CHARACTERIZATION OF HEAT TREATMENT INDUCED CHANGES IN Li-Na BETA-ALUMINA SINGLE CRYSTALS

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ABSTRACT

Single crystals of lithium-sodium beta alumina with 40 to 95% substitution of Li⁺ for Na⁺ were annealed in air and in vacuum at temperatures up to 1000°C. The specimens were examined before and after each heat treatment by pulsed NMR, Raman scattering, infrared absorption, and x-ray diffraction. After annealing at 600°C or above, the two original Raman bands due to Li⁺ vibrations merged into a single peak accompanied by a narrowing of spinel block phonon bands. The 1000°C annealing introduced a broad Li NMR response and substantially reduced narrow line Li intensity. X-ray diffraction patterns showed that a second phase grows epitaxially with the beta-alumina structure as a result of high temperature heat treatment. The present results suggest that the thermal induced changes observed are due to diffusion of lithium out of the conducting plane and into the spinel-block.

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INTRODUCTION

The ion exchange properties of sodium beta-alumina are well-known [1]. Depending on the cation composition of the molten salt and number of ion exchange steps, mixed-ion beta aluminas can be prepared having a wide range of cation compositions. One of the more important and interesting mixed-ion materials is Li-Na beta-alumina. It has been shown [2] that at compositions near 50% Li substitution, Li-Na beta-alumina is a good lithium ion conductor at ambient temperatures. The crystal structure of Li-Na beta-alumina has been recently studied by powder neutron diffraction techniques [3], and the Li ions were found to be located at positions displaced above and below the Beevers-Ross sites (above and below the conducting plane), as predicted by model calculations [4,5]. Recent NMR studies of polycrystalline Li-Na beta-alumina [6] have shown that marked changes in Li ion motion occur when samples are heated at elevated temperatures for relatively short times. The importance of this result to the potential application of Li-Na beta-alumina as a Li ion solid electrolyte has motivated an investigation of the effects of heat treatment on single crystals of this material. In this work, we describe the results of NMR, Raman scattering, infrared absorption, and x-ray diffraction studies of Li-Na beta-alumina single crystals (40 to 95% lithium-ion substitution) which have been heated in air and in vacuum at temperatures from 200 to 1000°C for times from one hour to 7 days. The changes seen in the behavior of Li ions are attributed to diffusion of these ions out of the conducting plane into the spinel block, with the concomitant formation of a second phase.

EXPERIMENTAL PROCEDURES

Single crystal specimens of lithium-sodium beta-alumina with 40 to 95% substitution of Li for Na were prepared by ion exchange of sodium beta-alumina parent materials (obtained from Union Carbide Crystal Products Department), having a nominal composition varying from 1.15 Na2O · 11 Al2O3 to 1.22 Na2O · 11 Al2O3. Samples of less than 80% Li exchange were prepared by ion exchange in LiNO3 at 410°C, while specimens containing more than 80% substitution were first heated in molten AgNO3 and then in a mixture of LiNO3/LiCl at 350°C. The extent of ion exchange was determined by careful (10 µg sensitivity) weight change measurements and by chemical analysis for Li. After ion exchange,
specimens were washed with water (2 minutes or less), dried, and stored in a vacuum oven until an initial set of characterization measurements could be made by NMR, X-ray diffraction, infrared absorption, or by Raman scattering. Specimens were then heated on a platinum screen in air or in vacuum for times from 30 min. to 7 hrs. and for temperatures from 200 to 1000°C. Characterization measurements were repeated after each heat treatment.

Pulsed NMR measurements of $^7\text{Li}^+$ were made at 10.5 MHz with the c-axis oriented parallel ($\theta=0^\circ$), at 45° ($\theta=45^\circ$), or perpendicular ($\theta=90^\circ$) to the static applied magnetic field ($H_0$). Free induction decay (FID) curves, spin lattice relaxation times ($T_1$), and observed line widths ($T_2^*$) were measured at room temperature. The 90° pulse width was approximately 3.6 μsec. $T_2^*$ was determined from the FID as a function of temperature between 175 K and 455 K, and line widths [7] were calculated assuming a Lorentzian line shape. $T_1$ was measured by the inversion recovery technique.

