,10] Other more recent applications include combustible gas sensors,[11−15] as well as solid-state optical devices.[16,17]

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A novel application of β-alumina materials in the energy field is as solid electrolyte in solid oxide fuel cells.[18] However, a major problem is the necessary ion exchange of the sodium ions of Na−β″-alumina to protons to be used in fuel cells, which functions well in single crystals but *not* in polycrystalline samples.[19] Dense polycrystalline Na-β″-alumina used as precursor to proton-conducting β″-alumina for use in fuel cells, suffers structural damage on account of its (dense) microstructure and the anisotropic expansion of its crystal lattice during ion exchange. The materials fail because of high mechanical stresses.

II. Motivation for This Study

As pointed out in the literature,[20] K−β″-alumina is the ideal precursor to proton-conducting β″-alumina to be used in fuel cells, on account of the similarity in ionic radius between H_3O^+ ($r = 1.38$ Å) and K^+ ($r = 1.40$ Å). This similarity in size between these two ions constrains any mechanical stress built up during ion exchange. It is also the difference between forming a finished ceramic piece as opposed to a mere handful of powder. However, unlike the sodium β-alumina system, which is the more traditional one, the literature is not clear on the feasibility of directly synthesizing 100% pure K−β″-alumina. Currently, the state of the art in sodium β-alumina synthesis is the direct, routine, fabrication of both β- and β″-alumina species. In contrast, direct synthesis of K−β″-alumina is still disputed, and it is either concluded to be impossible,[21] or improbable.[22] The fact is, that this same conclusion had been reached previously for sodium β-alumina, when basic scientific knowledge was still lacking. Historical developments simply proved the initial conclusion wrong. The same might be true for the potassium analog.

The goal of this paper is to develop a direct synthesis route to both K−β- and K−β″-alumina in the K_2O-Al_2O_3 quasi binary. The use of so-called "dopants" or "stabilizers" will be the subject of another study.[23] In addition, this work seeks to prove that transition aluminas are the most effective in preparing pure K−β″-alumina and that both K−β- and K−β″-alumina can be targeted independently, depending on the suitability of the transition alumina or precursor thereof. This suitability of the original raw material is expressed in terms of the oxygen ion stacking of the transition alumina.

III. Strategy

This paper focuses on the preparation of phase-pure K−β- and K−β″-alumina by direct synthesis in the $K_2O-Al_2O_3$ quasi-binary. The main theme is structural interrelations between precursor materials and the final β-alumina products and the effects of precursor chemistry has on the formation of the different potassium β-alumina type phases. The results of similar work performed in the analogous sodium system are used to choose the starting materials. In addition, the high-temperature behavior of the phase-pure K−β- and K−β″-alumina phases are investigated in order to assess their thermal stability, which in the case of binary β-aluminas is often quoted as "insufficient". We will show that in contrast to the case of α-alumina, where any precursor-related effects are eliminated by its crystallization at around 1250 °C, precursor-related effects are still noteworthy for β-alumina and of major importance to its behavior at temperatures well above its crystallization point.

IV. Previous Studies

The traditional problem in the processing of β-alumina has always been the retention of the better-conducting β″-alumina phase over the unwanted β-phase. These phases differ in both stoichiometry and crystal structure, but are related (Figure 1). The main characteristics for β-alumina (ideal formula $R_2O{:}11Al_2O_3$) are its two-block structure (2-fold screw axis), and its conduction planes which act as perfect mirror planes between the respective spinel blocks. β″-Alumina, on the other hand (ideal formula $R_2O{:}5Al_2O_3$), is a three-block structure, with the individual spinel blocks rotated over 120° with respect to one another (3-fold screw axis), and the conduction planes no longer are mirror planes. Ideally, two cations per conduction plane per unit cell exist in β″-alumina, against one for β-alumina. This gives rise to the higher conductivity of β″-alumina compared to β. The spinel blocks in both β- and β″-alumina are comprised of four oxygen layers in cubic-close-packing, but only in β″-alumina does this packing continue without interruption (no mirror planes) throughout the structure.

Traditional synthesis of sodium β-alumina always relied on α-alumina (corundum) as its aluminum source, mainly because of its good sintering characteristics. Zone sintering was developed to prepare sodium β-alumina ceramics of high density.[24] However, these materials had poor β″-alumina phase characteristics and had to be given postsinter anneals at temperatures below the sintering temperature, to optimize their β″-alumina phase content.[25] Further developments attempted to optimize the β″-alumina phase content, *without* the concurrent danger of anomalous grain growth as experienced in postsinter anneals, and these include ζ-processing,[26] seeding with prereacted β″-alumina powders,[27] and two-peak firing schedules.[28] However, none of these methods ever produced phase-pure Na−β″-alumina.

Further attempts employed wet-chemical synthesis techniques and/or the use of transition aluminas to prepare phase-pure Na−β″-alumina. Sol/gel-synthesis,[29] and alkoxide hydrolysis and coprecipitation[30] were used to increase the homogeneity of reaction mixtures and thereby to create a tendency toward β″-alumina. However, these attempts failed, and instead of β″-

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Table 1. Chemical and Physical Characteristics of Aluminum Oxide, Hydroxide, and Oxyhydroxide Starting Compounds

mineral name	crystallographic notation	Al_2O_3 content (wt %)	trace analysis (ppm) Na	Si	Fe	Ca	Mg	surface area (m^2/g)	median particle size (μm)
gibbsite[a]	γ-$Al(OH)_3$	65.5	<1600	500	140			3–5	1.3–2.2
bayerite[b]	α-$Al(OH)_3$	64.0	100	250	400			295	13
boehmite[c]	γ-AlOOH	83.1	944	235	222	84	<66	41	17
pseudoboehmite[d]	γ-AlOOH	75.4	100	250	300			262	15
corundum[e]	α-Al_2O_3	100.0	<4	114	126	6	24	11	0.46
corundum[f]	α-Al_2O_3	100.0	1000	80	600	100	<10	0.05	88

[a] Martinal OL-104, Martinswerk, Bergheim, Germany. [b] Bayerite, Condea Chemie, Hamburg, Germany. [c] Cera Hydrate, Alcan Chemicals Europe, Chalfont Park, Gerrards Cross, UK. [d] Pural SCF, Condea Chemie, Hamburg, Germany. [e] Ceralox-APA0.5, Condea Chemie, Hamburg, Germany. [f] Fused alumina, Aldrich Chemical Co., Milwaukee, WI.

