CHEMICAL ANALYSIS AND STRUCTURAL INVESTIGATIONS OF SODIUM- AND LANTHANIDE ION-EXCHANGED BETA-ALUMINAS

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ABSTRACT. Flux grown crystals of Na\(^{+}\)-\(\beta\)-Al\(_2\)O\(_3\) and Na\(^{+}\)-\(\beta''\)-Al\(_2\)O\(_3\) have been analysed chemically by electron probe microanalysis (EPMA) indicating a wide variety of the sodium content for both compounds. For the analytical measurements certain conditions have to be observed because of the high mobility of the sodium ions in these materials. The structure of a neodymium-exchanged Na\(^{+}\)-\(\beta\)-Al\(_2\)O\(_3\) crystal with the analytical composition Na\(_{0.08}\)Nd\(_{0.38}\)Al\(_{11}\)O\(_{17.10}\) has been investigated by X-ray diffraction methods and shows a high disorder of the ion distribution in the conduction planes.

1. Introduction

After the fundamental work of the researchers at the Scientific Laboratory of the Ford Motor Company in the field of \(\beta\)-aluminas [1-6] these materials became one of the most promising family of fast ionic conductors 20 years ago, when the first conference on solid ionic conductors was held in Belgirate (Italy). Especially the refined crystal structures of Na\(^{+}\)-\(\beta\)-Al\(_2\)O\(_3\) and Na\(^{+}\)-\(\beta''\)-Al\(_2\)O\(_3\) [5, 2] as well as the ion exchange possibilities of the sodium ions [1] has given rise to a wide interest in the production of other \(\beta\)-alumina isomorphs and their chemical and physical properties.

After the systematic studies of Yao and Kummer [1] in which they replaced the sodium ions in Na\(^{+}\)-\(\beta\)-alumina by monovalent and partially by divalent cations the monovalent isomorphs were studied extensively [7, 8]. The high ionic conductivity of Na\(^{+}\)-\(\beta''\)-Al\(_2\)O\(_3\) promised good ion exchange behaviour of this material as well [6]. Indeed, after the exchange with monovalent cations [9] various divalent ions of the earth alkali metals and transition metals could be incorporated into Na\(^{+}\)-\(\beta''\)-alumina [10-13] during the 1980's. Also trivalent cations were able to replace the sodium ions by ion exchange [14-16] and the possibility to use lanthanide halides as the ion
exchange medium led to interesting laser materials [17, 18]. Nearly 10 years later
the successful ion exchange with lanthanide ions into Na⁺-β-alumina was described
[19] and until today more than 30 different cations were incorporated into the
Na⁺-β-aluminas and therefore the literature cited here can only be a small selection.

In this contribution we present some basic analytical aspects and results on flux
grown single crystals which we use for our ion exchange experiments. Furthermore,
we show the crystal structure of a highly neodymium-exchanged Na⁺-β-Al₂O₃ single
crystal.

2. Materials and Methods

For our investigations on the ion exchange of sodium ions with rare earth ions in β-
and β'-alumina [19-21] we have grown crystals of both compounds by high tempera-
ture solution growth as described previously [22]. These crystals have been analysed
by electron probe microanalysis (EPMA) to clarify the compositional range for
β-aluminas after spontaneous crystal growth between 1600 °C and 1700 °C. For the
EPMA measurements a Cameca CAMEBAX microprobe was used, operating with
15 kV accelerating voltage and 18 nA beam current.

The ion exchange also was carried out with commercially available crystals [19].
The grown crystals as well as the ion-exchanged compounds were characterized by
X-ray powder diffraction methods. For a single crystal study a small crystal was
cut from a larger parent crystal. The intensity measurements were performed at
room temperature with a four circle diffractometer (AED-2, Siemens-Stoe). The
refinements are reported in detail elsewhere [23].

3. Results and Discussion

The quantitative analyses show a high sensitivity to the applied electron beam (figs.
1 and 2). The count rate of Na increases rapidly upon electron irradiation, while
the count rate of the companion cations decrease (fig.1). Such an unusual target
behaviour is also observed for sodium in sepiolite [24] and in Na₂O-FeO-SiO₂-glass
[25]. In both cases the sodium ions are only weakly bound and show a high grade
of free mobility. This target behaviour may lead to surface damages [22] and because
the weak bonding of ions is a common fact for all fast ion conductors it should be
considered during chemical analyses with EPMA in general. In order to get stable
conditions for quantitative analyses, the beam was defocused to 20 µm (fig. 2) and
the counting time was reduced to 2 s for Na.

In the case of Na⁺-β-alumina a compositional range from Na₁.₄₀Al₁₁O₁₇.₂₀ to
Na₁.₇₃Al₁₁O₁₇.₃₇ was found after crystal growth. This corresponds to a Na:Al ratio
of 1:6.4-7.8 which is in agreement with other crystals grown by the Czochralski