Polarized Raman scattering measurements were made at 12 and 300 K using the apparatus and techniques described previously [5]. The 488.0 nm line of an argon ion laser operating at an output power of 1200 mW was the excitation source. The sample was cooled to 12 K using a closed cycle refrigerator. Raman spectra were recorded step-wise under computer control at 2 cm$^{-1}$ intervals, with a counting time of either 20 or 40 sec/point. The scattering geometry was described by $a(cc)a'$, where $a$ and $a'$ are orthogonal axes in the (001) plane, and $c$ is parallel to the crystallographic c-axis. Previous measurements[5] of Raman scattering from $^6\text{Li}^+$ and $^7\text{Li}^+$ ions in Li beta-alumina showed that the Li$^+$ ion vibrational modes occur in the region between 340 and 400 cm$^{-1}$, and the largest scattering intensity from these modes was observed for (cc) polarization. Infrared absorption measurements of single crystals were made in the region from 2000 to 4000 cm$^{-1}$ at 300 K using a Fourier transform spectrometer. Samples of from 0.2 to 0.5 mm thick (measured along the c-axis) were mounted in a 4x beam condenser such that the infrared radiation was incident on the (001) face.

Transmission X-ray Laue patterns and X-ray precession diagrams were made by standard methods using Mo Kα radiation. Lattice parameters were calculated from diffraction spot spacings measured on the precession films.

Several heat-treated specimens were heated in water vapor at 200°C for 200 hrs in order to determine the role of water in the changes observed. These specimens were then reexamined by Raman scattering, infrared absorption, and NMR.
RESULTS

Nuclear Magnetic Resonance

The characteristic $^7$Li NMR free induction decays (FID) obtained at room temperature from specimens before and after 1000°C heat treatment in air are shown in Fig. 1. Before heat treatment (Figure 1a) the FID is relatively long lived, indicating the presence of a narrow line (159 Hz). After heat treatment, the FID reflects a substantial reduction in the $^7$Li narrow line intensity (Fig. 1b) and the appearance of a broad line (13.9 KHz) $^7$Li signal (Fig. 1c). This behavior was followed as a function of treatment temperature in a second sample. This specimen was heated in air stepwise for 4 hrs at 350, 560, 690 and 900°C and for 7 hrs. at 1000°C. The results in Fig. 2 show that the $^7$Li narrow line intensity was not substantially influenced at 690°C (step III) or below; however, a very significant decrease in narrow line intensity occurred at 900°C (step IV), and all narrow line intensity was gone after the 1000°C (step V) treatment. Although narrow line intensities changed with heat treatment, the line widths did not.

The spin lattice relaxation time, $T_1$, at room temperature for $\theta=90°$ was about 30 msec for the narrow line lithium signal prior to heat treatment. After Step IV heat treatment, $T_1$ for the broad-line lithium signal was significantly larger; however, no reliable determinations of its true value could be made because of the poor signal to noise ratio and because of the fast nature of the decay. The increase in $T_1$ and the line broadening which occurred after heat treatment at 900°C and above suggests that at these elevated temperatures, there is a change in the local environment of the spins.

No significant changes in narrow line $^7$Li line width were caused by the step-wise heat treatment procedure. These data are shown in Table I. The orientation dependence of the line width is consistent with other work [8], and the trend of increasing line width with increasing rotation angle was observed in all measurements. No entries are present in Table I for step five since the narrow line lithium intensity was zero after this treatment.

The $^7$Li line width measured vs temperature prior to specimen heat treatment is shown in Fig. 3. The strong narrowing trend over the observed temperature range is indicative of reduced Li$^+$ motion in the conducting plane. As seen in Fig. 3, essentially the same results were obtained with polycrystalline samples [6].
The divergence of the two curves seems to be caused by the magnetic field inhomogeneities associated with the different sample volumes in the two experiments. Both curves are bounded by the $^7\text{Li}^+$ line width observed for $^7\text{Li}^+$ in a volume of aqueous solution corresponding to the solid specimen volume. One of the NMR samples which had been annealed at 1000°C was heated in $\text{H}_2\text{O}$ vapor at 200°C for 7 days. The changes in the FID curves induced by the initial heat treatment were not affected by the treatment in water vapor. The significance of this result will be apparent later.

