

Production and characterization of polycrystalline (Na, Ca) β "-alumina

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Polycrystalline (Na, Ca) β "-aluminas with different calcium contents were produced from commercial Na β "-alumina (Ceramtec Inc.) by ion exchange in suitable mixtures of NaNO₃ and Ca(NO₃)₂. The extent of crack and pore formation could be reduced by increasing the calcium content gradually from one equilibrium concentration in the solid electrolyte to the next higher one. The equilibrium distribution curve was determined for the polycrystalline materials and compared with measurements on single crystals. Thermogravimetric measurements were made on fully-exchanged samples. The curves of the specific conductivity versus the extent of exchange suggest that the Na⁺ ion is the conducting species in a wide range of soda content. The transition to the predominant conduction by the Ca²⁺ ion occurs in a relatively narrow region at high extents of exchange.

1. Introduction

The sodium ions which are located in relatively open conduction planes in β - and β "-aluminas can be easily replaced by other ions [1-3]. It was shown [4,5] in the last decade that this exchange can also be carried out with numerous divalent and trivalent ions in single crystals of β "-alumina. While the ion exchange is principally feasible for the same ions in polycrystalline β "-alumina, it is met with an additional difficulty: corrosive attack leads to the formation of cracks and pores. Previous work on polycrystalline β "-aluminas is referenced and discussed with respect to the issue of pore and crack formation in ref. [6,7].

The properties of fully exchanged specimens of Ca β "-aluminas produced in different ways, were described in [6-10]. The present paper extends the previous work [6-10] by studying the whole composition range of isomorphs between Na β "-alumina and nearly fully exchanged Ca β "-alumina. In addition, a production technique was applied which yielded less corrosive attack for Sr [11] and Ba [12] β "-aluminas than the direct conversion in chloride melts, used previously in our ion exchange experiments [6,7].

2. Experimental

Rectangular pieces (1.0×0.5×0.1 cm) of polycrystalline Na β "-alumina (lithia-stabilized betalyte from Ceramtec Inc.), were dried for several hours at temperature of 170°C. Polycrystalline samples and some single crystals (magnesia stabilized, made by Prof. B. Dunn's group at UCLA) were exchanged in molten salt mixtures of NaNO₃ and Ca(NO₃)₂ at 570°C for five to ten hours. The equilibrium content of calcia in the solid electrolyte was increased stepwise. Salt layers adhering after the exchange were removed by washing of the specimens in diluted HNO₃ in an ultrasonic bath.

Thermogravimetric measurements were made with a nearly fully-exchanged sample to obtain information on the amount of residual salt in pores and deep cracks.

The extent of exchange was computed from the weight change. The respective results were compared with those obtained by instrumental neutron activation analyses (INAA). The conductivity of the cell graphite/(Na, Ca) β "-alumina/graphite was determined as a function of composition and temperature between room temperature and 500°C by a four-probe technique.

The new results are compared in section 4 with previous work [6-10].

3. Results

The micrograph in fig. 1a represents a specimen, exchanged in $\text{Ca}(\text{NO}_3)_2$ to 97%. Au films of 100 nm were sputtered onto the surface to improve the visibility. Fig. 1b shows a sample with a Ca content of about 20%. The pictures were taken at a magnification of 116 \times .

Fig. 2 contains the thermogravimetric results for a piece exchanged to 98%. The upper curves reflect the behavior during the first three runs with the same specimen. For comparison a curve was recorded for $\text{Ca}(\text{OH})_2$. Different scales had to be used for the abscissa.

Values of the extent of exchange, determined by weight change or INAA, are compared in fig. 3. In addition the data for the single crystals are given there.

The conductivity is plotted in fig. 4 as a function of the exchange for different temperatures. The conductivity measurements were only made up to 500°C. If the temperature range is extended to higher

temperatures, a hysteresis in the conductivity-temperature curve for the ascending and descending branch of the measurements is observed. The described effect is under study. An interpretation cannot be offered at present.

Arrhenius plots were constructed for samples with a given composition. The activation energy was computed for the temperature range in which the plots were linear. It is plotted versus the extent of exchange in fig. 5.

