A Thermogravimetric and NMR Study of β-Aluminas

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The Na^+ tracer diffusion coefficient and the ^{27}Al NMR spin lattice relaxation time in Na β-alumina display an anomalous temperature dependence near 470 K. These phenomena are related to absorption of water which takes place when the temperature is decreased below 470 K. Water absorption processes in pure and partially substituted β-aluminas are studied by thermogravimetric analysis. Their effects upon conductivity are qualitatively discussed.

Introduction

Recent careful measurements of the sodium tracer diffusion coefficient (D_T) in Na β-alumina by Kim et al. [1] revealed the presence of a "jog" or a "transition region" in the $\ln D_T$ versus T^{-1} curve near 470 K, while no other physical anomaly was reported in the same temperature region. Such an effect causes a large fluctuation of the Haven ratio (H_R), thus reducing the ability of this parameter to discriminate among different models of cation dynamics in β-alumina [2, 3].

The purposes of this paper are the following:

i to show that the ^{27}Al NMR spin lattice relaxation time also has an anomalous behavior near 470 K,

ii to give the results of thermogravimetric analyses of β-aluminas that reveal an absorption of H_2O which begins near 470 K in Na β-alumina and near 650 K in Li-containing aluminas,

iii to qualitatively relate the intake of H_2O to the discontinuity in the $\ln D_T$ versus T^{-1} curve.

Experimental

Na β-alumina has the formula $(Na_2O)_x \cdot 11\,Al_2O_3$ with $x = 1.22$ for our samples ($x = 1$ for the stoichiometric compound). It is a layered compound with sodium ions contained in a low density plane between slabs of compact aluminum oxide spinel blocks.

Single crystals of melt-grown Na β-alumina were cut from a boule supplied by Union Carbide. Cation exchange was accomplished by submerging the crystals in molten nitrate baths as described by Kummer [4]. The extent of cation substitution was controlled by measuring the weight changes and through neutron activation analysis. Standard NMR pulse techniques have been applied to measure the recovery of the magnetization due to the ^{27}Al central transition in β-alumina single crystals. Since the recovery is not exponential, we will indicate by T_{10}^{-1} the average decay rate in an interval close to the time origin during which the magnetization changes by 30% of its equilibrium value. The temperature was controlled at ± 2 K.

Thermogravimetric analyses in the range 300–900 K have been made using a Dupont TGA 950 system with maximum sensitivity of 0.01% (sample weight $\cong 50$ mg; heating rate $q = 3\ \mathrm{K\,min^{-1}}$). Most analyses have been performed on small crystals (size 63–88 μm) obtained by crushing larger crystals in an agate mortar. Examination of the samples with a stereoscopic microscope showed grains with very similar dimensions along directions perpendicular and parallel to the c-axis.

Results and Discussion

Figure 1 reports ^{27}Al T_{10} versus T at 21 MHz in a crystal of Na β-alumina with the c-axis parallel to the magnetic field.

The data have been collected while increasing T in two experiments which entirely covered the displayed T-interval. The crystal was exposed to usual

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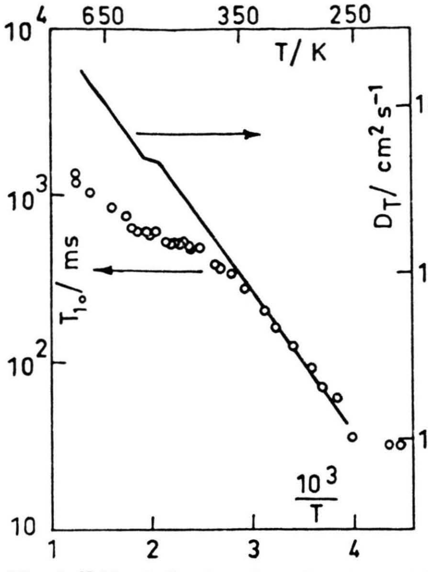

Fig. 1. ^{27}Al spin lattice relaxation times at 21 MHz and Na$^+$ tracer diffusion coefficients in Na β-alumina.

room atmospheric conditions during the 10 months between experiments. The solid curve of Fig. 1, which represents the experimental D_T data tabulated by Kim et al. [1], is included for comparison. Over the T-region explored, the relaxation is caused by electric field gradient (efg) fluctuations at the alumina positions which result from cation motion in the conducting plane.

