Conductivity fluctuations and contact noise observed in ceramic and single crystal silver $\beta''$ alumina are very similar to those in sodium $\beta''$ alumina. The current noise spectral density varies as $f^{-3/2}$, indicative of diffusion noise, and is thermally activated with an activation energy of 0.5 eV, significantly smaller than for sodium $\beta''$ alumina. In both materials, single crystal specimens are noisier than the ceramics and the granular nature of the ceramics does not seem important in the diffusion noise process. The standard expression for diffusion noise is unable to account for either the observed noise magnitude or the temperature dependence.
CURRENT NOISE IN SODIUM 6° ALUMINA CERAMICS AND SINGLE CRYSTALS

by

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ABSTRACT

Conductivity fluctuations and contact noise observed in ceramic and single crystal silver $\beta''$ alumina are very similar to those in sodium $\beta''$ alumina. The current noise spectral density varies as $f^{-3/2}$, indicative of diffusion noise, and is thermally activated with an activation energy of 0.5 eV, significantly smaller than for sodium $\beta''$ alumina. In both materials, single crystal specimens are noisier than the ceramics and the granular nature of the ceramics does not seem important in the diffusion noise process. The standard expression for diffusion noise is unable to account for either the observed noise magnitude or the temperature dependence.

I. INTRODUCTION

Conductivity fluctuations in ceramic\textsuperscript{1} and single crystal\textsuperscript{2} sodium $\beta''$ alumina have been attributed to diffusion noise of the mobile sodium ions. The observed current noise levels appear to be similar for both polycrystalline samples and single crystal specimens, indicating that grain boundary effects are not important. In both cases, the measured noise levels are much greater and the temperature dependence is much stronger than can be accounted for by the standard expression for diffusion noise\textsuperscript{3}. Preliminary
results on silver β" alumina ceramics show conductivity fluctuations very similar to those observed in the sodium conductors. The present work examines current noise in a wider range of polycrystalline silver samples and in single crystals in order to establish more firmly the similarities and differences between the diffusion noise properties of silver and sodium ions in the β" alumina structure.

II. EXPERIMENTAL TECHNIQUE

The experimental approach is essentially identical to that employed in the case of sodium β" alumina, and is facilitated by the ease with which silver ions can be exchanged for sodium ions in this structure. Both commercial sodium β" alumina ceramic (90.4% Al₂O₃, 8.85% Na₂O, 0.75% Li₂O) specimens and single crystals are converted to silver β" alumina by ion exchange in molten 50% AgNO₃/NaNO₃ at 300°C for eight hours. Weight change of the samples indicates 98% of the mobile sodium ions are replaced by silver ions.

The corners of square ceramic samples 1x1x0.3 cm³ are sealed into the sides of four plastic test tubes holding liquid electrodes to provide diagonally opposing corner current terminals and transverse noise contacts. Satisfactory low noise ohmic contacts are 5-M AgNO₃ solution in water or 0.05-M AgNO₃ solution in glycerin. Single crystal samples are smaller than ceramic specimens but large enough to make the same technique possible. The same noise apparatus employed in previous studies consisting of a PAR 113 preamplifier and a digital FFT analyzer is used to measure noise signals at the various contacts.
III. NOISE SPECTRA

Typical contact noise (i.e., I=0) and transverse current noise spectra for a ceramic specimen and for two different electrode materials are illustrated in Fig. 1. Both electrode materials produce low contact noise, although occasionally much greater low-frequency noise levels are observed, as shown. Significantly, the transverse current noise levels are seen to be independent of electrode material and contact noise levels as expected for a bulk noise effect. The slope of the bulk current noise spectrum is near -1.5, characteristic of diffusion noise, and the high frequency noise is attributable to Nyquist noise of the sample. In all respects, these results are essentially the same as for sodium \( \beta^n \) alumina\(^1\), except that measured noise voltages are one to two orders of magnitude greater.

