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Compositional Change in NH_4^+ β-Alumina during NH_4^+ Ion Exchange

N. IYI, Y. YAJIMA, AND S. KIMURA

National Institute for Research in Inorganic Materials, Namiki 1-1, Tsukuba-shi, Ibaraki 305 Japan

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K β-aluminas ($K_{1.2}Al_{11.0}O_{17.10}$) with different thickness (100 μm and 500μm in the *c*-plane) were subjected to NH_4^+ ion-exchange at 210°C. The starting *c*-axis parameter was about 22.87 Å. The *c*-axis parameter of the 100-μm specimen decreased to c = 22.84 Å in 4 weeks and maintained this *c*-parameter up to 8 weeks. It can be interpretted as the degradation of the nonstoichiometric NH_4^+ β-alumina into a stoichiometric one during the ion-exchange because the *c*-parameter of the stoichiometric NH_4^+ β-alumina is 22.84 Å. On the other hand, 500-μm specimen showed little sign of decomposition after ion-exchange for 8 weeks. The difference in behavior was attributed to the size of the starting specimens and the reaction was assumed to be a diffusion-controlled decomposition.

Introduction

Ammonium (NH_4^+)β-alumina is one of the most interesting materials for its high-proton conductivity (*1*). NH_4^+ β-alumina has been produced by NH_4^+ ion-exchange reaction of Na^+ or K^+ β-alumina in molten NH_4NO_3 bath at about 200–210°C (*2, 3*). The resulting NH_4^+ β-alumina is known to have a composition of $(NH_4)_{1+x}Al_{11}O_{17+x/2}$ ($x \approx 0.2$–0.3) (*4*), retaining the nonstoichiometry of the precursor β-alumina. The structure study revealed excess NH_4^+ ions exist in the conduction plane as well as a Frenkel defect of the Al^{3+} ion and interstitial O^{2-} compensating for excess cation charge (*5–7*).

In our previous paper (*7*), however, it was shown that stoichiometric NH_4^+ β-alumina was obtained under a certain ion-exchange condition, and the possibility of elimination of the excess cations during NH_4^+ ion exchange was pointed out in the β-alumina system. In the structure-related β-gallate system, it was already reported by Ikawa *et al.* (*8, 9*) that β-gallate lost excess NH_4^+ ions together with interstitial oxygen ions during the NH_4^+ ion-exchange reaction, giving stoichiometric NH_4^+ β-gallate, $(NH_4)_{1.0}Ga_{11.0}O_{17.0}$.

The aim of this study is to clarify factors influencing the degradation of NH_4^+ β-alumina into a stoichiometric one during NH_4^+ ion exchange. Factors such as (i) the size of the crystal and (ii) the amount of excess cation in the starting β-alumina were considered in the present study.

Experimental

To examine the size factor, two sizes of $K_{1.2}$ β-alumina single crystals (thickness in the basal plane: 500 μm and 100 μm) were used for NH_4^+ ion exchange. For monitoring of the composition, the lattice parameters were measured because it was shown that the *c*-parameter decreases from 22.87 to

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22.84 Å according to the decrease of excess cations from $x = 0.2$ to $x = 0.0$ (stoichiometric) (7).