4. Discussion

The micrographs in fig. 1a and 1b reveal that corrosive attack is still occurring under the present conditions of ion exchange. This effect is more pronounced at high exchanges (compare the formation of the crack in the sample of fig. 1a). However, the attack is less severe than for the "zetalyte material", used previously [6,7].

The thermogravimetric curves in fig. 2 demon-

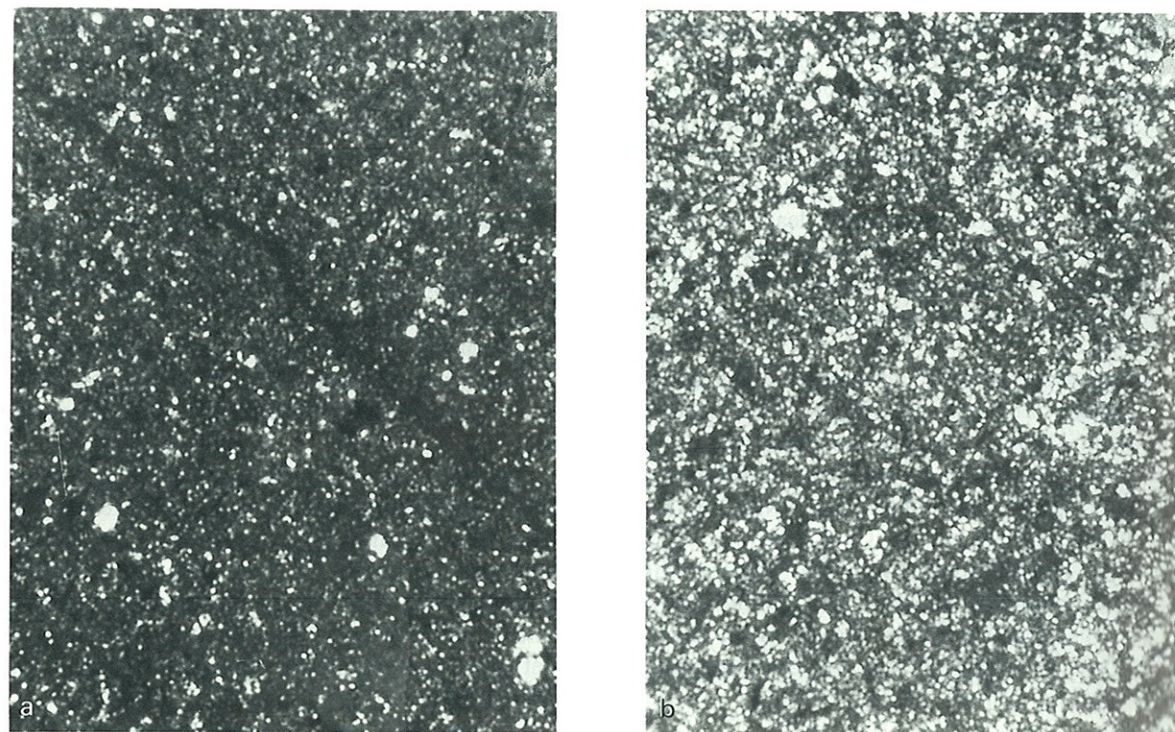


Fig. 1. Micrographs of nearly fully exchanged sample (a) and partially exchanged sample (b).

