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Preparation of Ca-β''-Al_2O_3 from Alumina Gel

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Abstract

Using aluminium nitrate solution containing calcium and magnesium cations, and saturated ammonium oxalate solution in concentrated ammonium hydroxide as precipitating agent, alumina gel was prepared. The gel was calcined at different heating rates up to 400°C and then at different temperatures and soaking times. The calcination products successively appeared as aluminium oxides, calcium aluminate and calcium-beta''-alumina. The obtained calcium-beta''-alumina crystallites were plate-shaped and the direction perpendicular to the crystallite surface was parallel to the Z-axis. It was found that the kinetics of calcium-beta''-alumina synthesis depends on the presence of a molten salt during the gel thermal treatment. The mechanism of calcium-beta''-alumina formation is proposed as a reaction between formerly produced calcium aluminate and aluminium oxide of the alpha form. Sintered bodies prepared from the calcium-beta''-alumina powder were characterized by good ionic conductivity.

1 Introduction

For many years, compositions containing β- and β''-alumina have aroused interest as ionic conductors.[1,2] They are potential materials for batteries,[3] sensors,[4] electrochemical probes[5] and for investigation of thermodynamic data in oxide systems.[6] There are several preparation routes that allow β- and β''-alumina powders, sintered bodies and monocrystals to be obtained. In the case of β-aluminas containing monovalent cations, direct high-temperature synthesis, often followed by sintering of the resulting powder, is the simplest way leading to the polycrystalline material. The precursors usually applied in such a case are sodium and lithium carbonate, aluminium oxides of the α- or γ-form[7,8] as well as bayerite, gibbsite or boehmite.[9] The zetha-process is a type of direct synthesis in which compositions of formula $M_2O{\cdot}5Al_2O_3$ (where M = Na and/or Li) are used as a precursor.[10] Thermal decomposition of the appropriate nitrate mixtures is also a useful process.[11] It has recently been found that the sol–gel technique gives good results in the preparation of β-alumina fine powders,[12–14] thin films and coatings.[15]

To prepare β''-Al_2O_3 containing ions of a higher valence state, the sodium ions in Na-β''-Al_2O_3 can be exchanged for di- or trivalent ions.[16] It is also possible to use the direct, high-temperature reaction of aluminium oxide, calcium and magnesium carbonates.[17,18]

It has been found that β''-aluminas containing divalent cations transform at elevated temperatures to the magnetoplumbite structure, which shows no ionic conductivity.[19] This has been found from ionic conductivity measurements in relation to the thermal history of samples[20] and X-ray diffraction studies.[21] The mechanism of the β''-Al_2O_3 to magnetoplumbite structure transformation is not explained as well as the conditions under which this transformation takes place. According to Schaefer and Weppner[22] it occurs at a temperature of ~1400°C during 20 h soaking, whereas Kirchnerova *et al.*[21] state that it can be observed at temperatures >1000°C. These facts suggest that only low-temperature synthesis of the divalent β''-aluminas can be applied. The above-mentioned ion exchange technique cannot secure the proper microstructure of the material, since changes in the microstructure and grain habit have been reported[22] to occur during the ion exchange process.

The aim of the present work was to study the preparation of magnesium-stabilized calcium-beta''-alumina ceramics using aluminium hydroxide gel as a precursor.

2 Experimental

1·2 M aluminium nitrate solution was used. The proper amounts of calcium and magnesium carbonates were added to this solution. The molar ratio of the components was 6 : 1 : 0.6, as recalculated to aluminium, calcium and magnesium oxides, respectively. Saturated ammonium oxalate solution in concentrated (~26 wt%) ammonium hydroxide was applied as the precipitating agent. It was found that the concentration of the saturated ammonium oxalate in the concentrated ammonium hydroxide is about 0·06 mol l^{-1}. Such a solution secures the quantitative precipitation of calcium oxalate. Also, the concentration of the hydroxide ions secures the quantitative precipitation of magnesium hydroxide. Chemical analysis corroborates these statements.

