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Chu Kun Kuo and James J. Brophy

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**Department of Physics
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Salt Lake City, UT 84112**

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CONDUCTIVITY FLUCTUATIONS IN MIXED Na/Ca β'' ALUMINA

by

Chu Kun Kuo* and James J. Brophy
Physics Department
University of Utah
Salt Lake City, Utah 84112

ABSTRACT

Conductivity fluctuations in mixed Na/Ca β'' alumina ceramics for different values of the Na/Ca ratio are observed to be similar to diffusion noise of the mobile ions seen in Na, Ag, and Pb β'' alumina. Measured noise levels increase two orders of magnitude in changing from 100% Na to 100% Ca ions in the structure. In mixed Na/Ca ceramics the noise is greater for NaI solution current electrodes than for CaBr_2 solution current electrodes. These differences are attributed to different correlation effects between the mobile ions.

INTRODUCTION

Experimental measurements of current noise in sodium¹, silver², and lead³ β'' alumina are characteristic of conductivity fluctuations arising from diffusion noise of the mobile ions. The observed differences in noise levels between the mobile ion species and the fact that the observed noise levels are much greater than can be accounted for by the standard expression for diffusion noise⁴ is attributed to correlation effects between the mobile ions. There is as yet little quantitative understanding of the phenomenon, however.

Crystal structure studies⁵ of the β'' aluminas have presented evidence for two-dimensional ordering of the mobile ions in the conduction planes. In the case of Na β'' alumina, the change in coherence length with temperature accounts reasonably well for the non-Arrhenius behavior of the conductivity⁶. Similarly, non-linear Arrhenius plots in the case of Ca β'' alumina are attributed to order-disorder interactions among the mobile ions and vacancies, which are expected to strongly influence the rates of ion/vacancy diffusion⁷.

The present study examines the conductivity and the conductivity fluctuations of mixed Na and Ca ions in the β'' alumina structure. The presence of mixed monovalent-divalent mobile ion compositions is expected to alter significantly ion/ion correlations and the diffusion noise levels. Correspondingly, experimental determination of diffusion noise

provides new information about the ionic interactions. The work is facilitated by the ease with which mobile ion species can be exchanged in β'' -alumina.

EXPERIMENTAL TECHNIQUE

Sodium β'' -alumina (90.4%, Al_2O_3 , 8.85% Na_2O , 0.75% Li_2O) ceramic specimens⁸ approximately $0.5 \times 0.5 \times 0.15 \text{ cm}^3$ are ion exchanged by immersion in a calcium chloride-calcium nitrate eutectic melt (43:57 by mole) at 550°C for times ranging from 0.25 to 48 hours. The samples are then annealed in air at 550°C for five hours and subsequently at 800°C for three hours to homogenize the calcium distribution. As discussed below, further annealing at 800°C for six hours does not change the measured noise properties, indicating that the Na/Ca distribution is homogenous after the three-hour treatment.

This is confirmed by electron microbeam analysis of the samples⁹. As summarized in Table 1, the measured $\text{Ca}/(\text{Ca}+\text{Na})$ mole ratio increases with exchange time and is substantially the same in the center compared to the edge of the sample, except in the case of the 48-hour exchange sample. In the latter case there exists a very calcium-rich surface layer which is not reduced by the 800°C heat treatment, suggesting prepenetration of the exchange melt into the ceramic. The $\text{Ca}/(\text{Ca}+\text{Na})$ mole ratio at the center of the 48-hour sample is essentially the same as the (uniform) ratio of the three-hour exchange sample, which indicates that the calcium ion exchange in the three-hour sample is complete.

For noise measurements, the corners of the square samples are sealed into sides of four plastic test tubes containing appropriate liquid electrode materials. In the case of mixed Na/Ca specimens, test tubes at diagonal corners are filled with a solution of NaI in propylene carbonate and a solution of CaBr_2 in propylene carbonate, respectively. This permits comparison of Nyquist noise measurements at the sodium electrodes with those at the calcium electrodes and transverse current noise measurements with current introduced at either the sodium or calcium electrodes. Sodium β'' -alumina samples are provided with four NaI electrodes, and Ca β'' -alumina samples (three-hour exchange) with four calcium bromide electrodes.

Noise measurements are undertaken using a PAR 113 preamplifier and a digital FFT analyzer. Both electrode solutions yield low noise contacts after aging for twenty-four hours such that bulk Nyquist noise of the samples is observed at frequencies above about three Hertz. All measurements are carried out at room temperature.

