**Title:** Diffusion Noise in Annealed Na, Ag and Pb Beta Aluminas (UNCLASSIFIED)

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DIFFUSION NOISE IN ANNEALED Na, Ag, AND Pb$\beta$ALUMINA

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Abstract

Conductivity fluctuations in Pb$\beta$alumina arising from diffusion of the mobile ions are observed to increase linearly with annealing time at a temperature of 130$^\circ$C after quenching from 550$^\circ$C. Simultaneously, the conductivity as measured by Nyquist noise decreases linearly. No effect of annealing on conductivity fluctuations or conductivity is found for either Na$\beta$alumina or Ag$\beta$alumina. The increase in conductivity fluctuations for Pb$\beta$alumina can be interpreted in terms of a decrease in effective ion density for diffusion noise.

INTRODUCTION

Several x-ray and neutron crystal structure studies$^1$ of the $\beta$aluminas have presented evidence for two-dimensional ordering of the mobile ions in the conduction planes, with room temperature coherence lengths ranging from 10 to 200$\AA$. In the case of Na$\beta$alumina, the change in coherence length with temperature accounts reasonably well for the non-Arrhenius behavior of the conductivity$^2$. It has been observed that annealing heat treatment can introduce changes in site occupancies by the mobile ions and in the long-range order$^3$. For example, while rapidly-cooled Pb$\beta$alumina has the highest room temperature conductivity of the divalent $\beta$aluminas, slow cooling or annealing at modest temperatures (130$^\circ$C) leads to decreases in conductivity of many orders of magnitude$^4$.

Conductivity fluctuations in the $\beta$aluminas$^5,6$ are ascribed to diffusion noise of the mobile ions. The magnitude of the noise is
much greater and the temperature dependence different from that predicted by the standard expression for diffusion noise, and these discrepancies may be a result of correlation effects between the mobile ions. Experimentally observed diffusion noise is similar for different mobile ion species, but differs quantitatively, which also could be attributable to differences in ionic correlations.

This study examines the effect of annealing heat treatments on conductivity fluctuation diffusion noise in single crystal and ceramic Na, Ag, and PbB' alumina. These mobile ion species are chosen because of the differences in correlations between the ions and because of the expected differences in the effect of annealing upon correlation effects. The experimental work is facilitated by the ease with which mobile ions can be exchanged in the B' alumina structure.

EXPERIMENTAL TECHNIQUE

Sodium B' alumina (90.4% Al₂O₃, 8.85% Na₂O, 0.75% Li₂O) ceramic specimens and single crystals approximately 5x5x0.5 mm³ are converted to AgB' alumina or PbB' alumina by ion exchange in molten 50% AgNO₃/NaNO₃ at 300°C for 8 hours or by immersion in molten PbCl₂ at 550°C for 24 hours under a partial pressure of oxygen. Weight change of the converted samples indicates essentially complete exchange of silver or lead ions for the mobile sodium ions. The corners of the samples are sealed into the sides of four plastic test tubes containing appropriate liquid electrode materials to provide diagonally opposing corner current contacts and transverse noise contacts. This configuration reduces the possible influence of contact current noise on conductivity fluctuations observed at the transverse contacts.

Low noise, ohmic contacts are provided by 0.5M NaI propylene carbonate solution, 5M AgNO₃ aqueous solution, or saturated aqueous Pb(NO₃) in the four test tubes. In each case, contact noise is negligible after aging for several hours. Transverse noise voltages
are measured with a PAR 113 preamplifier and a digital FFT PC analyzer\textsuperscript{14}.

Before mounting, each sample is heated in a Helium atmosphere at 550°C and quenched by surrounding it with a water-cooled metal sleeve. Some samples are heated in air and quenched on a metal block to increase the cooling rate. The samples are then annealed in air at 130°C for various times up to 30 hours. Periodically, the Nyquist noise and diffusion noise levels are determined after pouring the appropriate electrode solution into the test tubes. Fresh electrode solution is used after each annealing interval.