The Al–Ca–Mg nitrate solution was introduced slowly into the vigorously stirred precipitating solution; the amount added was a 10% excess, based on the stoichiometric proportion. The precipitated slurry was filtered off and the filtrate subjected to chemical analysis. The precipitated gel was dried at 70°C and calcined at temperatures up to 400°C. Two heating rates were applied: 1 and 10°C min^{-1}. During this operation the total decomposition of ammonium nitrate takes place. Powders prepared by the described procedure were examined by scanning electron microscopy (SEM) and by differential thermal analysis (DTA) using a heating rate of 6°C min^{-1} at temperatures >400°C. Changes of the powder morphology and phase composition during calcination at 1000–1350°C for a soaking time of at least 1 h were followed by transmission electron microscopy and X-ray diffraction.

On the basis of the results obtained, conditions for the preparation of a larger quantity of the pure β''-alumina phase powder were determined. The precipitated gel was filtered, dried, heated at the rate of 1°C min^{-1} up to 400°C and then calcined at 1350°C for 3 h. The obtained powder was ground for 12 h in dry acetone using zirconia grinding media and a rotary-vibratory mill. After milling the powder was dried at 70°C and isostatically pressed under 350 MPa, and then sintered at 1550°C for 2 h. The four-probe a.c. and impedance spectroscopy methods were used to determine the electrical properties of the sintered bodies. The impedance spectra were recorded using a system based on the Tesla 508 impedance meter, with platinum electrodes sputtered on two faces of the pellets. The preparation routes of the calcium-beta"-alumina powders and sintered bodies are presented in Fig. 1.

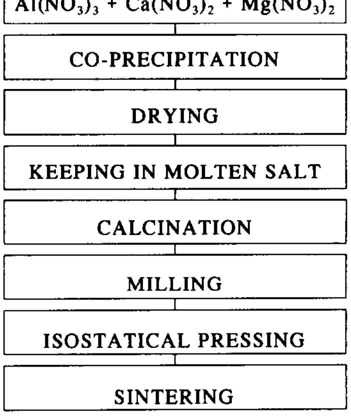

Fig. 1. Preparation routes.

3 Results and Discussion

The X-ray diffraction patterns of the dried gels show the peaks of ammonium nitrate and a wide increase of the background characteristic for amorphous material. No peaks of calcium oxalate and magnesium hydroxide were detected. It follows from the diffraction patterns (Fig. 2) that during heating the following calcination products successively appear: calcium aluminate $CaO{\cdot}2Al_2O_3$, γ-, θ- and α-aluminium oxides, and calcium-beta"-alumina.[23] The DTA curves show the ammonium nitrate decomposition and an endothermic peak at ~400°C that can be attributed to the decomposition of aluminium hydroxide. There are two probable reasons why calcium oxalate and magnesium hydroxide were not detected. The first is the small percentage by weight of these substances and the second is the formation of other compounds by the calcium and magnesium, not simply oxalate and hydroxide. This later phenomenon was often found in co-precipitated materials.

The rate of temperature increase up to 400°C strongly influenced the amount of Ca-β''-Al_2O_3 produced during further heating. Comparison of the diffraction patterns of powders heated at various rates up to 400°C and then calcined at 1300°C

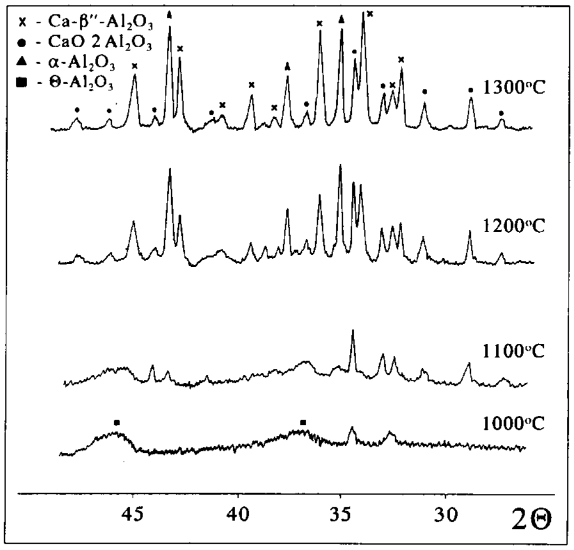

Fig. 2. Diffraction patterns of the powders calcined for 1 h at different temperatures.