Low frequency contact noise arises from nonequilibrium chemical reaction noise\(^7\) and aging effects similar to those in sodium \( \beta^n \) alumina are observed. Current noise in silver \( \beta^n \) alumina is much more stable with respect to time, and only relatively minor changes attributable to electrochemical effects are seen. Also, as shown in Fig. 2, transverse and longitudinal (two-terminal) current noise levels are the same, which means that contact current noise effects are small compared to bulk conductivity fluctuations, a rather surprising result in view of the presence of contact noise and in distinct contrast to the results for sodium \( \beta^n \) alumina.

Essentially identical results are found for single crystal specimens. Also, the absence of contact current noise enables examination of tiny single crystals by two-terminal noise measurements. For example, Fig. 3 shows
noise spectra for a 0.5x0.3x0.1 cm$^3$ crystal. In all cases, the current noise levels are stable, show a spectral shape of $f^{-3/2}$, and increase as the square of the current.

A few ceramic specimens inadvertently heated to high temperatures (800°C) for several hours experienced a decrease in room temperature conductivity by factors of four to five, together with a darkening of the surface. This effect has previously been reported$^8$, but no chemical or structural change has been detected to account for the decrease in conductivity. The current noise spectra of darkened samples are similar to those of the normal ceramic, except that the noise levels are lower.

IV. TEMPERATURE DEPENDENCE

As in the case of sodium $\beta''$ alumina, the various noise processes are thermally activated in both ceramic and single crystal specimens, Fig. 4. Experimentally determined activation energies and noise levels are tabulated in Table I to facilitate comparison with sodium $\beta''$ alumina results. The sign of the activation energy for contact noise is consistent with a thermally-activated chemical reaction at the contacts$^7$, but there is no apparent reason for the difference between ceramic and single crystal samples. Unfortunately, comparable data for sodium $\beta''$ alumina is not available, due principally to the unstable contact noise levels in this material.

The activation energies for Nyquist noise agree with conductivity values$^5,8,9$ for both single crystal and ceramic specimens and for both silver and sodium $\beta''$ alumina. That for the darkened ceramic also follows
<table>
<thead>
<tr>
<th>Sample</th>
<th>$S(V,1)/V^2$ Hz$^{-1}$</th>
<th>Activation Energy, eV</th>
<th>Contact Noise</th>
<th>Nyquist Noise</th>
<th>Current Noise</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag Ceramic (Darkened)</td>
<td>1.0x10$^{-12}$</td>
<td>-0.96</td>
<td>0.18</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.3x10$^{-14}$</td>
<td>-</td>
<td>0.22</td>
<td>0.61</td>
<td></td>
</tr>
<tr>
<td>Ag Single Crystal (Two Terminal)</td>
<td>7.4x10$^{-12}$</td>
<td>-1.81</td>
<td>0.16</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.8x10$^{-11}$</td>
<td>-0.76</td>
<td>0.16</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>Na Ceramic</td>
<td>5.0x10$^{-13}$</td>
<td>-</td>
<td>0.30</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Na Single Crystal</td>
<td>7.3x10$^{-12}$</td>
<td>-</td>
<td>0.33</td>
<td>1.3</td>
<td></td>
</tr>
</tbody>
</table>

TABLE I

CERAMIC AND SINGLE CRYSTAL NOISE
from conductivity data. The activation energy for current noise is much smaller in silver \(\beta^s\) alumina than in sodium \(\beta^s\) alumina, and single crystal and ceramic data are consistent in both cases.

The first column in Table I compares the relative noise levels of the various samples by forming the ratio of the conductivity fluctuation spectral noise power density \(S(V,1)\) at a frequency of one Hertz to the square of the dc voltage across the sample, \(V^2\). This is a satisfactory approach apart from sample geometry effects which are expected to be small. On this basis, the relative current noise power is significantly greater in the case of single crystals for both materials and the silver conductors are somewhat noisier than the sodium counterparts. The relative current noise power is least in darkened silver \(\beta^s\) alumina. The greater stability of measured noise in the case of silver \(\beta^s\) alumina compared to sodium materials makes the observed difference between single crystals and ceramic specimens much more certain than previous results.