EXPERIMENTAL RESULTS

Typical experimental noise spectra for Na\textsuperscript{+}alumina and Ag\textsuperscript{+}alumina are shown in Figures 1 and 2. These data are in good agreement with previous results\textsuperscript{5} in that the conductivity determined from the Nyquist noise level agrees with literature values, and the -3/2 slope of the conductivity fluctuation spectra is characteristic of diffusion noise. In neither case is there a difference in either Nyquist noise or diffusion noise resulting from annealing.

The results are quite different for Pb\textsuperscript{2+}alumina, Figures 3 and 4. Here both the Nyquist noise level (hence the resistivity) and the diffusion noise level are observed to increase linearly with annealing time. The Nyquist noise level before annealing is considerably greater than that calculated from the sample dimensions and literature values of the conductivity. Single crystals do not exhibit this discrepancy\textsuperscript{6}, which may mean that the lead ions are not uniformly distributed in the ceramic samples.
DISCUSSION

In one dimension, the standard expression for the noise voltage spectral density, $S(V,f,T)$, of conductivity fluctuations due to diffusion is $^7$

$$
\frac{S(V,f,T)}{V^2} = 2 \frac{\langle \Delta N^2 \rangle}{N^2} \left( \frac{2D}{L^2} \right)^{1/2} \left[ 1 - \exp(-r)(\cos r + \sin r) \right] \omega^{-3/2}
$$

$$
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \qua
On this basis, annealing heat treatments that increase the mobile ion order are expected to influence both the Nyquist noise level, through a decrease in conductivity, and the diffusion noise level, as observed. The absence of either effect in Na and AgB\textsuperscript{2+}alumina means that annealing does not lead to such ordering in these materials.

Equation (2) may be used to calculate an effective ion density from the experimental data. It is assumed that the measured change in conductivity results from a decrease in the diffusion constant with annealing time and the diffusion constant is determined using the Einstein relation,

\[ D = \frac{(kT/e)\mu}{kT/ne^2} \sigma \]  

where \( k \) is Boltzmann's constant, \( T \) is the temperature, \( e \) is the electronic charge, \( \mu \) is the ionic mobility and \( \sigma \) is the conductivity. The calculated effective ion density decreases with annealing, as shown in Figure 5 for two different PbB\textsuperscript{2+}alumina ceramic samples.

The decrease in effective ion density seems to be conceptually in keeping with ordering of the mobile ions. A more quantitative understanding awaits a treatment of diffusion noise that accounts for correlations between the mobile ions. In addition, it is important to repeat the experiments with PbB\textsuperscript{2+}alumina single crystals to eliminate the possible disturbing influence of grain boundaries.

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FIGURE CAPTIONS

Figure 1. Nyquist noise and diffusion noise spectra of a NaB"alumina single crystal after quenching from 550°C and after annealing for 6 hours at 130°C.

Figure 2. Nyquist noise and diffusion noise spectra of a AgB"alumina ceramic sample after quenching from 550°C and after annealing at 130°C for 30 hours.

Figure 3. Nyquist noise and diffusion noise spectra of a PbB"alumina ceramic sample after quenching from 550°C and after annealing at 130°C for 12.5 hours.

Figure 4. Increase in diffusion noise and Nyquist noise with annealing time for two PbB"alumina ceramic samples.

Figure 5. Decrease in effective ion density with annealing time for the same samples as in Figure 4.
Figure 1

Noise Spectral Density
in Volts²/Hertz

FREQUENCY IN HERTZ

10⁻¹⁶
10⁻¹⁴
10⁻¹²
10⁻¹⁰

Na β" Alumina Single Crystal

Annealing Time (hours)

- 0
- 6

Figure 1
Figure 2
Figure 3

Annealing Time (hours)

\[ I = 38 \mu A \]

\[ I = 0 \mu A \]

\[ Pb \beta'' \text{ Alumina Ceramic} \]
Figure 4
Figure 5

Pb Ceramic

Sample #2

Sample #3

Effective Ion Density (cm⁻³)

Annealing Time (hours)
END
DATE
FILMED
9-88
DTIC