alumina, Na-β-alumina tended to form. Similar approaches that used γ-alumina as aluminum source to increase the reactivity of starting mixtures also failed.[31–33] In this case, Na-β/β''-alumina intergrowths were formed with a high degree of stacking faults. This then led to some discussion as to the suitability of transition aluminas in general to prepare phase-pure β''-alumina.[34]

The most recent achievements in the processing of sodium β-alumina can be traced back to the 1968 study of Yamaguchi and Suzuki on the crystal structure of β- and β''-alumina. These authors used aluminum trihydroxide (unspecified) to prepare phase-pure K–β''-alumina.[3] However, this study was largely ignored. In 1977, Foster and Scardefield patented the use of θ-alumina for the preparation of 100% Na-β''-alumina.[35] Another 1977 patent by Eddy and Rhodes of the General Motors Corp.[36] claimed the use of boehmite to the same result, while Morgan in 1982 patented the use of bayerite.[37] Duncan et al.[38] used boehmite or mixtures of boehmite with α-alumina and prepared single-phased Na–β''-alumina. Van Zyl et al.[39,40] claimed the use of cubic-close-packed aluminum oxides, or precursors thereof, in the preparation of 100% Na–β''-alumina, while Hartung[41] simply claimed the use of *all* aluminum hydroxides, oxyhydroxides, and transition aluminas, to the same effect, with the exception of diaspore. Almost all available alumina raw materials have now been used and patented to prepare 100% pure Na–β''-alumina.

V. Experimental Procedure

5.1. Powder Preparation. Powder mixtures according to the molar range $K_2O{:}5Al_2O_3$ to $K_2O{:}11Al_2O_3$ were prepared by attrition milling various kinds of alumina raw materials, their chemical and physical characteristics are listed in Table 1, together with potassium hydroxide (p.A., Merck, Darmstadt, Germany) in doubly distilled and demineralized (DDD) water using solid α-alumina spheres as milling media (1–2 mm in diameter). Appropriate amounts of raw materials were weighed to give approximately 60 g of oxides after calcination. After the attritor milling (1 h) the powder suspensions were separated from the milling media over stacked 160 and 30 μm sieves. Suspensions were collected in 1.5 L stainless steel pans and dried in air at 60 °C. The dried powders were then hand-crushed in an alumina mortar and subsequently calcined in air between 400 and 1700 °C, at every 100 °C. The powders calcined below 1400 °C were calcined for 1 h, the powders calcined above 1400 °C were calcined with soak times ranging from 10 min to 24 h. The heating rate in all cases was 5 °C/min. Calcining furnaces were electrically heated and microprocessor controlled. To contain the powders, open α-alumina crucibles that had been prereacted with $KAlO_2$ to form K–β-alumina were used. No further precautions were taken against potassium evaporation.

5.2. Powder Characterization. Powder characterization involved scanning electron microscopy (Stereoscan 200, Cambridge Instruments, Cambridge U.K.), simultaneous thermal analysis (Netzsch STA 409, Netzsch Gerätebau GmbH, Selb, Germany), specific surface area analysis by the BET method (Micromeritics Gemini, Norcross, GA), and qualitative, as well as quantitative X-ray diffraction analysis (Siemens D5000-spectrometer equipped with an OED detector, Siemens, Karlsruhe, Germany). SEM samples were prepared by sprinkling the powders on Al stubs coated with graphite. The samples were then coated with gold. STA was carried out under stagnant air atmosphere with empty alumina crucibles as reference (heating rate 5 °C/min). BET-samples were outgassed overnight at 200 °C under flowing nitrogen atmosphere. The specific surface area of selected samples was then measured by five-point BET analysis using N_2 as adsorbate and He as carrier gas. Standard X-ray diffractograms were recorded using Cu Kα radiation, utilizing a scanning width of 6 to 80° 2θ, with a stepwidth of 0.02°, and a scanning time of 10 s.

For quantitative X-ray diffraction analysis, the following equations were used to calculate the weight percentages w_α, w_β, and w_γ in ternary mixtures of phases α, β, and γ:

$$w_\alpha = \frac{1}{[1 + (I_\beta/I_\alpha)(I_\alpha/I_\beta)_{0.5} + (I_\gamma/I_\alpha)(I_\alpha/I_\gamma)_{0.5}]} \tag{1}$$

$$w_\beta = 1 - w_\alpha[1 + (I_\gamma/I_\alpha)(I_\alpha/I_\gamma)_{0.5}] \tag{2}$$

$$w_\gamma = 1 - w_\alpha - w_\beta \tag{3}$$

These equations can easily be adapted to binary mixtures. The subscripts 0.5 denote intensity ratios belonging to calibration samples of 50:50 mixtures (by weight) of the corresponding pure phases. Integrated peak intensities for α-alumina were measured against its (113) peak (100% in JCPDS card No. 10-173), for β-alumina against the (017) peak (100% in JCPDS card No. 39-50, and 75% in JCPDS card No. 31-960), and for β''-alumina against the $(01\underline{11})$ peak (40% in JCPDS card No. 21-618). Powders were stored in desiccators, but measured under air.

VI. Results and Discussion

6.1. Raw Materials. Alumina raw materials have been characterized by SEM, STA, and BET. Figure 2

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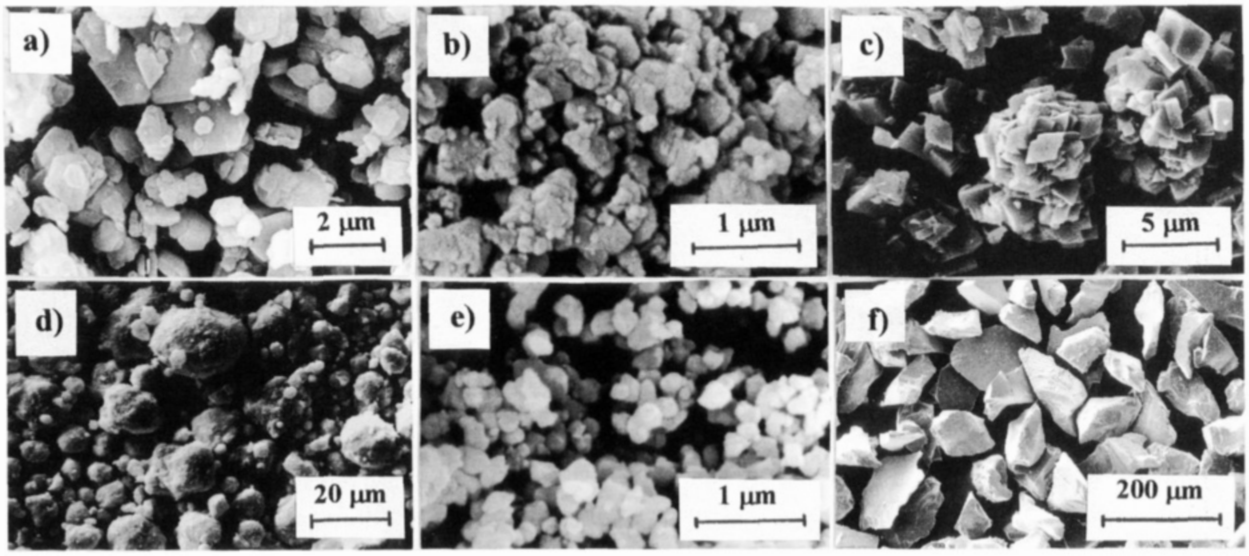

