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## **The Dispersion of Dielectric Constant and Resistivity in Stannic Oxide Ceramics<sup>1</sup>**

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In recent years there have been many studies made of the electrical properties of metal oxides in crystalline, thin film, and pressed powder forms. Extensive work has been done at Oklahoma State University on both natural and artificial stannic oxide crystals (Kohnke, 1962) and the investigation is presently being extended to include stannic oxide in ceramic form. This paper presents the results of a preliminary study of these ceramics. In this study, electrical measurements were made that might indicate the effects dependent upon differences in the physical characteristics of a ceramic and a single crystal. Before evaluating the measurements, the techniques of forming and firing suitable samples will be reviewed since these constituted a large part of the preliminary study.

In general, the forming and firing of a ceramic body is a technological problem involving several variables. The first problem was to find a

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procedure to produce compact unfired samples from the stannic oxide powder. The best results were obtained when the dry powder was mixed in a slurry with acetone, dried for 24 hours, and pressed in small disks using pressures from 10,000 to 15,000 p.s.i. The resultant samples, which were very cohesive and had densities of about 4 gm/cc, were then placed in an alumina dish to be fired.

When firing a ceramic there are four main variables that determine the maturity of the sample: 1) amount and kind of impurity in the powder; 2) nature of the heat treatment before and after the maximum firing temperature; 3) maximum firing temperature; and 4) time at the maximum firing temperature. Fig. 1 shows the relationship of relative density (the ratio of the measured density to the theoretical density) to firing time at a fixed temperature of 1246C. Using the experimental lattice parameters of  $a = 4.72 \text{ \AA}$  and  $c = 3.16 \text{ \AA}$  (Wyckoff, 1951), the theoretical density was calculated to be 7.11 g/cc. Fig. 2 shows the relationship of relative density to firing temperature at a fixed time of 4 h. From Figs. 1 and 2, the optimum firing conditions involving the least time and temperature, for the zinc-doped sample can be set at 1350C for 25 h. There appears to be no significant dependence of density on time or temperature for the reagent-grade specimen in this temperature range although Goodman and Gregg (1960) have reported significant powder densification about 1600C. The electrical measurements reported in this paper were made on a representative sample of pure stannic oxide having a relative density of 0.64 and on a sample of doped material having a relative density of 0.91.

When making standard AC bridge measurements of dielectric samples it is customary to characterize the specimen in terms of an equivalent circuit as shown in Fig. 3-a, where  $C$  represents the capacitance and  $R$  the leakage. Measuring this capacitance and resistance as a function of the frequency of the applied field and eliminating geometrical factors leads to values for the dielectric constant and resistivity which are plotted

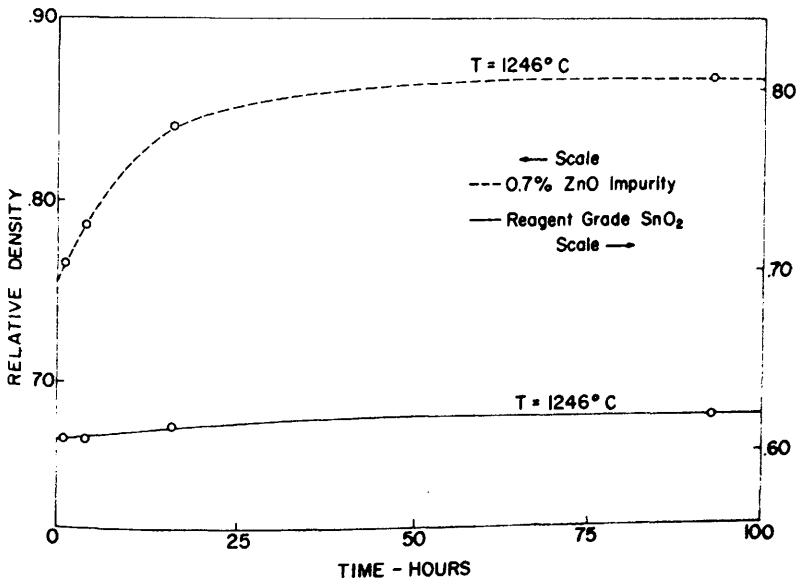


Fig. 1. Relative density and firing times at 1246C.