The starting specimens, $K_{1.2}$ β-alumina, were derived from a large crystal of $Na_{1.2}$ β-alumina. $Na_{1.2}$ β-alumina (Toshiba Monoflux) crystals of the same batch were confirmed to have a composition of $Na_{1.20}Al_{11.0}O_{17.1}$ by chemical analysis (7). This means a 20% excess of Na^+ over stoichiometry. $Na_{1.2}$ β-alumina single crystals used for ion-exchange were sliced into bars with 0.5 mm thickness in the c-plane. Conversion of $Na_{1.2}$ β- into $K_{1.2}$ β-alumina was conducted by the conventional K^+ ion exchange in molten KNO_3 at 380°C for 4 days. The Na and K content was checked by line scanning of sections of the exchanged bars by using an EPMA (electron probe microanalyzer, Shimadzu), and no remaining Na^+ ion was detected. Half of the resulting crystals were further polished to thin bars with 100 μm thickness in the c-plane. Pairs of 100- and 500-μm crystals were placed in Pt mesh bags, and NH_4^+ ions were substituted for K^+ by ion exchange in molten NH_4NO_3 at 210°C. Crystals (500 μm) picked up 3 days after the immersion still contained about 10% of the initial K ions in the middle of the crystal; however, those of 7 days immersion were revealed to be completely exchanged into NH_4^+ β-alumina throughout the crystal by EPMA. Crystals were picked up weekly up to 8 weeks. In the present paper, the resulting specimens are designated as NH4-100 and NH4-500 for the crystals of 100 and 500μm thickness, respectively. The resulting crystals were all clear and no extra damage due to the ion exchange was observed. The lattice parameters were determined on the basis of 2θ data (22 reflections within $2\theta = 50$–$90°$, Mo$K\alpha1$ radiation, $\lambda = 0.70926$ Å) collected on an automatic four-circle diffractometer (AFC-3, Rigaku Denki Co.). The accuracy of the lattice parameters had been checked by a single Si crystal measurement, and the lattice parameters were calculated using the least-square method.

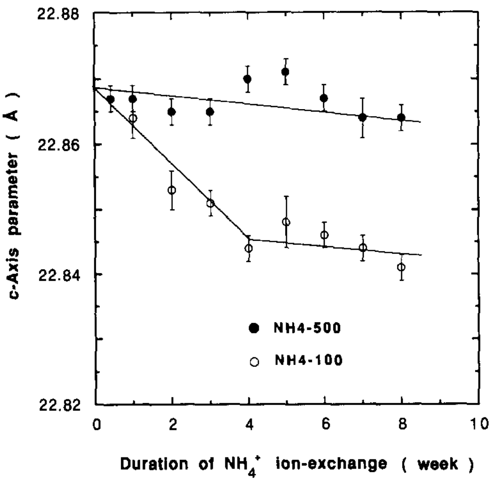

FIG. 1. The c-axis parameters plotted against the duration of NH_4^+ ion-exchange for NH4-100 (crystal of 100 μm thickness) and NH4-500 (crystal of 500 μm thickness).

Refinements of the crystal structure were carried out on a single crystal NH4-100 (4 weeks ion exchange) to check the interstitial ions. Using rectangular crystals, intensity data were collected on an automatic four-circle diffractometer (AFC-3, Rigaku Denki Co.) using graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71068$ Å). The ω-2θ scanning was used for intensity data collections up to $2\theta = 120°$. The final set of 1111 nonzero independent reflections below were corrected for Lorenz polarization and absorption effects. Refinement was conducted in the usual manner (7). The final anisotropic refinement gave a R-value of 0.023 ($wR = 0.026$, $w = 1/\sigma F^2$) for the stoichiometric NH_4^+ β-alumina model. Final difference maps showed random peaks and depressions within the range -0.3 to $+0.6$ eÅ^{-3}.

Results and Discussion

Figure 1 shows the change of the c-axis parameters during NH_4^+ ion exchange. The

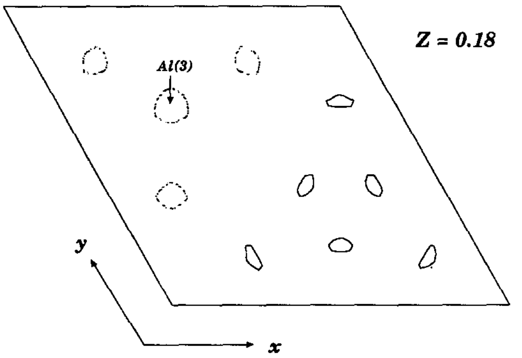

FIG. 2. The difference Fourier section showing the electron density at $z = 0.18$ for NH4-100 after ion-exchange for 4 weeks ($R = 0.030$). Contour lines are drawn with interval of 0.20 eÅ^{-3}. Dashed contour lines indicate negative electron density. Zero contours are omitted.