for 1 h shows an increased amount of β''-phase in the material heated at a slower rate. Rapid heating leads to the violent reaction yelding brown nitrogen oxide vapour. During the slow temperature increase, this salt melts at ~180°C and then decomposes at ~230°C. It was found that the co-precipitated gel subjected to prolonged heating at 200°C under cover also results in a higher Ca-β''-Al_2O_3 phase content in the product calcined at 1300°C than observed without this operation.

SEM studies of the powder morphology, after total removal of ammonium nitrate, revealed that both powders (i.e. heated at different rates) are composed of ~0·2 μm grains linked to each other. However, in the powder heated at 1°C min^{-1} these grains are linked more closely than in the rapidly heated sample. This is illustrated by the microphotographs presented in Fig. 3. This difference in powder morphology and phase composition can most probably be attributed to the way in which the ammonium nitrate decomposition takes place. It cannot be excluded that products of the precipitation partially dissolve in the molten salt. This may lead to better homogeneity of calcium and magnesium in the alumina gel. Rapid heating does not allow the liquid phase long enough to act on the co-precipitate. It was also found that differences in the phase composition of the powders heated at different rates were only of kinetic character. This phenomenon is illustrated by the mutual intensity changes of the α- and β''-alumina reflections (Fig. 4).

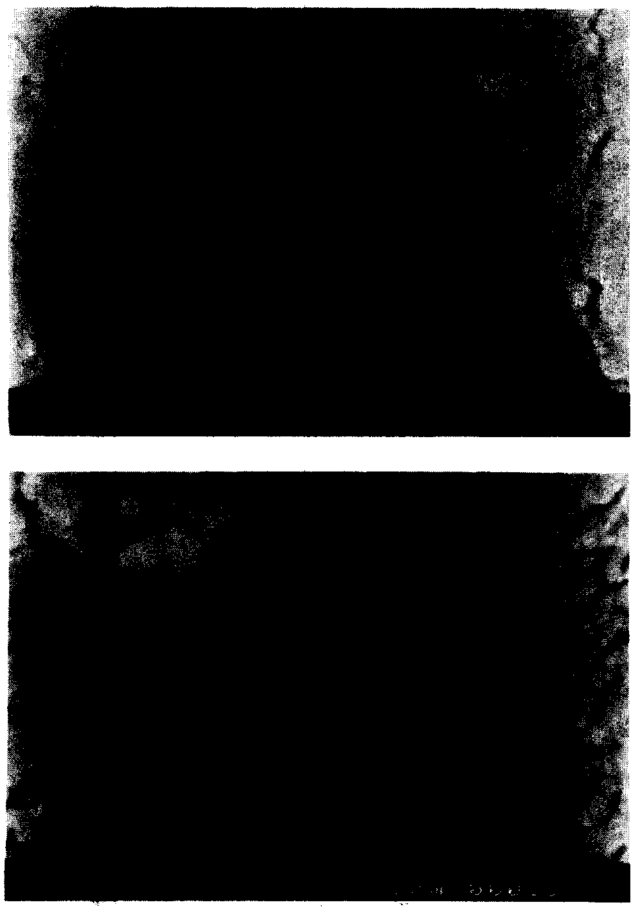

Fig. 3. SEM pictures of the powders heated to 400°C at different rates: (a) 1°C min^{-1} and (b) 10°C min^{-1}.