Raman and Infrared Measurements

The Raman spectra of a 95% $^7\text{Li}$ substituted crystal before and after heat treatment at 800°C in vacuum for 1 hr is shown in Fig. 4. By comparison with the frequencies observed for a $^6\text{Li}^+$ substituted sample, the two overlapping bands near 370 cm$^{-1}$ in curve (a) were assigned to localized vibrational modes of $\text{Li}^+$ ions parallel to the c-axis [5]. The appearance of two bands may be caused from two different environments about the $\text{Li}^+$ ions. The broad band near 440 cm$^{-1}$ does not appear in the spectrum of $\text{Na}$ beta-alumina and was therefore attributed to a mode involving $\text{Li}^+$ motion. The shift in frequency of this band with substitution of $^6\text{Li}^+$ for $^7\text{Li}^+$, however, was much less than predicted for a pure $\text{Li}^+$ motion. After annealing the crystal, the Raman spectrum (curve b) showed several distinct changes: The two $\text{Li}^+$ bands (resolved into two overlapping Gaussian components) at $\sim 390$ and 370 cm$^{-1}$ were replaced by a single band centered at 375 cm$^{-1}$. The intensity of the broad band at $\sim 440$ cm$^{-1}$ diminished considerably, and the intensity of the neighboring phonon peak at 431 cm$^{-1}$ also decreased, accompanied by a decrease in its frequency to 426 cm$^{-1}$. Finally, the width [7] of the phonon peak at 323 cm$^{-1}$ decreased from $\sim 15$ cm$^{-1}$ before annealing to $\sim 9$ cm$^{-1}$ after annealing. On annealing the crystal at 950°C in vacuum for 1 hr., the width of the $\text{Li}^+$ band at 375 cm$^{-1}$ decreased slightly, while no additional changes in the position or shape of the phonon peaks at 426 and 323 cm$^{-1}$ were apparent.

Recent studies [9] have shown that substitution of $\text{Li}^+$ for $\text{Na}^+$ in beta-alumina causes an increase in the concentration of $\text{H}_2\text{O}$ in the conducting plane and an increase in the stability of the hydration state so formed. The infrared transmission spectra of a 90% $\text{Li}^+$ substituted crystal in the region from 4000 to 2500 cm$^{-1}$ is shown in Fig. 5. The spectrum of the as-prepared specimen (curve a) shows two sharp
absorption bands at 3520 and 3400 cm\(^{-1}\) and a broader absorption band at 3180 cm\(^{-1}\). These bands are assigned to stretching modes of H\(^2\)O located in two or more nonequivalent sites in the conducting plane. Curves (b), (c), and (d) show the results obtained after annealing the specimen in vacuum for 1 hr. at 500°C, 1 hr. at 600°C, and for 9 hrs. at 600°C, respectively.

After annealing at 500°C, one absorption band of much lower intensity appears at 3420 cm\(^{-1}\), while the formerly intense band at 3180 cm\(^{-1}\) appears as a relatively weak feature. Annealing at 600°C (curve c) causes a reduction in intensity of the 3420 cm\(^{-1}\) peak, and a new peak appears at 3750 cm\(^{-1}\). We attribute the latter feature to OH\(^-\), which may have been formed by decomposition of H\(^2\)O. On annealing the sample either at higher temperatures for 1 hr. or for longer times at 600°C or above (curve d), the intensity of the 3750 cm\(^{-1}\) band increases, while the intensity of the 3420 cm\(^{-1}\) band decreases. In curve (d) of Fig. 5, the two weak bands at 3520 and 3400 cm\(^{-1}\) appear as a result of partial rehydration of the sample from exposure to air.

In the samples studied so far, we have found that the intensity of the 3750 cm\(^{-1}\) band remains unchanged on annealing at 1000°C for several hours.

The dehydration process illustrated by the infrared data in Fig. 5 can be reversed by heating a dehydrated sample in H\(^2\)O vapor at 200°C. However, although the infrared spectrum of curve (a) is recovered, the Raman spectrum of curve (b) in Fig. 4 remains unchanged. This result shows that the changes observed in the Raman spectrum of Li\(^+\) ions after annealing are not caused by loss of H\(^2\)O from the sample. Furthermore, as noted above, the re-hydration of an NMR sample did not affect the changes seen in the FID curves that were caused by the initial heat treatment.