EXPERIMENTAL RESULTS

Typical Nyquist noise and current noise spectra are illustrated in Figures 1 and 2 for a mixed Ca/Na sample and for a Ca β ''alumina sample. Both types of spectra are similar to those seen for the other β ''aluminas^{1,2,3}. The room temperature conductivity of Ca β ''alumina calculated from the Nyquist noise level in Figure 2 using the Nyquist expression and sample dimensions is $8.3 \times 10^{-7} \text{ (ohm-cm)}^{-1}$, about forty percent less than single crystal data⁷. This close agreement indicates that grain boundary effects are minimal in these ceramic samples.

In the case of mixed ion samples the observed Nyquist noise level is essentially the same for the sodium electrodes as for the calcium electrodes and the conductivity calculated from the measured Nyquist noise is strongly dependent upon the Na/Ca ratio, as shown in Figure 3. The precipitous drop in conductivity for small percentages of the calcium ion has been reported previously¹⁰ for Ca β ''alumina. In Figure 3 the calcium percentages have been calculated from Table 1 taking the Ca/(Ca+Na) ratio of 14.8 to represent 100% calcium.

Nyquist noise measurements can also be used to monitor the annealing process after ion exchange. For example, the noise level of all samples is very large after exchange but before annealing, suggesting a high-resistance calcium-rich surface layer. The noise level drops orders of magnitude after the first heat treatment, but is not changed by the second anneal.

All current noise spectra vary as $f^{3/2}$, characteristic of diffusion noise⁴ and vary as the square of the current, indicating conductivity fluctuations. As seen in Figure 1, the observed transverse noise levels are larger when current is introduced through the sodium contacts compared to when the calcium electrodes are the current contacts.

DISCUSSION

The standard expression for the noise voltage spectral density, $S(f,V,T)$, arising from diffusion is given by⁴

$$\frac{S(V,f,T)}{V^2} = \frac{2}{N} \left(\frac{2D}{L^2} \right)^{1/2} \omega^{-3/2} \quad (1)$$

where V is the applied voltage across the sample, N is the number of diffusing ions, D is the diffusion constant, L is the sample length, and ω is the angular frequency. Equation (1) applies above a characteristic angular frequency given by $2D/L^2$ and Poisson statistics are assumed.

Inserting known values into Eq.(1) results in predicted noise levels that are many orders of magnitude smaller than those observed experimentally¹. The discrepancy is attributed to correlation effects between the mobile ions because the analysis leading to Eq.(1) assumes independent diffusing entities. In order to compare experimental results, it is useful to calculate an effective ion density from the data using Eq.(1). Since the diffusion constants for Na/Ca mixtures are not readily available, it is assumed that the variation in conductivity with calcium content shown in Figure 3 results from changes in an effective diffusion constant which can be calculated from the Einstein relation

$$D = (kT/e)\mu = (kT/ne^2)\sigma \quad (2)$$

where k is Boltzmann's constant, e is the electronic charge, μ is the ionic mobility, σ is the conductivity, and n is the mobile ion density, taken to be 10^{21} cm^{-3} .

The results of this approach are shown in Figure 4. The effective ion density decreases rapidly with increasing concentration of calcium mobile ions and is much smaller for the situation in which sodium ions are injected into mixed Na/Ca specimens at the sodium current electrodes compared to injection of calcium ions. Under the rather crude assumption that a smaller effective ion density implies greater mobile ion correlations, these results suggest that correlations are greater in $\text{Ca}\beta''$ -alumina than in $\text{Na}\beta''$ -alumina but that introducing calcium ions into Na/Ca mixed ion conductors reduces correlation effects. Further quantitative interpretation awaits development of an expression analogous to Eq.(1) in which ion-ion correlations are explicitly taken into account.

The change in conductivity with calcium content in Figure 3 does not give any indication of the mixed alkali effect, which predicts that the conductivity passes through a minimum as the calcium concentration increases¹¹. Previous results¹⁰ at 300°C show a slight minimum and the effect would be expected to be enhanced at the lower temperatures pertinent to the present results.

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* On leave from the Shanghai Institute of Ceramics, Chinese Academy of Sciences.