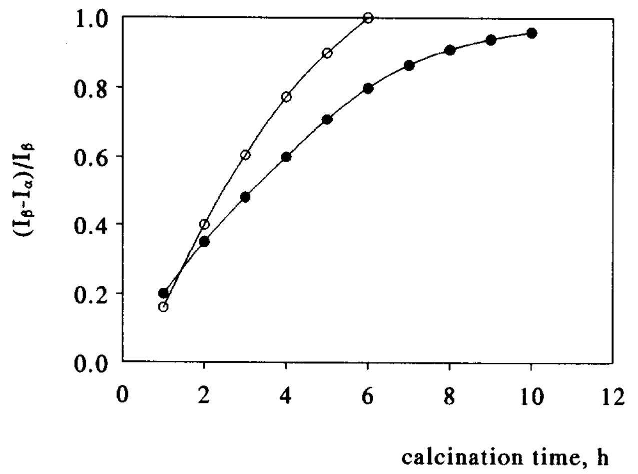

Fig. 4. Mutual intensity changes of the (1 0 4) reflection of α-Al_2O_3 and the (2 0 4) reflection of Ca-β''-Al_2O_3 measured in the powders heated to 400°C at different rates: 1°C min^{-1} (○) and 10°C min^{-1} (●).

The microphotographs in Fig. 5 illustrate the changes of powder morphology. Figure 5(a) shows the powder at the initial stage of the reaction obtained by calcining the gel at 1100°C for 1 h. By electron diffraction it was found that both the smaller (30 nm diameter) isometric particles and the larger (70 nm diameter) particles are composed of a mixture of calcium aluminate, $CaO{\cdot}2Al_2O_3$, and aluminium oxide of the θ-form. After calcination at 1200°C for 1 h plate-shaped crystallites appear, Fig. 5(b), their smaller dimensions being equal to those of the agglomerates of the isometric particles. It was established that the plate-like crystallites were calcium-beta''-alumina. In the powder calcined at 1300°C for 2 h (Fig 5(c)) plate-like crystallites, from 0·2 to 1·4 μm in size, were in the majority. In addition, using electron diffraction it was found that the direction perpendicular to the crystallite surface is parallel to the *Z*-axis of its crystallographic structure. An additional experiment showed that the α-alumina powder prepared by the same method, under the same conditions, was characterized by crystallites similar in size but isometric in shape.

In the case of the powder calcined isothermally at 1000°C, the reaction products that appear first are aluminium oxide of the γ-form and calcium aluminate, $CaO{\cdot}2Al_2O_3$. During the process calcium aluminate remains unchanged but the γ-alumina transforms into the θ- and α-forms. Calcination prolonged to 20 h results in a powder composed of a mixture of α-alumina and calcium aluminate. Traces of β''-alumina can be detected in samples calcined for up to 200 h. At calcination higher temperature changes of the phase contents are