**X-ray Diffraction Studies**

The precession photographs obtained from an untreated, 77% Li\(^+\) substituted single crystal showed the pattern expected for a beta-alumina structure. The diffraction data are consistent with the hexagonal space group, P6\(_3\)/mmc [10]. The lattice parameters, determined from film measurements, are \(a_0 = 5.59(1)\) Å and \(c_0 = 22.54(2)\) Å, and are close to those reported by Tofield and Farrington [3] for a 60% Li\(^+\) substituted polycrystalline sample of Li-Na beta-alumina, \(a_0 = 5.5923(4)\) Å and \(c_0 = 22.5576(6)\) Å.
Precession photographs were taken at two different orientations after heat treatment (1000°C for 7 hrs. in air) of the 77% substituted crystal. The results are shown in Fig. 6. In addition to the normal beta-alumina pattern, extra reflections were observed and are indicated in the figure. The extra reflections are close to the space group absences of the beta-alumina structure, but they correspond to a cubic structure with $a_0 = 7.89(1)$ Å, which is epitaxial with the beta-alumina structure. Adopting a rhombohedral description for the cubic structure, the corresponding hexagonal parameters are $a_0 = 5.58$ Å and $c_0 = 13.67$ Å. The matching of the hexagonal base planes is almost exact, and the $hk0$ reflections of the new material occur generally in coincidence with $hk0$ reflections of the $\beta$-alumina structure. The main differentiation occurs in $hkl$ reflections. However, even with $hkl$ reflections, near coincidence is often encountered because $5 \times 13.67$ Å is close to $3 \times 22.54$ Å.

The new substance or second phase is quite likely LiAl$_2$O$_4$, for which the cubic lattice parameters are $a_0 = 7.908$ Å when ordered and 7.925 Å when disordered [11]. The epitaxy is to be expected since both structures not only have the same close-packing arrangement of oxygens, but also have in common the arrangement of cations in the spinel blocks of the $\beta$-alumina structure. In terms of the cubic description of LiAl$_2$O$_4$, the epitaxial relations are

$$[121]_{\text{spinel}} || [100]_{\beta\text{-Al}_2\text{O}_3}, [011]_{\text{spinel}} || [110]_{\beta\text{-Al}_2\text{O}_3}, \text{and } [111]_{\text{spinel}} || [001]_{\beta\text{-Al}_2\text{O}_3}.$$

Weight Change

The weight change of the 77% Li$^+$ substituted sample was measured after each step-wise heat treatment. The results, recorded as percent weight loss, are listed in Table II. As can be seen from these data, the significant weight losses occurred during steps I and II (below 600°C), while much smaller losses occurred during steps III-V. From the infrared results discussed above and illustrated in Fig. 5, the weight losses occurring below 600°C can be attributed to removal of H$_2$O from the specimen. That the weight loss below 600°C is due to loss of H$_2$O and not to Li$_2$O is substantiated by the result that no significant loss in the $^7$Li$^+$ narrow line NMR intensity occurred after steps I and II or even after step III (Fig. 2).
DISCUSSION AND CONCLUSIONS

The results of the experiments described above support earlier work with polycrystalline specimens [6] and show that changes in the behavior of Li\textsuperscript{+} ions occur when Li-Na beta-alumina is heated at temperatures of \(-600\,^\circ\text{C}\) or above. These changes are not caused by the loss of H\textsubscript{2}O, nor are they reversible by re-hydration. The NMR data shows that the mobility of the Li\textsuperscript{+} ions, and hence their contribution to the ionic conductivity, is greatly reduced as a result of annealing above 700\,^\circ\text{C}. Evidence from the X-ray diffraction studies suggests that the changes observed in the magnetic resonance and Raman spectra are caused by the growth of a new phase having a spinel-like structure. The extra reflections observed after heat treatment are consistent with the epitaxial formation of LiAl\textsubscript{5}O\textsubscript{8} in the beta-alumina structure.

We believe that this work provides the first experimental evidence that lithium ion diffusion in beta-alumina is not confined to the conducting plane. Our experimental results can be explained with the following model. The Li-Na beta-alumina structure formed by ion exchange at moderate temperature [3] is inherently unstable at elevated temperatures. Stabilization occurs by diffusion of Li\textsuperscript{+} out of the conducting plane and into the interstices between the close packed oxygen layers of the spinel block. When complete, this Li\textsuperscript{+} diffusion results in the formation of a spinel-like Li compound such as LiAl\textsubscript{5}O\textsubscript{8}. This formation of a second phase necessitates decomposition of the conducting plane which must occur by Na\textsuperscript{+} diffusion between neighboring unit cells.