Figure 2. SEM micrographs of aluminum oxide, hydroxide, and oxyhydroxide starting compounds, featuring (a) gibbsite, (b) bayerite, (c) boehmite, (d) pseudoboehmite, (e) corundum, and (f) fused corundum.

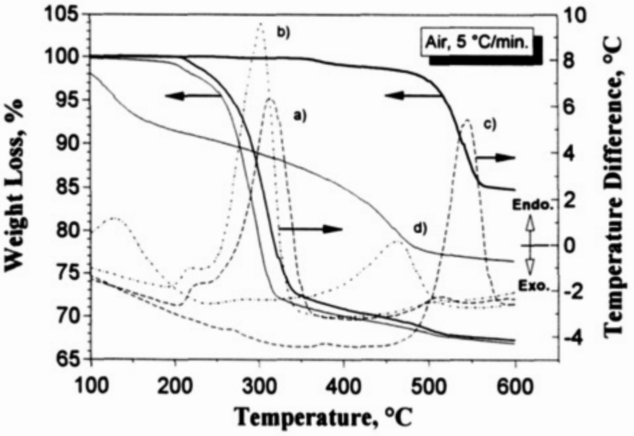

Figure 3. Simultaneous thermal analysis data of aluminum hydroxide and oxyhydroxide starting compounds, featuring (a) gibbsite, (b) bayerite, (c) boehmite, and (d) pseudoboehmite.

Table 2. Phase Composition (wt %) of Calcined K_2O:$5Al_2O_3$ Powder Mixtures Based on Different Alumina Precursors as a Function of the Calcination Temperature, As Measured by XRD[a]

alumina precursor	2 h, 1400 °C, β″	2 h, 1500 °C, β″	2 h, 1600 °C, β″	2 h, 1700 °C, β″
gibbsite	β/β″-intergr	β/β″-intergr	β/β″-intergr	0
bayerite	100	100	97	46
boehmite	100	96	70	13
pseudoboehmite	98	79	26	0
Condea corundum	11	10	3	0
Aldrich corundum	23[b]	12	5	0

[a] Entries list K−β″-alumina, complement is K−β-alumina. [b] With 14 wt % α-alumina.

shows the powder morphology of all raw materials used in this work. The corresponding chemical and physical characteristics are listed in Table 1. All powders show the characteristic hexagonal platelet, if with somewhat different scaling. Exceptions are the pseudoboehmite (Figure 2d) and fused alumina (Figure 2f) powders. The first is a spray-dried powder containing large soft agglomerates, while the latter consists of solid chunks (in the 200 μm range) of solidified alumina. The bayerite and α-alumina powders by Condea (Figures 2b,e) are very fine and submicron. Boehmite primary crystallites (Figure 2c) are on the order of 3 μm, although the agglomerates are larger (approximately 15 μm). This powder was prepared by hydrothermal synthesis and is highly crystalline in nature. The median particle sizes of the bayerite, boehmite, and pseudoboehmite powders, as listed in Table 1, clearly refer to their agglomerates.

Figure 3 shows the results of simultaneous thermal analysis. Gibbsite and bayerite lose their water of crystallization at around 300 °C. Boehmite does so only at around 500 °C, in agreement with the literature.[42−44] Pseudoboehmite dehydrates in between the first two, in that it loses its crystal water gradually, over a broad temperature range up to 500 °C. This is indicative of a highly disordered structure. BET data of alumina raw materials calcined in air over a temperature range of 400−1400 °C are listed in Table 3 in parentheses.

6.2 Structural Evolution. Figure 4 shows the evolution of potassium β-alumina type phases with temperature for K_2O:$5Al_2O_3$ powder mixtures prepared from different alumina precursors. With gibbsite, χ-alumina predominates at temperatures above 400 °C. β-Alumina appears above 700 °C, but with the exact type (β- or β″-alumina) remaining unclear. At 1300 °C, a clear K−β/β″-alumina intergrowth is formed on the basis of gibbsite as evidenced by the occurrence of both sharp and diffuse diffraction peaks.[29] Bayerite and likewise boehmite and pseudoboehmite forms well-developed phase-pure K−β″-alumina at 1300 °C. In the case of bayerite, η-alumina predominates above 400 °C, and this phase changes gradually into a β-alumina type phase above 700 °C (exact type unclear). In the case of boehmite, crystalline K−β″-alumina appears abruptly at 1300 °C. This abrupt appearance of β″-alumina may be due to the highly crystalline nature and relative coarseness of the boehmite powder (Figure 2c), and to its high thermal stability (Figure 3). Below 900 °C, the

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Table 3. BET Specific Surface Area of Calcined $K_2O{:}5Al_2O_3$ Powder Mixtures[a] Prepared from Different Alumina Precursors and as a Function of Calcination Temperature (m^2/g)

	low-temp range (1 h)					high-temp range (2 h)			
alumina precursor	400 °C	600 °C	800 °C	1000 °C	1200 °C	1400 °C	1500 °C	1600 °C	1700 °C
gibbsite	117 (237)	66 (148)	41 (96)	32 (34)	19 (17)	14 (4)	9	7	4
bayerite	186 (341)	91 (166)	49 (95)	32 (67)	21 (8)	20 (3)	11	8	4
boehmite	9 (3)	11 (66)	9 (19)	9 (11)	9 (3)	6 (1)	7	4	3
pseudoboehmite	112 (212)	96 (174)	80 (159)	59 (101)	18 (6)	11 (2)	6	3	1
Condea corundum	(9)	(7)	(7)	(8)	(5)	5 (3)	7	4	3
Aldrich corundum						1	2	1	<1

[a] Values in parentheses are just for the calcined alumina precursors, i.e., without the added potassium component.