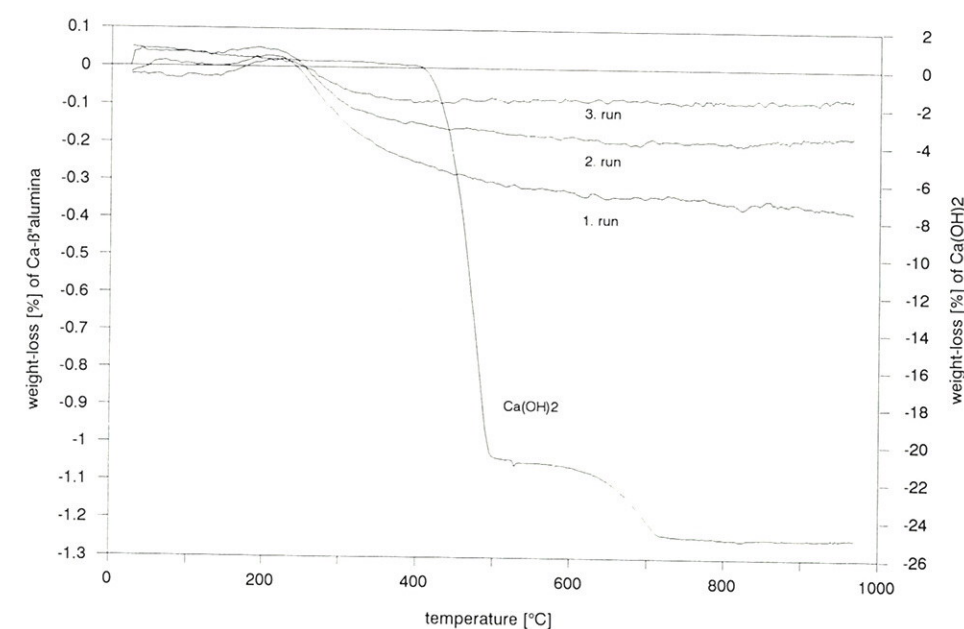


Fig. 2. Thermogravimetric results for nearly fully exchanged sample and for $\text{Ca}(\text{OH})_2$.

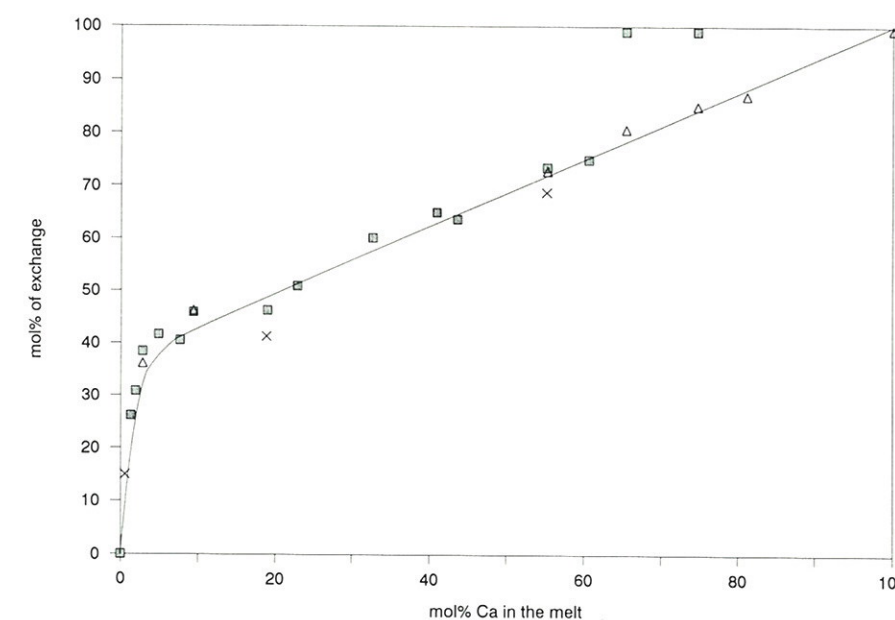


Fig. 3. Equilibrium distribution curve from weight change (\square) and INAA (Δ , \times) for polycrystalline sample and for single crystals by INAA.

strate a small weight loss in a relatively wide temperature range (200 to 1000°C). The weight loss decreases with the number of repetitive measurements.

It is concluded that the weight change is caused by the loss of water from the conduction planes. $\text{Ca } \beta''$ -alumina is hydrophobic like other alkali betas.