c-axis parameter of NH4-500 (specimen with 500 μm thickness in the c-plane) changed little up to 8 weeks; on the other hand, that of NH4-100 decreased to about 22.84 Å and maintained this value up to 8 weeks. The a-axis parameter was within the range 5.596–5.598 Å for all the specimens. It can be assumed that the NH4-100 decomposed into stoichiometric NH_4^+ β-alumina in 4 weeks and then remained in the stoichiometric composition on the grounds that:

(i) It was shown that the c-parameter of NH_4^+ β-alumina decreased as the excess NH_4^+ ions decreased and that the c-parameter of stoichiometric NH_4^+ β-alumina was 22.84 Å (*7*).

(ii) Difference Fourier sections on the basis of anisotropic refinement of the single crystal NH4-100 ($R = 0.023$) revealed no significant electron density at the *i*Al site (around (5/6, 2/3, 0.18)). (See Fig. 2. cf. Fig. 1a of Ref. (*7*).)

On the other hand, only a little change was observed in the nonstoichiometric composition of NH4-500 during the 8-week exchange period. As the difference between two specimens existed only in the size of the specimens, size factor is the cause of the difference in the exchange reaction. It indicates the thermodynamic instability of nonstoichiometric NH_4^+ β-alumina at the exchange temperature (210°C).

In our previous paper (*7*), the difference of the exchange reaction of two different K β-aluminas ($K_{1.2}Al_{11}O_{17.1}$ and $K_{1.5}Al_{11}O_{17.25}$) was reported. The former ($K_{1.2}$-β) was 500 μm in the c-plane and had 20% excess K^+ ions. The latter ($K_{1.5}$-β) was 100 μm in size and contained a large excess (50%) of K^+ ions. The nonstoichiometry was retained through NH_4^+ ion exchange in the case of $K_{1.2}$-β. However, stoichiometric NH^+ β-alumina, $(NH_4)_{1.0}Al_{11}O_{17.0}$, was derived from $K_{1.5}$-β. It contained only a stoichiometric amount of NH_4^+ ions and no interstitial Al and O ions were detected by the X-ray method. At that time, it was not determined whether (i) the amount of excess cation, or (ii) the size of the crystal caused the different exchange reaction. The present result clearly shows the main factor is the size of the single crystal used for ion exchange.

The crystallinity of the single crystals was retained through the degradation reaction, so the present reaction can be thought of as a special case of the topotactic decomposition. The decomposition might proceed from the surface (perpendicular to the c-plane), and the excess species, NH_4^+ and interstitial O^{2-}, may diffuse out to the crystal surface along the c-plane. As the conduction of these species in the resulting stoichiometric region is not good, the decomposition reaction would be controlled by the diffusion process. This type of decomposition is known to follow the parabolic law $\alpha^2 = (k/x^2)\, t$ (where α is the fraction of product, $2x$ is the thickness of the crystal, and t is time) (*10*). A fraction of the product is in reverse proportion to the square of the crystal dimension, which causes a striking size-effect. More quantitative discussion is not, however, possible because the standard deviations of the c-axis parameter are large compared with the change of the c-parameter.

So far, two methods, heat treatment (~500°C) of ammonium β-alumina (*5*) and reduction of Ag β-alumina (*11*), were known to obtain stoichiometric β-alumina. Prolonged ion exchange of thin crystals in NH_4NO_3 may offer an alternate way to yield stoichiometric β-alumina, although the resulting crystals are little in size. it is reasonable to assume that higher exchange temperature also enhances the degradation of NH_4^+ β-alumina. This should be clarified in the future. NH_4^+ β-alumina cannot be assumed a priori to retain the nonstoichiometry of the starting β-aluminas through ion exchange.

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