For a Larmor frequency, ω_L, smaller than the characteristic jump frequencies τ_j^{-1} we should have

$$T_{10} \propto \tau_j^{-1} \propto D_T . \qquad (1)$$

Between 240 and 350 K, this equation holds true (see Figure 1). Below 240 K, the temperature dependence of T_{10} flattens as τ_j^{-1} becomes comparable with ω_L and T_{10} approaches the temperature ($\sim$190 K) where it reaches a minimum (not displayed in the Figure).

Above 350 K, the T_{10} versus T^{-1} curve displays a jog similar to that reported for D_T. The possibility that efg fluctuations driven by vibrations are responsible for this jog can be excluded. Vibrations would give $T_{10} \propto T^{-2}$ while the experiment indicates that T_{10} still increases with increasing temperature at $T = 700$ K.

A jog smaller than that of Fig. 1 has been observed near 470 K for the ^{27}Al T_{10} in Ag β-alumina [5]. In partially substituted crystals containing Li$^+$, K$^+$, Tl$^+$ and Rb$^+$ a ^{27}Al T_{10} minimum occurs near, or above, 470 K [5]. Thus a relaxation effect similar to that reported in Fig. 1 would be difficult to observe.

Figure 2 reports TG experiments performed on Na β-alumina in controlled atmospheres after a "first run" *. In some first runs in air a noticeable weight increase occurred near 370 K.

For experiments carried out in air (relative humidity 55%), the sample looses 0.9 ± 0.05% of weight when heated (curve a) then it returns to the initial weight when cooled to room temperature (RT) (curve b). A sequence of several temperature cycles on the same sample does not significantly alter this behavior.

Figure 2 reports also (dashed lines) experiments performed using a flux of dry air and dry nitrogen, oxygen, carbon dioxide or helium on samples equilibrated in air for one day. After a common desorption process (curve c), no absorption phenomenon is apparent when returning to RT (curve d), so showing that Na β-alumina intakes H_2O vapour only. When air was mixed with the gas stream at $T \leqq 330$ K, the samples returned to their original weight. Samples left for hours under vacuum at RT did not loose weight; a partial weight loss occurred when the temperature was raised to 330 K, but the desorption process in vacuum was completed only for $T \geqq 500$ K.

Typical thermogravimetric recordings on the sample of Li(50%)-Na(50%) β-alumina in air are shown in Figure 3. Trace a (dashed line) is a first run while traces b and c represent a cooling-heating cycle performed immediately following the first run.

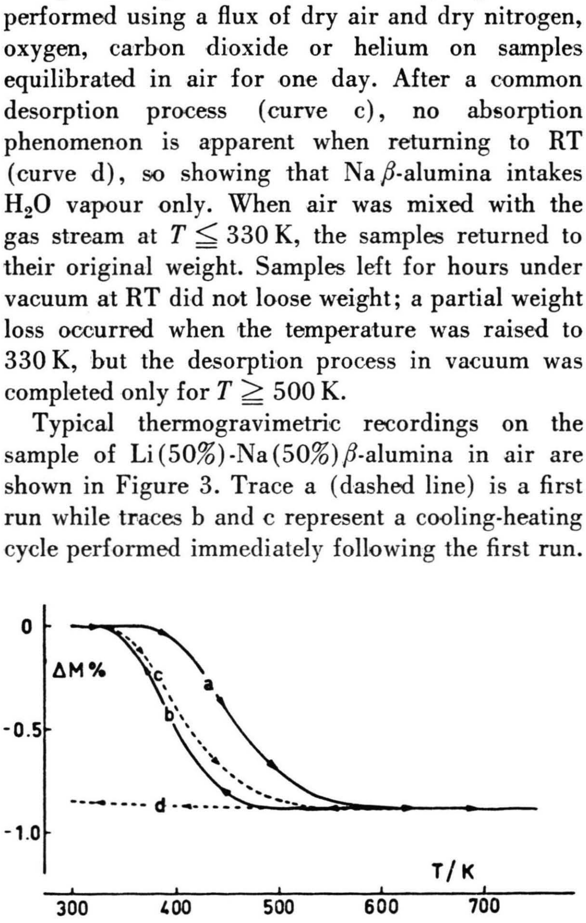

Fig. 2. Percentage weight changes of small Na β-alumina crystals in different atmospheres; full lines: cycle in air; dashed lines: cycles in dry air and dry N_2, O_2, He and CO_2.

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* By "first run" we indicate a thermogravimetric analysis performed on a newly prepared sample, obtained from crystals left for months in air.