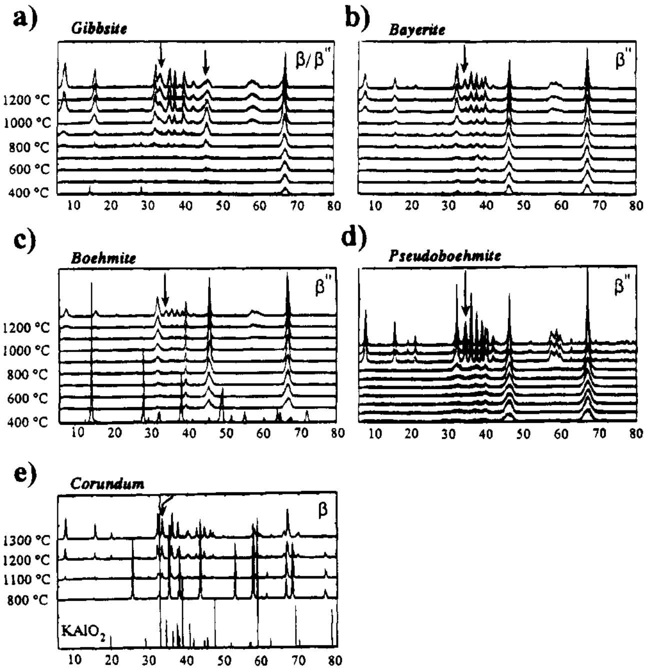

Figure 4. Temperature-dependent phase formation of the transition and β-alumina type phases in the potassium-doped $K_2O{:}5Al_2O_3$ composition, determined by the type of alumina-precursor: (a) gibbsite (b) bayerite, (c) boehmite, (d) pseudoboehmite, and (e) fine-grained corundum. Calcination time: 1 h, degrees 2θ scale, intensity in arbitrary units. $KAlO_2$-standard published previously by Brumakin et al.[47].

X-ray diffraction pattern of the β-alumina mixture based on boehmite (Figure 4c) is still very vague and contains only major peaks of γ-alumina next to minor peaks of a β-alumina type phase (exact type unclear). Above 900 °C, the intensity of the peaks increases, and pure β''-alumina results at 1300 °C. This material is fully crystallized at 1400 °C. With pseudoboehmite a similar abrupt formation of K$-\beta''$-alumina as with boehmite occurs, at temperatures that are between 1000 and 1100 °C. These temperatures are 200 °C lower than in the boehmite case. However, in the case of pseudoboehmite, minor β-alumina diffraction peaks are no longer observed below 1000 °C, and instead only broad peaks of γ-alumina are present. K$-\beta''$-alumina on the basis of pseudoboehmite appears directly at 1100 °C from a γ-alumina structure and is immediately well-crystallized. α-Alumina is stable up to 800 °C, and at that temperature forms β-alumina along with $KAlO_2$. The formation of $KAlO_2$, apparently unique to the α-alumina case, can be understood by considering that unlike the transition aluminas, the α-alumina is dense and potassium ions must progressively diffuse into this dense material. Reaction zones then appear, depending on the local potassium ion concentration. $KAlO_2$ will form on the surface of the α-alumina grains, where the potassium ion concentration is highest, followed by β-alumina more toward the interior of the grains. An unreacted core of α-alumina exists at the lower temperatures, and the transformation of this core region into β-alumina competes at higher temperatures with the interface reaction between $KAlO_2$ and β-alumina to β''-alumina. Above 800 °C, in the case of potassium-doped corundum, $KAlO_2$ is observed to react with β-alumina to form K$-\beta''$-alumina but only in trace amounts.

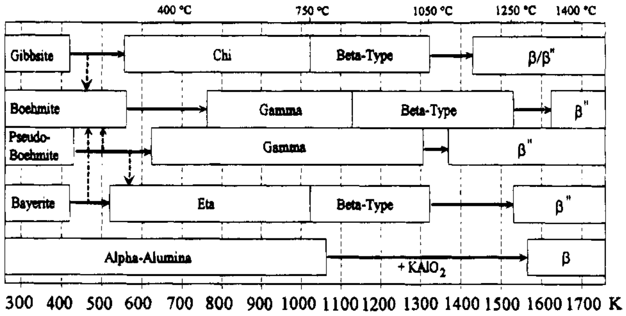

Figure 5. Proposed dehydroxylation sequence of potassium-doped aluminum hydroxides and oxyhydroxides based on the results shown in Figure 4. Arrows indicate ranges of transition. Corundum, α-alumina, is the only raw material that does not contain water.

The results of Figure 4 are redrawn in the Alcoa-like presentation of Figure 5. Below approximately 750 °C, Figure 5 is identical to the dehydroxylation sequence proposed by Alcoa laboratories for pure aluminum hydroxides and oxyhydroxides in air.[43,44] The presence of the potassium component tends to stabilize the respective transition aluminas, and is responsible for the formation of β-alumina type phases on the place of α-alumina. Only at sufficiently high temperatures are the β-alumina type phases crystallized well enough so that they can be properly identified.

The explanation to the different reactivity of the various alumina raw materials toward either β- or β''-alumina, as witnessed by Figure 5, can be traced to the pioneering work of Poulieff et al.[31] These authors commented on the similarity between the oxygen ion packing in β''-alumina and γ-alumina, yet were unable to prepare phase-pure Na-β''-alumina. The first to recognize the importance of the oxygen ion stacking of the alumina precursors to the reaction kinetics of β-alumina formation and then to systematically investigate this effect for the case of Na-β''-alumina were Van Zyl et al.[39,40] These authors were able to prepare 100% phase-pure Na$-\beta''$-alumina on the basis of precursors with cubic-close-packed oxygen ion sublattices.

The crystal structure of each alumina raw material and transition alumina is invariably important to the structural evolution of K–β-alumina. The choice of the alumina raw material is important only insofar as it determines the crystal structure of the transition aluminas that form upon dehydroxylation.

All aluminum hydroxides and oxyhydroxides and also corundum place aluminum ions in octahedral interstices. However, they can be distinguished on the basis of their oxygen ion stacking sequence. Gibbsite consists of $[Al_2(OH)_6]_n$ double layers with oxygen ions stacked in the sequence –AB–BA–AB–, which is cubic-close-packed (prefix γ). The oxygen stacking sequence of bayerite is –AB–AB–AB–, which is purely hexagonal (prefix α). Boehmite consists of $[2AlOOH]_n$ double layers, not unlike gibbsite, with the oxygen ions stacked in the sequence–ABC–ABC–, which is cubic-close-packed (prefix γ). Pseudoboehmite is a structurally disordered boehmite containing more water than its crystalline counterpart. Corundum, finally, has its oxygen ions stacked in an hexagonal sequence which is identical to that of bayerite.