The results discussed here help explain the observation [12] that high temperature annealing decreases Li\textsuperscript{+} conductivity in Li\textsuperscript{+} substituted sodium beta-alumina. Our present interpretation suggests that the high Li\textsuperscript{+} conductivity reported [2] for Li-Na beta-alumina may be degraded at elevated temperature by eventual Li\textsuperscript{+} trapping in the spinel block.
REFERENCES


7. Full width at one-half peak height.


**TABLE I**

LINE WIDTH OF THE NARROW LINE $^7\text{Li}^+$ SIGNAL (159 Hz)

<table>
<thead>
<tr>
<th>Step</th>
<th>$\theta=0^\circ$</th>
<th>$\theta=45^\circ$</th>
<th>$\theta=90^\circ$</th>
<th>Annealing(b) Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>405</td>
<td>303</td>
<td>221</td>
<td>350</td>
</tr>
<tr>
<td>II</td>
<td>340</td>
<td>290</td>
<td>136</td>
<td>560</td>
</tr>
<tr>
<td>III</td>
<td>453</td>
<td>258</td>
<td>197</td>
<td>690</td>
</tr>
<tr>
<td>IV</td>
<td>396</td>
<td>306</td>
<td>226</td>
<td>900</td>
</tr>
<tr>
<td>V</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1000</td>
</tr>
</tbody>
</table>

(a) Calculated full width at one-half band maximum measured after each heat treatment.

(b) Treatment times were 4 hrs. for Steps I-IV and 7 hrs. for Step V. Specimens were quickly entered and removed from a furnace operating at the treatment temperature. Insertion and withdrawal times were only about five minutes at the highest treatment temperatures.
### TABLE II

WEIGHT CHANGE AFTER HEAT TREATMENT

<table>
<thead>
<tr>
<th>Step</th>
<th>% Weight Loss</th>
<th>Annealing Temperature (°C)</th>
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<tbody>
<tr>
<td>I</td>
<td>0.22</td>
<td>350</td>
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<tr>
<td>II</td>
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<td>560</td>
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<tr>
<td>III</td>
<td>0.07</td>
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</tr>
<tr>
<td>IV</td>
<td>0.03</td>
<td>900</td>
</tr>
<tr>
<td>V</td>
<td>0.02</td>
<td>1000</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1. $^7$Li Free Induction Decay (FID) curves at 25°C obtained from (a) untreated (2 pulse/sec), (b) heat treated (2 pulse/sec), and (c) heat treated (1 pulse/5 sec) Li-Na beta-alumina. Larmor frequency equal to 10.5 MHz. The increase $T_1$ of the broad line $^7$Li of (c) makes its presence undetectable in (b) because of the increased pulse rate.

Fig. 2. Fast Li$^+$ intensity versus heat treatment temperature for the stepwise heat treatment experiment. Step I—350°C for 4 hrs., Step II—560°C for 4 hrs., Step III—690°C for 4 hrs., Step IV—900°C for 4 hrs., Step V—1000°C for 7 hrs.

Fig. 3. Observed linewidth versus temperature for single crystal and polycrystalline [6] Li-Na beta-alumina before heat treatment. The strong motional narrowing observed is indicative of fast Li$^+$.

Fig. 4. Raman scattering from a 95% Li$^+$ substituted single crystal of beta-alumina before (a) and after (b) heat treatment at 800°C in vacuum for 1 hr.

Fig. 5. Infrared transmission spectra of a 90% Li$^+$ substituted single crystal of beta-alumina. The infrared light was incident on the 001 face. The curves are measurements made on the as-prepared sample (a) and after heating in vacuum for (b) 1 hr. at 500°C, (c) 1 hr. at 600°C, and (d) 9 hrs. at 600°C.

Fig. 6. Unfiltered X-ray precession patterns for heat treated Li-Na beta-alumina. The arrows indicate extra reflections caused by the spinel-like Li compound formed during heat treatment. The reflection indices for the cubic phase are: upper pattern—upper right (333), lower right (115), center (004), left (115); lower pattern—upper (113), lower (333).
Fig 2.
UNTREATED SINGLE CRYSTALS
UNTREATED POLY-CRYSTALS
Fig. 5

$Na_{0.1}Li_{0.9}B\text{-}Al_2O_3$

$T = 300^\circ K$