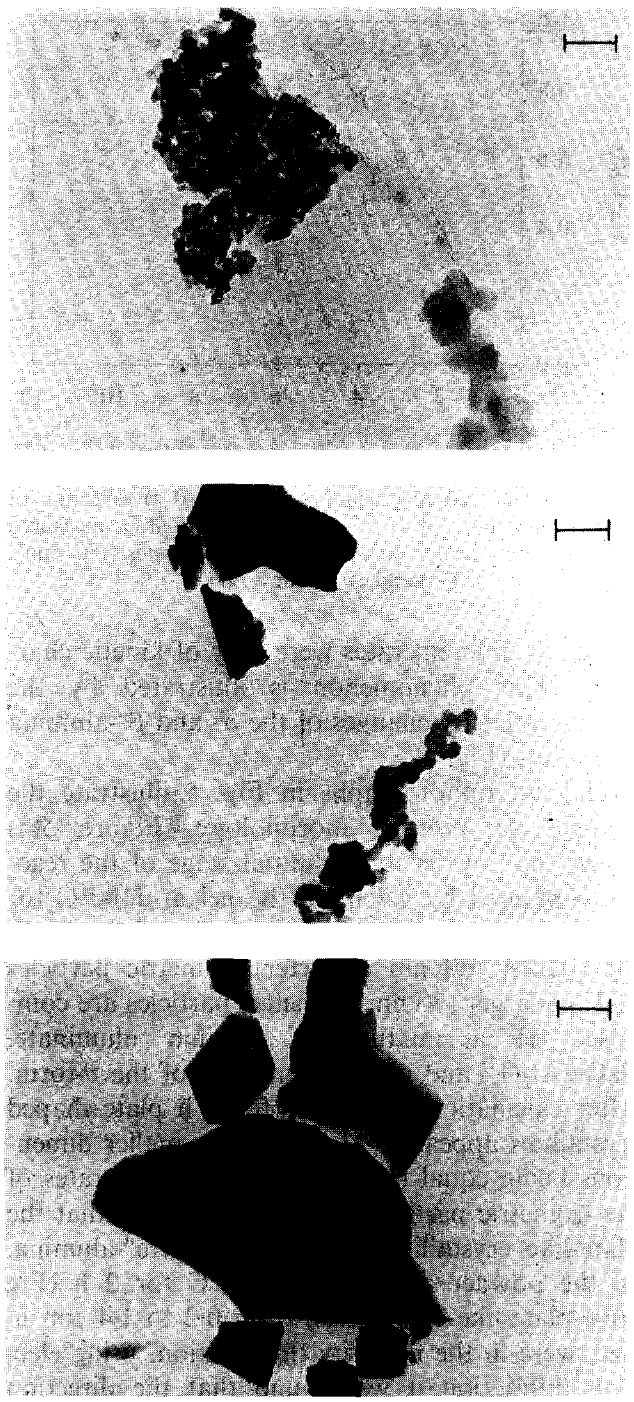

Fig. 5. Morphology of the powders calcined: (a) at 1100°C for 1 h, (b) at 1200°C for 1 h and (c) at 1300°C for 2 h. Scale bars: 150 nm (a and b) and 0·2 μm (c).

similar, although they occur much more rapidly. At 1200°C both α- and β''-alumina appear practically simultaneously.

Based on the facts as described above, the mechanism of calcium-β''-alumina formation can be proposed as follows. During heating the alumina hydroxide gel decomposes into a low-temperature form of aluminium oxide. A part of this oxide reacts with calcium oxalate to give calcium aluminate. Further heating transforms the aluminium oxide into its higher temperature forms. At the same time, individual crystallites of both aluminium oxide and calcium aluminate link together to form agglomerates. Then, α-alumina reacts with calcium aluminate and forms the β''-alumina phase. The reaction starts at the interphase boundary, the β''-alumina nucleus is then increased by the diffusion of calcium cations from calcium aluminate to the aluminium oxide. The preferential directions of the β''-alumina crystallite growth would be the ones along the plane perpendicular to the Z-axis. The irregular, not completely hexagonal, plate-like appearance of the Ca-β''-Al_2O_3 particles (see Fig. 5(c)) suggests their formation through coalescence from the smaller crystallites. The occurrence of the β''–alumina phase at 1000°C only when aluminium oxide is completely transformed into the α-form suggests that, for the synthesis of Ca-β''-Al_2O_3, the formation of the crystalline structure of aluminium oxide with a densely hexagonally packed anion sublattice is necessary.

The sintered bodies obtained from the β''-alumina powders were characterized by the microstructure presented in Fig. 6. It is evident that the grains of the material are not isometric, suggesting that the original crystallite shape has been preserved, at least to some extent.

The dependence of conductivity on temperature is presented in Fig. 7. The activation energy of the

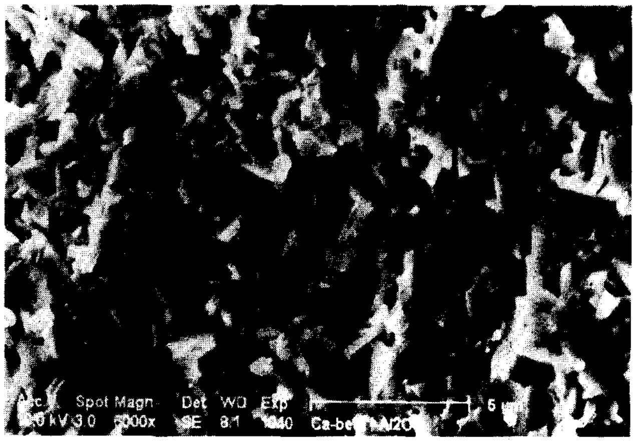

Fig. 6. Fracture surface of Ca-β''-Al_2O_3.