In the undoped state, heating aluminum hydroxides and oxyhydroxides results in the formation of α-alumina (corundum) via a number of transition aluminas. These transition aluminas have been designated χ-, κ-, η-, γ-, δ-, and θ-alumina arbitrarily. The crystal structures of the transition aluminas η-, γ-, δ-, and θ-alumina all consist of a cubic-close-packed oxygen ion sublattice. Any structural changes between these phases therefore involve only the rearrangement of cations, while the oxygen ion array is constant, i.e., these transformations are topotactic (or displacive). The driving force behind the γ- to δ- to θ-alumina transformation is reduction of surface area and tetrahedral ordering.[45] The crystal structure of χ-alumina is not well-known. However, the χ- to κ-alumina phase transformation is reconstructive, and κ-alumina consists of an oxgen sublattice of –ABAC–CABA– stacking sequence, which is both cubic *and* hexagonal in nature. The final transformation to α-alumina of all transition aluminas is also reconstructive. In general, reconstructive phase transformations are slow and occur by nucleation and growth.

In the case of the potassium-doped alumina raw materials, the dehydroxylation sequence presented in Figure 5 is valid. Boehmite, pseudoboehmite, and bayerite form transition aluminas with exclusively cubic-close-packed oxygen ion arrays. These give rise to the formation of β″-alumina. Gibbsite leads to a β/β″-alumina intergrowth because of the reconstructive phase transformation of the χ-alumina to κ-alumina and on to β-alumina. κ-Alumina contains both cubic *and* hexagonally close-packed oxygen ions. The part of the oxygen ions that is cubic-close-packed is responsible for the formation of β″-alumina, but the part that is hexagonally close-packed forms β-alumina. The result is a β/β″-alumina intergrowth. Corundum finally, contains oxygen ions solely in hexagonal stacking. The necessary reconstructive transformation of that oxygen lattice to a cubic-close-packed oxygen sublattice is responsible for the formation of mainly β-alumina.

The failure of conventional synthesis and of the first attempts to utilize γ-alumina for the preparation of phase-pure Na-β″-alumina can now be understood. Both are a classical case of "wrong precursor in the wrong place". Conventional synthesis focused on α-alumina, mainly because of its good sintering characteristics. However, it is a poor precursor with which to investigate the optimization of β″-alumina phase formation. In the case of the earliest attempts to use "γ-alumina",[31] it must have been a transition alumina based on gibbsite rather than on boehmite.

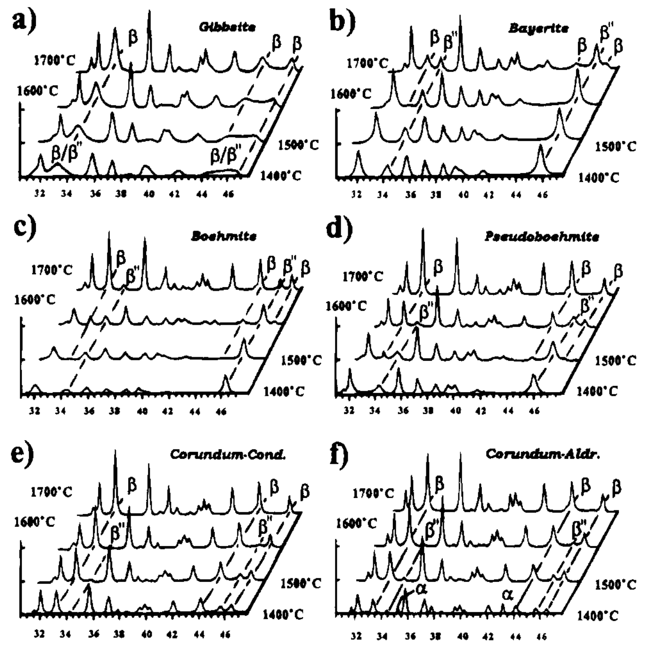

Figure 6. Phase evolution of K–β- and K–β″-alumina type phases in the K_2O:$5Al_2O_3$ composition, dependent on the type of alumina-precursor: (a) gibbsite, (b) bayerite, (c) boehmite, (d) pseudoboehmite, (e) fine-grained corundum, and (f) coarse-grained corundum. Calcination time: 2 h; degrees 2θ scale, intensity in arbitrary units.

6.3. Thermal Behavior. Figure 6 shows the phase evolution of K–β- and K–β″-alumina, between 1400 and 1700 °C in powders of K_2O:$5Al_2O_3$ starting composition prepared from various alumina raw materials. The results of quantitative X-ray diffraction analysis are listed in Table 2. It is clear that phase-pure K–β-alumina develops at 1700 °C from the gibbsite, corundum, and pseudoboehmite precursors. Also, it is only the pseudoboehmite precursor that leads to phase-pure K–β-alumina at 1700 °C, notwithstanding its behavior at 1400 °C (where phase-pure β″-alumina was formed). The trend in the K–β-alumina formation rate for the various alumina precursors, starting from fully crystallized K–β″-alumina at 1400 °C, is as follows: pseudoboehmite > boehmite > bayerite. This trend, however, is *not* mirrored in the specific surface area data belonging to these powders (see Table 3), and thus cannot be expected to be caused by alkali vaporization. The trend followed by the specific surface area data of these powders is given by bayerite > boehmite > pseudoboehmite. This is opposite to the observed order. Thus, the trend observed in the different rates of K–β-alumina formation for the various alumina precursors as witnessed in Figure 6 and recorded in Table 2 has *no* underlying physical meaning. It therefore must be a structural one. This section places emphasis on the structural causes to observed differences in thermal behavior between potassium β-aluminas prepared from different precursors. In particular the behavior of