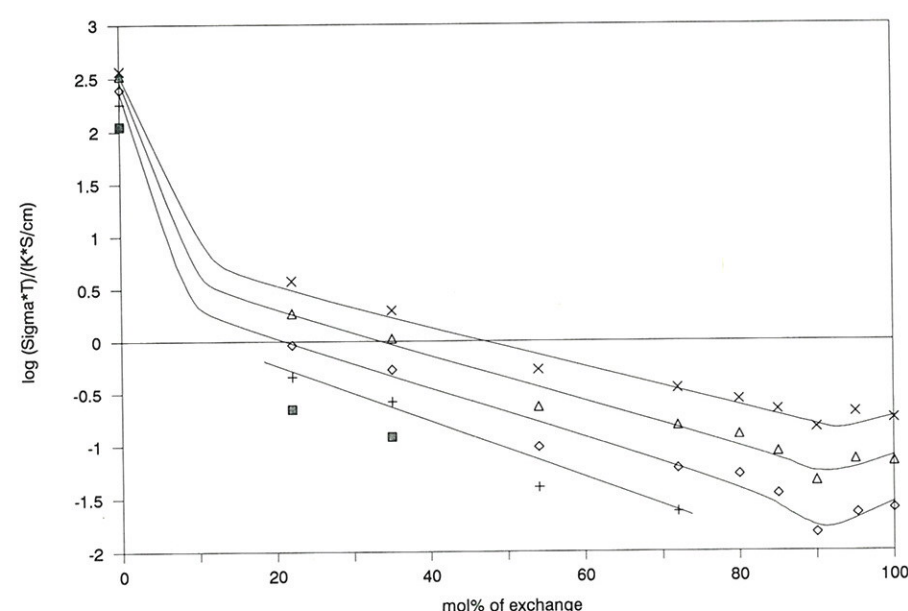


Fig. 4. Specific conductivity as a function of composition at different temperatures: (x) 500°C; (Δ) 450°C; (\diamond) 400°C; (+) 350°C; (\square) 300°C.

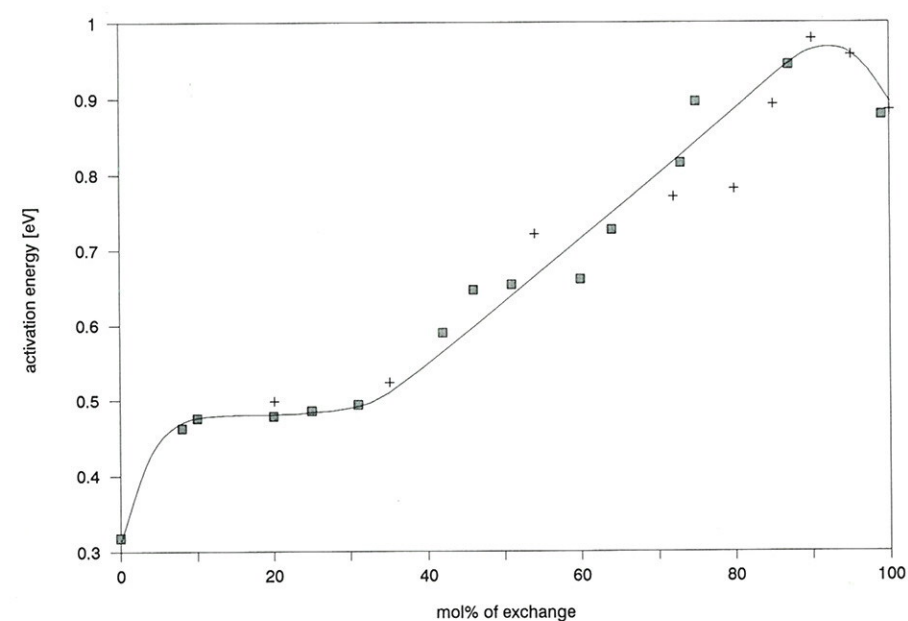


Fig. 5. Activation energy of conduction of polycrystalline (Na, Ca) β'' -aluminas as a function of composition for two experimental runs, carried out in an interval of about a year: (\square) first run; (+) second run.

Another possibility is that residual salts, not removed by the extensive washing procedure, are evaporated from deep pores and cracks. The comparison of the shape of the upper three curves with that of the lower curve for a $\text{Ca}(\text{OH})_2$ suggests that the decomposition of $\text{Ca}(\text{OH})_2$, formed as an intermediate product in the washing procedure, cannot be responsible for the weight loss of the Ca β'' -alumina sample.

There is satisfactory agreement at exchanges below 60% between the extent of exchanges, obtained from weight change measurements or INAA (see fig. 3.). Above 60% two effects may lead to erroneous values of the exchange from weight change:

(a) Residues in pores and cracks will lead to a lower value of the computed exchange because the weight of the exchanged samples decreases with increasing Ca content.

(b) Loss of crystallites of the polycrystalline samples during the ion exchange will yield a higher exchange.