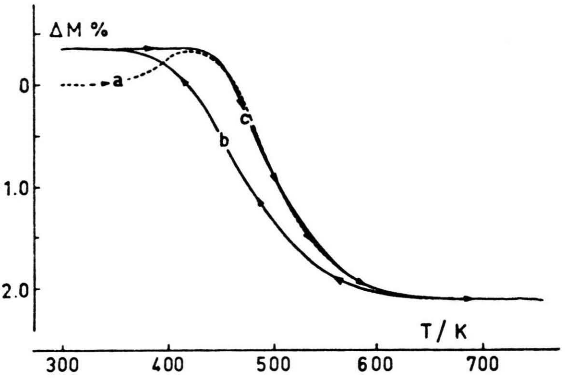

Fig. 3. Weight change in a first run (dashed curve a) and subsequent temperature cycle (b, c) of Li-Na(50%) β-alumina crystals in air.

After the first annealing, completely reversible absorption-desorption processes (traces b and c) occurred, even when the sample was left for a full day in RT air between measurements.

A behavior similar to that of Fig. 3, with a higher percentage of weight change, is displayed by a crystal of nominal ** composition Li (85%) – Ag (15%), while almost no weight change occurs in crystals containing K, Rb, Tl, and Ag.

Table 1 lists the compositions of the crystals studied, together with the percentages of weight change occurring in heating-cooling cycles performed in air.

Several measurements were made on single crystals weighing $\cong$ 100 mg.

For Na β-alumina, weight losses of $0.35 \pm 0.2\%$ were observed in the first run. The process was apparently irreversible since no thermogravimetric changes were noted in experiments performed several days after annealing.

For Na-Li single crystals in air the behavior of trace a in Fig. 3 was reproduced in first runs and some weight increase occurred while cooling. Both phenomena were depending upon the heating-cooling rate. The above observations suggest that the main effect of a high surface-to-volume ratio is to allow a faster intake of H_2O when temperature is decreased.

Table 1. Weight Changes and c-Lattice Parameters of Exchanged β-aluminas.

Ion(s)	ΔM % [a]	c/Å [b]
Ag	0.07	22.498
Na	0.9	22.530
Li-Na (50%)	2.5	22.570
Li-Ag (15%)	3.3	22.570
K-Na 45%)	0.05	22.729
Rb-Na 45%)	$\simeq 0$	22.883
Tl-Na (40%)	0.07	22.93

[a] For annealed small crystals (size 63–88 μm) in air.

[b] The values refer mostly to completely exchanged β-aluminas [4].

The intake of H_2O does not appear to be correlated with the greater space available, at RT, in the conduction plane which accompanies the introduction of cations larger than Na^+ (see Table 1).

For Na β-alumina this process is very selective (no absorption of other gases is evident) and the number of absorbed H_2O molecules approximately equals the number of sodium atoms in excess of stoichiometry: therefore it may be deduced that water absorbed forms a 1 : 1 complex with Na^+ as suggested by Roth et al. [6].

The H_2O absorption-desorption phenomenon may be related to the presence of a "transition region" in the $\ln D_T$ vs $1/T$ curve. Kim et al. [1] annealed to 673 K all their large crystals ($\cong 1\ \text{cm}^3$) before measurements. However, annealing and conductivity measurements were both performed under a $1.33 \cdot 10^{-4}$ Pa vacuum and it may be safe to assume that no equilibration with H_2O occurred below 470 K. Instead, tracer diffusion by non-destructive profiling above 300 K was performed in air allowing a partial equilibrium with H_2O to be reached during the time of the experiment.

Since the D_T values below 470 K are greater than those expected from extrapolating the higher temperature D_T curve, the presence of H_2O seems to increase the sodium mobility: such an enhancement may be explained by considering that H_2O intake causes an expansion along the c-axis, as our first results indicate.

The reason that ^{27}Al T_{10} seems more sensitive than D_T to H_2O intake is believed to be due to the fact that NMR experiments were performed on a sample in equilibrium with H_2O.

As regards the intake of H_2O in Li-containing β-aluminas, the water content increases with Li^+

** The crystal underwent two substitutions: first, more than 99% of Na^+ was exchanged with Ag^+ in molten $AgNO_3$. Then Ag β-alumina was exchanged in a $LiNO_3$-LiCl bath, where it underwent 85% of the weight loss expected for the complete Ag$\rightarrow$Li substitution. However, neutron activation showed that 2–3% of cations were Na^+, probably due to Na impurities of the second bath.

concentration, and NMR data of Walstedt et al. [7] show higher lithium mobility in annealed samples than in those exposed to air.

Both these facts indicate that the process of H_2O absorption by Li-Na β-aluminas is somewhat different from that of Na β-alumina. Work is in progress to explain these differences.

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