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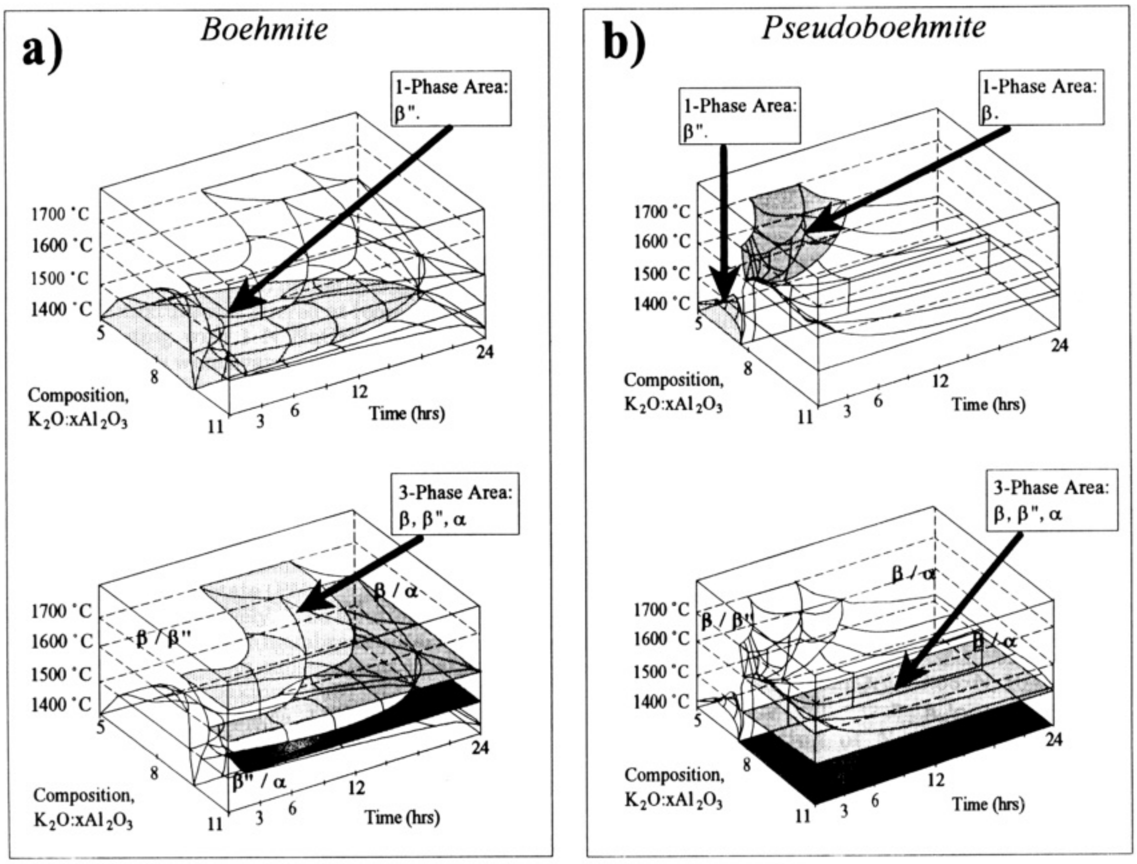

Figure 7. Phase relations in the $K_2O-Al_2O_3$ quasi-binary. Schematical representation of the thermal stability of single-phased binary K−β- and K−β''-alumina as a function of calcination time and temperature, dependent on the type of alumina-precursor: (a) boehmite and (b) pseudoboehmite. Top-row diagrams place emphasis on the K−β- and K−β''-alumina single-phased regions, while the lower-row diagrams highlight the three-phase regions of K−β-/K−β''-/α-alumina, respectively . Two-phase regions are indicated, side faces at 10 min calcination time were checked by X-ray fluorescence.[48]

K−β''-alumina prepared from pseudoboehmite will be compared to the behavior of K−β''-alumina prepared from crystalline boehmite, at temperatures higher than 1400 °C.

The results of calcining $K_2O{:}5Al_2O_3$, $K_2O{:}8Al_2O_3$, and $K_2O{:}11Al_2O_3$ powder mixtures based on boehmite and pseudoboehmite alumina precursors are plotted in Figures 7 and 8. These powders were calcined between 1400 and 1700 °C for time periods up to 24 h. Both figures are based on quantitative X-ray diffraction analysis, the results of which are listed in Table 4. Figure 7 shows that there *is* a tremendous difference in the thermal behavior between the K−β-aluminas prepared from either boehmite or pseudoboehmite.

Figure 7 shows the stability ranges of binary K−β- and K−β''-alumina based on boehmite (Figure 7a) and pseudoboehmite (Figure 7b) alumina precursors as a function of composition, temperature, and calcination time. The two diagrams vary widely. K−β''-alumina forms both in the boehmite and in the pseudoboehmite case. However, it is much more stable in the first. This can be seen by the effect of holding a specimen at a constant temperature, for example, at 1400 °C. K−β''-alumina founded on boehmite is not affected by holding at 1400 °C for times up to 24 h. This is in sharp contrast to the K−β''-alumina phase based on pseudoboehmite, which forms K−β-alumina relatively fast, even at 1400 °C. Phase-pure K−β-alumina is *not* found with boehmite and is present only in the pseudoboehmite case. The character of the multiple-phase regions is in each case similar. The single-phase region of K−β''-alumina founded on boehmite is flanked by β/β'' and β''/α two-phase regions on the alkali-rich and alkali-poor side, respectively. A $\beta/\beta''/\alpha$-alumina three-phase region connects both these two-phase regions at higher temperatures and toward lower alkali contents. The three-phase region changes into a two-phase region of β- and α-alumina, when due to alkali vaporization β-alumina transforms to α−, and β''-alumina to both β- and α-. In the case of pseudoboehmite, the three-phase region of $\beta/\beta''/\alpha$-alumina is already present at lower temperatures (<1600 °C), and phase-pure K−β-alumina results at 1700 °C. The two-phase region of β''/α-alumina on the alkali-poor side in the case of pseudoboehmite also does not exist.

Figure 8 takes some of the data presented in Figure 7 and Table 4. At first, Figure 8a compares the behavior of the boehmite based $K_2O{:}5Al_2O_3$ powder mixture with the $K_2O{:}8Al_2O_3$ powder mixture prepared from the same precursor. The exceptionally stable 1:8 boehmite based K−β''-alumina powder mixture (see also Figure 7), takes up to 4 h longer at 1600 °C to reach the same β-alumina phase content as the 1:5 boehmite powder at that temperature. The drop at 1700 °C for both powders after 12 h of calcining is due to α-alumina forming. An explanation for the different behavior of the two powder mixtures may be that two different stabilization mechanisms are operational in the two respective K−β''-aluminas, affecting their stability. Figure 8b compares the 1:5 binary K−β''-alumina powder mixture based on boehmite with that based on pseudoboehmite. The 1:5 pseudoboehmite-based mixture is clearly less stable