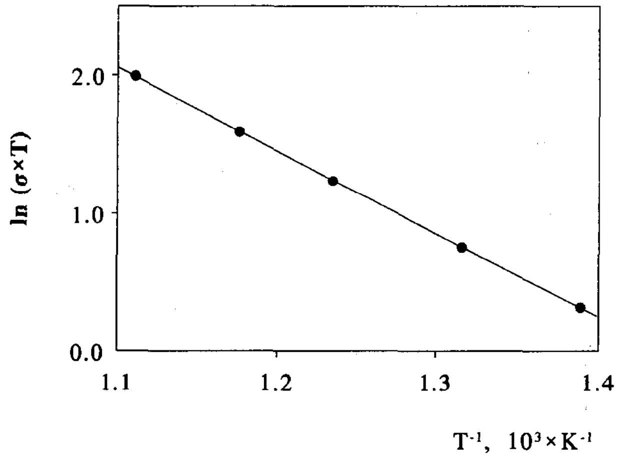

Fig. 7. Temperature dependence of Ca-β''-Al_2O_3 conductivity.

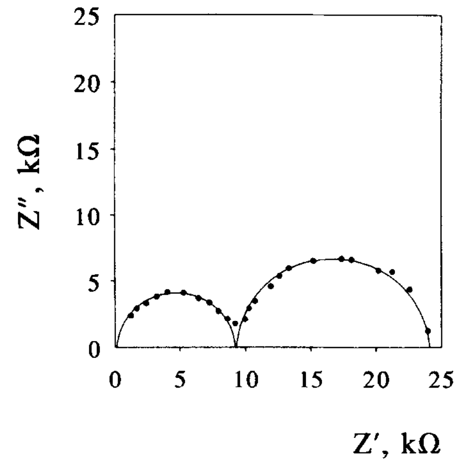

Fig. 8. Impedance spectra of Ca-β"-Al_2O_3 measured at 300°C.

conductivity process determined on the basis of this dependence is 50·1 kJ mol^{-1}. The impedance spectra recorded at 300°C are presented in Fig. 8 and yield the following values of conductivity: bulk conductivity $\sigma_b = 2{\cdot}40 \times 10^{-5}\ (\Omega\ cm)^{-1}$; grain boundary conductivity $\sigma_{gb} = 1{\cdot}50 \times 10^{-5}\ (\Omega\ cm)^{-1}$. Both the diagrams and the calculated values are characteristic of β"-alumina type conductors.[19,24]

4 Conclusions

The observations made during this study allow the following conclusions to be drawn.

(1) The application of alumina gel and the co-precipitation–calcination method allow a material with beta"-alumina structure to be obtained.
(2) The kinetics of the beta"-alumina synthesis depends on the presence of a molten salt during the precursor thermal treatment.
(3) The probable mechanism of calcium-beta"-alumina formation is the reaction between formerly produced calcium aluminate, $CaO{\cdot}2Al_2O_3$, and aluminium oxide of the alpha-form.
(4) Sintered bodies obtained from the powder prepared in this manner are characterized by good ionic conductivity.

The fact that material with the Ca-β"-Al_2O_3 structure and good ionic conductivity can be prepared via direct high-temperature synthesis leads to the conclusion that more work should be done to address the problem of metastability of that phase and its high-temperature degradation. To describe these phenomena in detail the following factors should be taken into consideration: the effect of the stabilizing cation type, the effect of contamination, the stabilizing effect of microstructure, and the kinetics of the degradation process.

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