TABLE 1

Exchange Time Analysis

Exchange Time In Hours	Ca/(Ca+Na)	
	Center	Edge
0	0	0
0.25	3.13	4.56
1.5	3.92	3.92
3.0	13.4	14.6
48.0	14.8	432.0

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FIGURE CAPTIONS

1. Nyquist and diffusion noise spectra of a mixed Na/Ca β ''alumina ceramic.
2. Nyquist and diffusion noise spectra of Ca β ''alumina ceramic.
3. Conductivity of mixed Na/Ca β ''alumina as a function of the concentration of calcium ions.
4. Effective ion density of mixed Na/Ca β ''alumina as a function of the concentration of calcium ions.

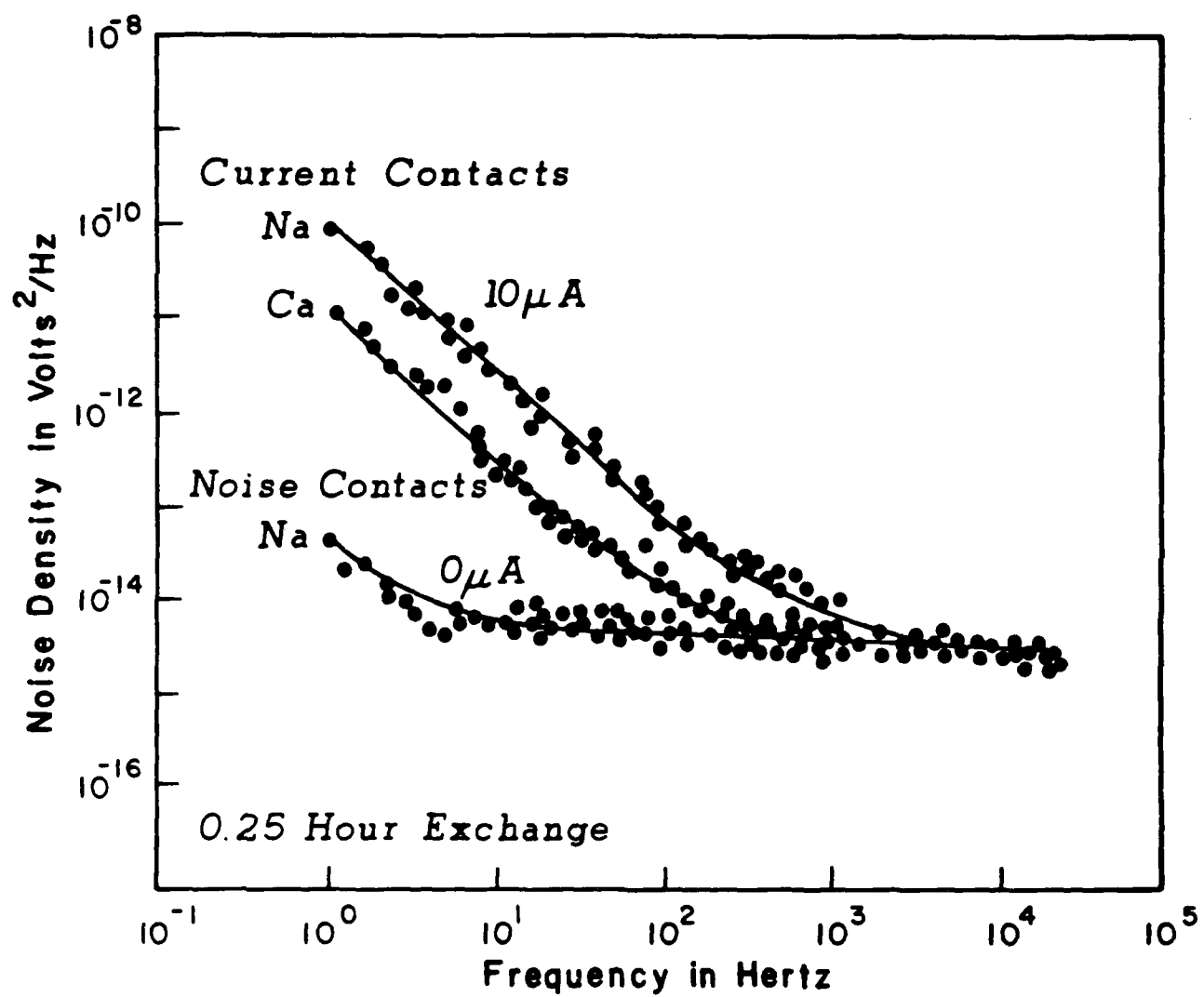


Figure 1

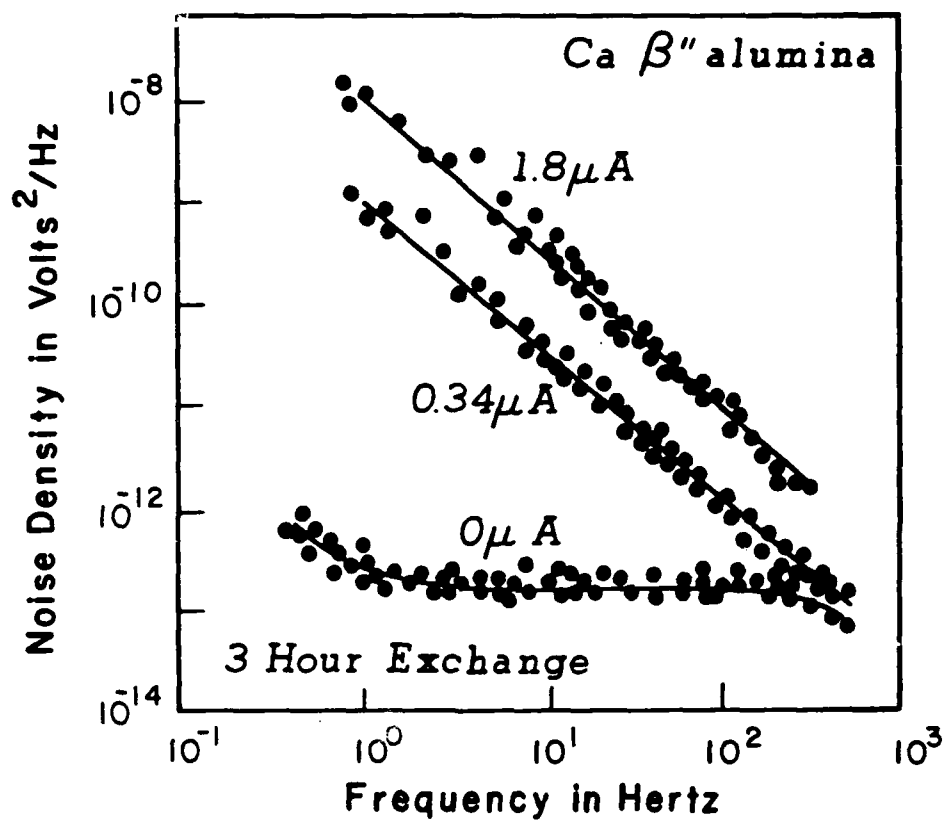


Figure 2

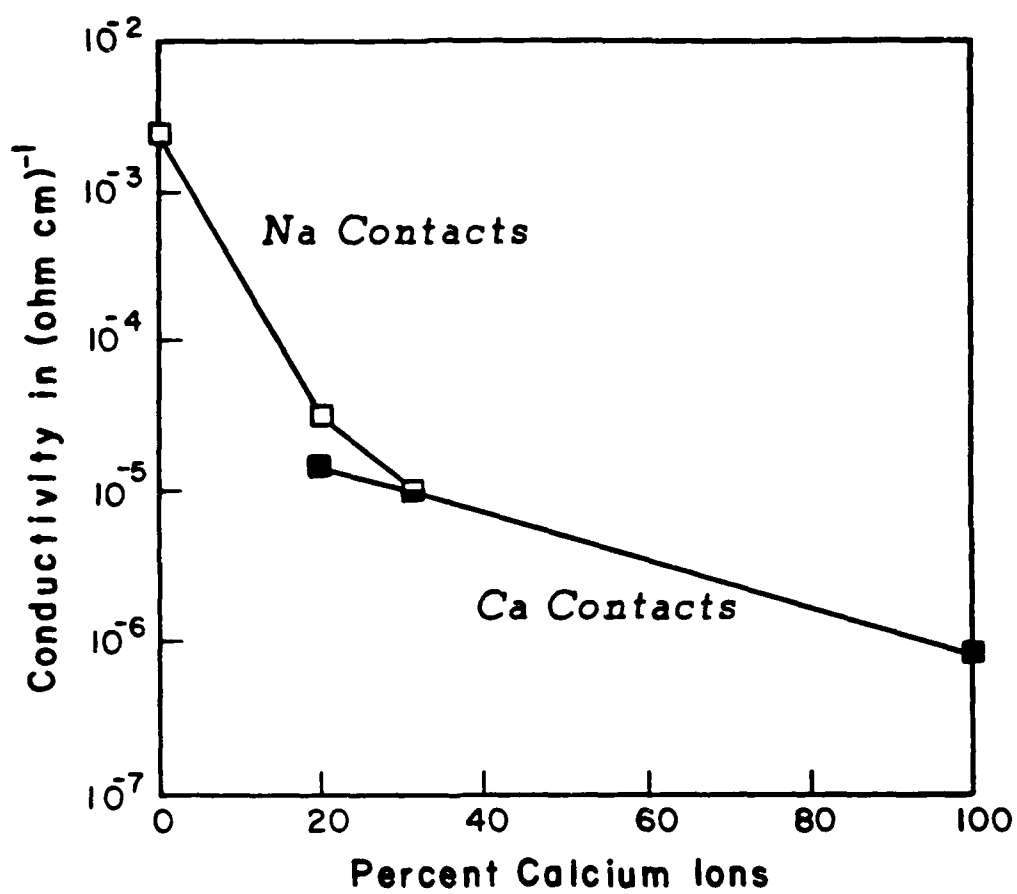


Figure 3

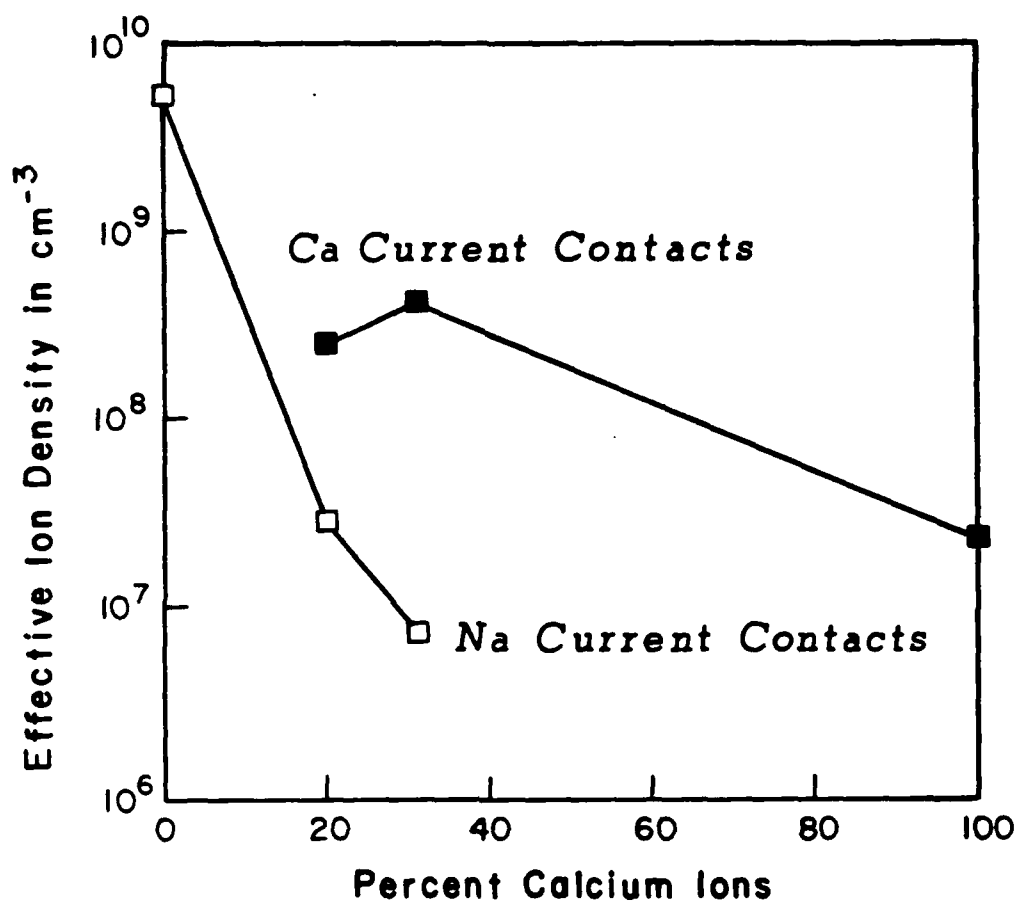


Figure 4