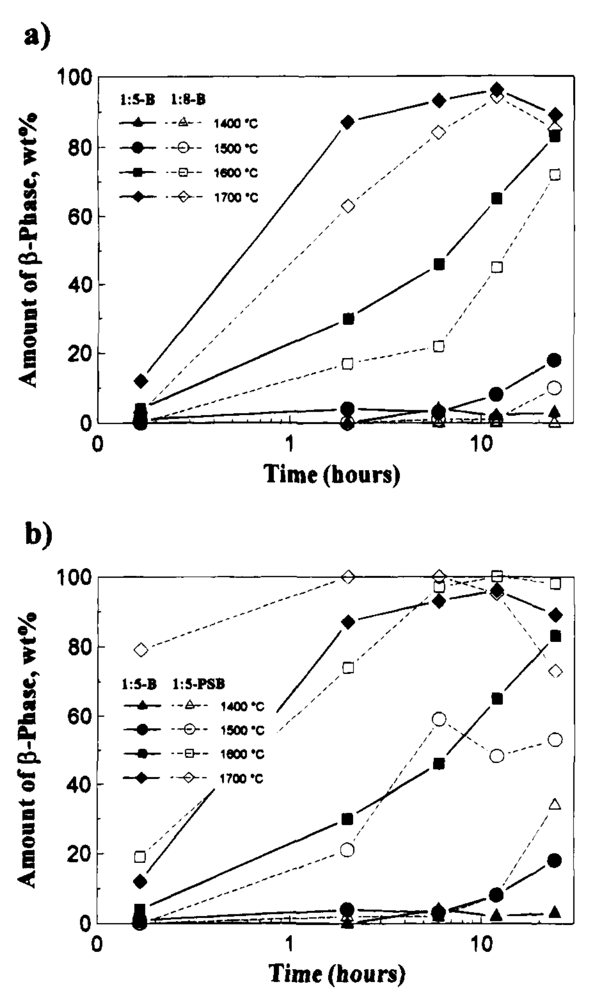

Figure 8. Kinetic evaluation of K–β-alumina phase formation in the $K_2O–Al_2O_3$ quasi-binary on the basis of boehmite and pseudoboehmite alumina precursors and as a function of (a) composition and (b) the type of alumina precursor.

than the 1:5 boehmite-based mixture. It seems to run 100 °C "behind" the pseudoboehmite mixture over the temperature range investigated. This may be an indication to differences in alkali vaporization. However, the respective boehmite and pseudoboehmite based samples shown in Figure 8b are identical in chemical composition to within 1 mol % K_2O, as found by quantitative X-ray fluorescence. These data are not presented here but are part of the second paper in this series on the direct synthesis of binary K–β- and K–β″-alumina. The main theme of part 2 is the experimental assessment of the $K_2O–Al_2O_3$ quasi-binary phase diagram.[48]

Figure 7 and Table 4 essentially prove that precursor chemistry still influences the thermal behavior of binary K–β″-alumina above 1400 °C. The cause for this effect must lie in the original crystal structure of the respective starting compounds. At temperatures where in the case of α-alumina the crystallization of α-alumina itself would have already eradicated any reference to the original raw materials, these precursor-related effects are still noteworthy in the case of β-alumina. Pseudoboehmite is a disordered structure when compared to boehmite. This can be recognized in the STA-data presented in Figure 3, where boehmite loses all its water of crystallization at one point and at a relatively high temperature but where pseudoboehmite loses its water of crystallization gradually over a broad temperature range. The first is indicative of a highly ordered structure, whereas the latter is characteristic of a highly disordered structure. The transition aluminas that are prepared from pseudoboehmite inherit this disordered structure, and as a result so do the β-aluminas prepared from them. Even though pseudoboehmite forms K–β″-alumina at 1400 °C, following the path of boehmite, the structure is inherently undermined by defects, and these lead to the subsequent (fast) transformation of the K–β″-alumina to K–β-alumina at higher temperatures. Structural defects undermine the stability of the K–β″-alumina phase.

6.4. Formation of Dense K–β-Alumina Artifacts. The morphology of the various K–β- and K–β″-alumina powders prepared in this work are shown in Figure 9. Figure 9a,b shows SEM micrographs of K–β-alumina powders based on pseudoboehmite and coarse-grained corundum. Both were prepared at 1700 °C. The anisotropic nature of the β-alumina grains is clearly visible. Figure 9c,d shows K–β″-alumina powder based on pseudoboehmite and boehmite, prepared at 1400 and 1600 °C, respectively. It is evident that an extensive amount of coarsening occurs in the case of pseudoboehmite (compare Figure 9a to Figure 9c, and see also Table 3). In contrast, the K–β″-alumina based on boehmite remains relatively fine and equiaxed. The first case is disastrous to sintering.

The use of high heating rates during the sintering of conventionally prepared sodium β-aluminas in order to achieve high densities, and the postsinter anneals to achieve high β″-alumina phase contents can now also be understood. In Figures 4 and 5 it was shown that with α-alumina, $KAlO_2$ forms next to β-alumina. When the $KAlO_2$ is *not* given the chance to react with β-alumina (i.e., using high heating rates), it can be retained at high temperatures to serve as the liquid phase in the densification process ($KAlO_2$–β-alumina eutectic at around 1640 °C[49]). Postsinter annealing is then required to fully convert $KAlO_2$ plus β-alumina, to β″-alumina. This works well only with α-alumina.

VII. Conclusions

This work proves that phase-pure K–β- and K–β″-alumina can be prepared directly in the K_2O-Al_2O_3 quasi binary. This fact was disputed in the literature. It also shows that precursor-related effects play a significant role in the formation *and* behavior of potassium β-alumina type phases.

Binary K–β″-alumina was prepared by direct synthesis due to the high homogeneity achieved by attrition milling potassium hydroxide with a suited aluminum hydroxide (bayerite) or oxyhydroxide (boehmite) precursor. A pronounced effect of precursor chemistry on the formation of K–β- and K–β″-alumina was established. Two groups of alumina precursors were identified based on their ability to form K–β″-alumina directly and at low temperatures. The first group comprises boehmite, bayerite, and pseudoboehmite. The latter group comprises α-alumina and gibbsite. Transition aluminas with a cubic-close-packed oxygen ion sublattice directly lead to the formation of β″-alumina. Precursor alumi-

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[48] De Kroon, A. P.; Schäfer, G. W.; Aldinger, F. Submitted to *Chem. Mater.*

[49] Schäfer, G. W., unpublished results.