V. DIFFUSION NOISE

In all cases the noise spectra are consistent with the universal \(3/2\) power law for diffusion noise. The spectral density, \(S(V,f)\), can be written

\[
\frac{S(V,f)}{V^2} = 4 \frac{\langle \Delta N^2 \rangle}{N^2} \left(\frac{D}{2L^2}\right)^{1/2} \omega^{-3/2}
\]

where \(\langle \Delta N^2 \rangle\) and \(N\) are the variance and average number of the diffusing species, \(D\) is the diffusion constant, \(L\) is a characteristic length and
\( \omega \) is the angular frequency. This expression is valid above a characteristic frequency, \( \omega_0 \), such that

\[
\omega_0 = \frac{2D}{L^2}
\]  

(2)

Below \( \omega_0 \) the spectrum flattens, becoming a constant in the case of three dimensional diffusion.

No departure from the 3/2 power law is seen in the experimental data for either single crystal or ceramic specimens at frequencies as low as \( 10^{-3} \) Hz. If the characteristic length \( L \) were equal to the average grain size \( 5 \times 10^{-4} \) cm, in ceramic samples, and taking \( D=10^{-7} \) cm\(^2\)/sec at room temperature, then the turnover frequency calculated from Eq. (2) is \( 0.13 \) Hz, which is not observed. Taking \( L \) equal to the sample length, 1 cm, the characteristic frequency becomes \( 3 \times 10^{-8} \) Hz, well below the range of investigation. Thus it appears that the granular nature of the ceramic specimens is not important in the diffusion noise process. This is consistent with the rather unusual result that single crystal specimens are noisier than the ceramics.

As in the case of sodium \( \beta^\prime \) alumina\(^{1,2} \), the measured noise levels are many orders of magnitude greater than predicted by Eq. (1). Furthermore, the sign and the magnitude of the temperature dependence cannot be easily accounted for either. The approach used in the case of sodium \( \beta^\prime \) alumina that the number of diffusing ions is thermally activated\(^1 \) is not quantitatively successful for either ceramic or single crystal silver \( \beta^\prime \) alumina. These results suggest that the deficiencies in Eq. (1) may arise
from ignoring possible correlation effects between diffusing ions. Such
correlations are expected to be considerable at the ion densities in these
materials, \(10^{22} \text{ cm}^{-3}\). If this approach is correct, then correlation effects
must also be able to account for the observed differences between ceramics
and single crystals as well as between the two materials.

VI. ACKNOWLEDGMENTS

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REFERENCES


6. Obtained from Ceramatec, Inc., Salt Lake City, Utah 84115.


FIGURE CAPTIONS

Fig. 1  Contact noise and transverse current noise of silver β" alumina ceramic with two different liquid electrodes.

Fig. 2  Transverse and longitudinal noise of a silver β" alumina ceramic with aqueous AgNO₃ electrodes.

Fig. 3  Noise spectra of a small, two-terminal single crystal sample.

Fig. 4  Temperature dependence of Nyquist noise (0µA, 5kHz), current noise (70 or 250 µA, 10 Hz), and contact noise (0µA, 10 Hz) for single crystal and ceramic silver β" alumina.
SAMPLE 2

0 µA

250 µA

Aqueous AgNO₃

Glycerin AgNO₃

Figure 1
Figure 2

Noise spectral density in volts^2/Hz

- **0 μA**
- **250 μA**

**SAMPLE 5**

- Transverse
- Longitudinal
Figure 3
Figure 4

NOISE SPECTRAL DENSITY IN VOLTS$^2$/HERTZ

$10^3 \frac{T}{T}$ IN °K$^{-1}$

- Singal Crystal
- Normal Ceramic
END

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