The results in fig. 3 suggest that the factor (b) is predominant here. The values for the exchanges in single crystal lie slightly lower than those for the po-

lycrystalline sample. Since a relatively small difference is observed it cannot be said at present whether a real effect is involved.

Initially the conductivity at constant temperature (see fig. 4) decreases very rapidly with the Ca^{2+} content. This decrease is assigned to an increase of the grain boundary resistance since it was found for the (Na, Ba) and (Na, Sr) isomorphs [12,13] that the intergranular resistance is more strongly affected by the composition than the intragranular resistance. A separation of intragranular and intergranular resistance was also attempted for the (Na, Ca) system in the exchange range below 20% by impedance spectroscopy. However, it failed in the said composition range as it was previously found [14] in a similar range for the (Na, Sr) system [14].

There is a minimum at about 90% exchange in the conductivity-composition curves. This minimum becomes more pronounced with decreasing temperature (see fig. 4). It is suggested in analogy to the results for the (Na, Sr) and (Na, Ba) isomorphs [11,12] that the conduction is largely due to Na^+ below 90% exchange. Above 90% exchange the conduction by Ca^{2+} ions becomes predominant. This

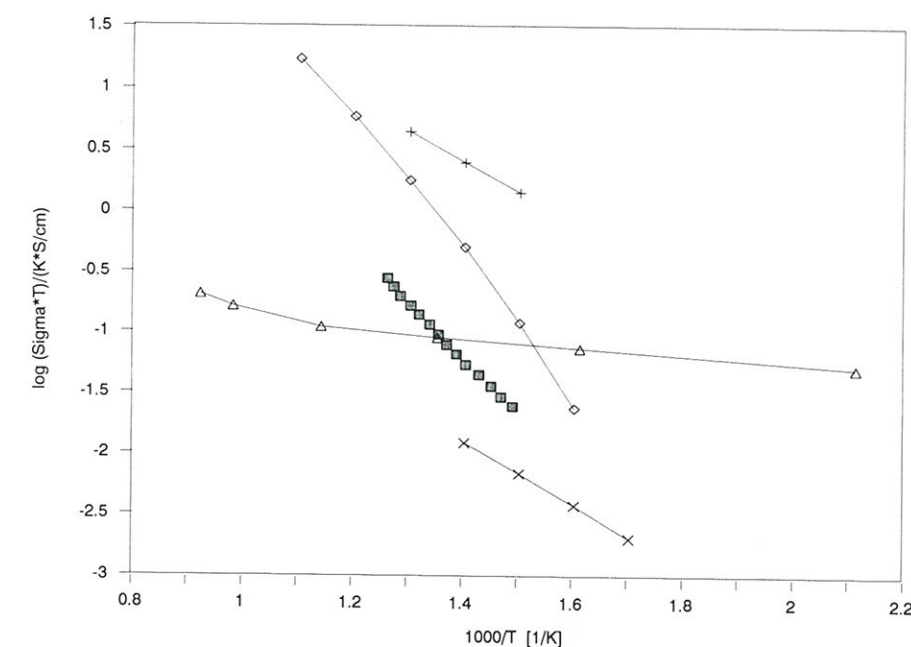


Fig. 6. Arrhenius plots of the data from different sources: (+), (x) ref. [8] $E_a = 0.53$ eV; (\diamond) ref. [9] $E_a = 1.15$ eV; (Δ) ref. [10] $E_a = 0.13$ eV; (\square) four probe, $E_a = 0.89$ eV.

interpretation is confirmed by the data in fig. 5. The activation energy of the conduction displays a maximum at 90% exchange.

Arrhenius plots, reported for polycrystalline Ca β'' -alumina [8–10] in the literature, are compared with our present results in fig. 6. The data from [8] and [9] differ in the absolute value from our data. This difference may be partly due to the different methods of measurements [14]. Nevertheless, the Arrhenius plots display a similar temperature dependence. The three materials were obtained by ion exchange. In contrast, the Ca β'' -alumina which was not prepared by ion exchange but by synthesis [10] behaves very differently. Our prior conductivity data [6] were not included in fig. 6 because the exchanged samples displayed a relatively large porosity. The conductivity values lie about a factor 10 below the new four-probe data in fig. 6.

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