Table 4. Phase Composition (wt %) of Boehmite and Pseudoboehmite-Based 1:5, 1:8, and 1:11 $K_2O{:}Al_2O_3$ Powder Mixtures, as a Function of Calcination Time (10 min−24 h) and Temperature (1400−1700 °C), As Measured by XRD

composition $K_2O{:}xAl_2O_3$	calcination time (h)	1400 °C			1500 °C			1600 °C			1700 °C		
		β	β''	α	β	β''	α	β	β''	α	β	β''	α
Boehmite													
1:5	0.16		100			100		4	96		12	88	
	2[a]		100		4	96		30	70		87	13	
	6	4	96		3	97		46	54		93	7	
	12	2	98		8	92		65	35		96	3	1
	24	3	97		18	82		83	17		89		11
1:8	0.16		100			100			100		3	97	
	2		100			100		17	83		63	37	
	6		100		1	99		22	78		84	16	
	12		100		1	99		45	55		94	5	1
	24		100		10	90		72	24	4	85		15
1:11	0.16		68	32		63	37	4	66	30	22	53	25
	2		70	30	2	63	35	34	40	26	74	7	19
	6		63	37	9	57	34	43	26	31	86		14
	12		62	38	17	52	31	55	13	32	79		21
	24		57	43	27	40	33	61	3	36	70		30
Pseudoboehmite													
1:5	0.16		100			100		19	81		79	21	
	2[a]	2	98		21	79		74	26		100		
	6	2	98		59	41		97	3		100		
	12	8	92		48	52		100			95		5
	24	34	66		53	43	4	98		2	73		27
1:8	0.16	6	73	21	19	62	19	63	28	9	100		
	2	6	72	22	36	28	36	100			100		
	6	16	74	10	64	23	13	99		1	89		11
	12	27	63	10	56	36	8	98		2	68		32
	24	40	48	12	54	39	7	96		4	14		86
1:11	0.16	20	25	55	25	20	55	47	15	38	70		30
	2	9	9	82	25	3	72	76		24	79		21
	6	25	7	68	41	11	48	79		21	75		25
	12	31	8	61	46	3	51	77		23	60		40
	24	27	9	64	54	20	26	69		31	41		59

[a] See also Table 2.

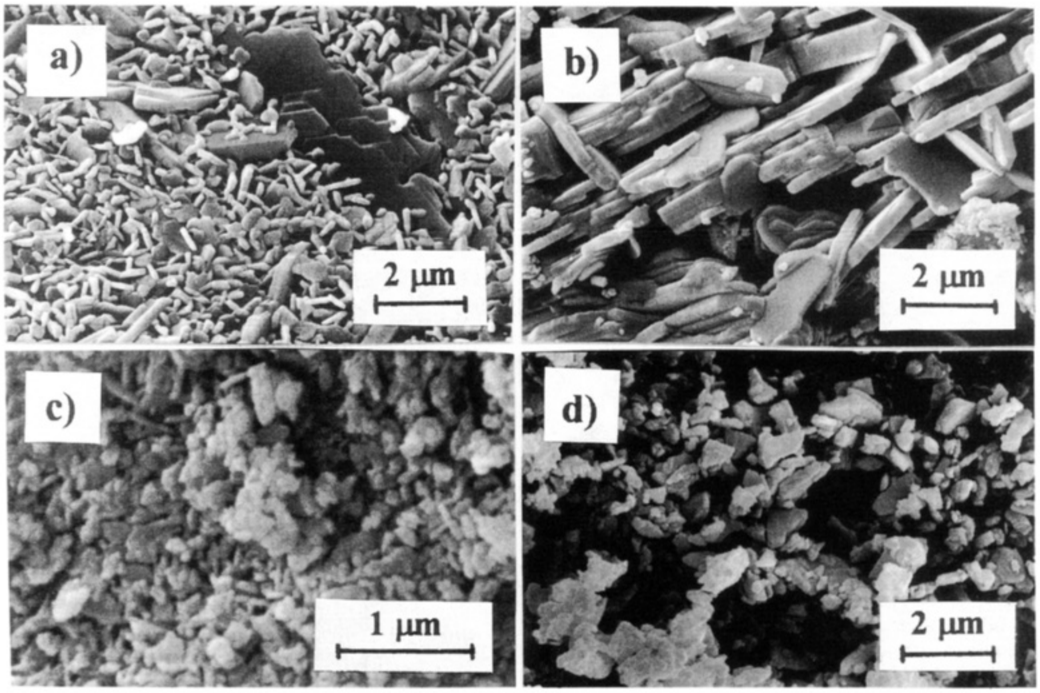

Figure 9. SEM-micrographs showing the morphological characteristics of K−β-alumina (top row) and K−β''-alumina (lower row) powders, prepared from the different alumina precursors used in this work: (a) pseudoboehmite, −1700 °C; (b) coarse-grained corundum, −1700 °C; (c) pseudoboehmite, 1400 °C; and (d) boehmite, 1600 °C.

nas (such as corundum) or transition aluminas (such as those based on gibbsite) which have a hexagonally close-packed oxygen ion array lead to the formation of β-alumina. The different behavior is caused by the necessary reconstructive phase transformation the precursors with the hexagonally close-packed oxygen ion array are forced to pass through in order to arrive at the cubic-close-packed oxygen ion array of the β-aluminas. These transformations are generally slow and introduce defects.

Alkali vaporization at higher temperatures favors the formation of β-alumina irrespective of the starting material. Also, corundum tends to form. K–β''-alumina prepared with pseudoboehmite is exceptionally unstable compared to the identical phase prepared with boehmite. Structural defects inherited from the pseudoboehmite are thought to destabilize the crystallized K–β''-alumina and at higher temperatures lead to its subsequent transformation to K–β-alumina. This is an effect similar to forcing a precursor material through a reconstructive phase transformation: both result in the formation of defects. As found by using both the boehmite and pseudoboehmite precursors, the stability range of K–β''-alumina is larger than that of K–β-alumina. This may indicate a difference in thermodynamic stability.

Although either boehmite or bayerite should be preferred over α-alumina in the fabrication of dense phase-pure K–β''-alumina artifacts, because of structural considerations microstructural considerations might make it necessary to use α-alumina in order to have liquid phase sintering. $KAlO_2$ forms on the surface of α-alumina grains when these react with potassium oxide, and the $KAlO_2$–β-alumina eutectic is responsible for the formation of a liquid phase. The validity of this approach has been proven in the literature and thus indirectly supports the work presented here.

VIII. Future Work

TEM-experiments are planned on dense K–β- and K–β''-alumina ceramics to definitely establish the effect of alumina precursors on the final crystal structure. Calorimetric measurements are necessary to investigate the thermodynamic stability of both K–β- and K–β''-alumina and to devise a phase diagram. So-called "stabilizers" or "dopants" can be used to alter the thermal stability of K–β-aluminas.

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