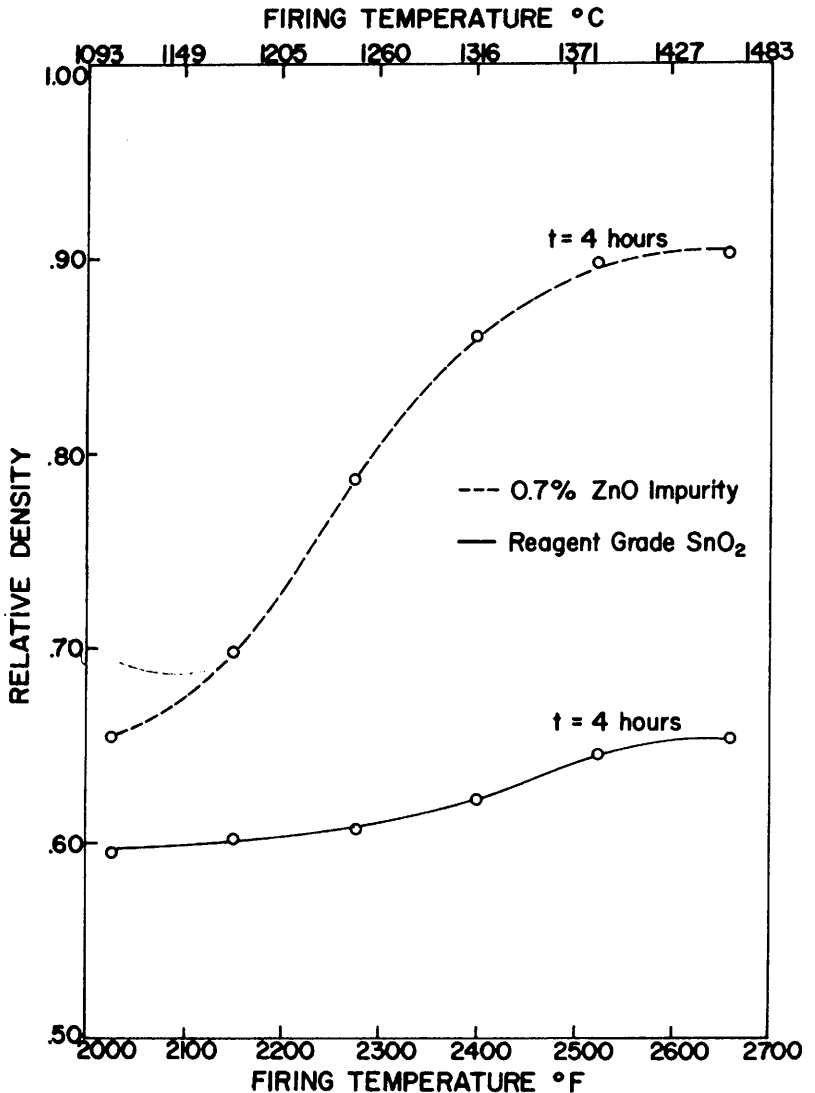


Fig. 2. Relative density and firing temperatures.

as a function of the frequency of the applied field in Figs. 4 and 5 for the two ceramic specimens. When measurements were made on a single crystal grown in the laboratory, however, no dispersion of the dielectric constant and a reduced dispersion in the resistivity were found. This suggests that at least part of the dispersion observed in ceramics may be due to their granular structure as opposed to the regular crystalline structure of the single crystal.

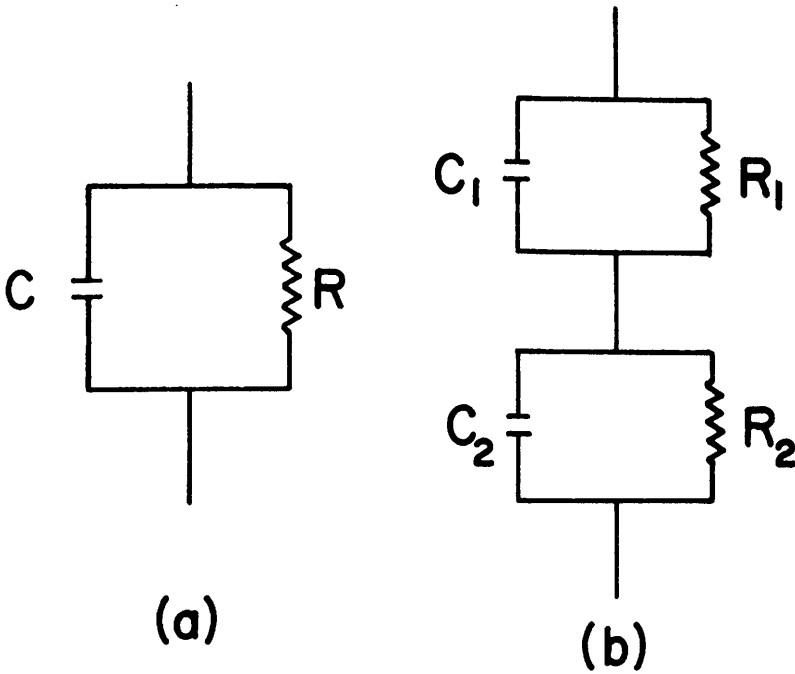


Fig. 3. "Equivalent-circuit" diagrams.

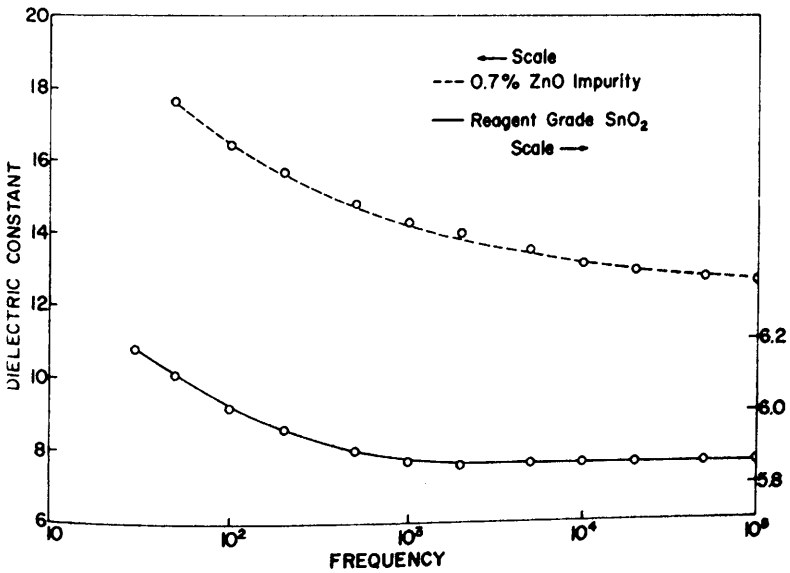


Fig. 4. Dielectric dispersion of specimens.

A ceramic sample may be looked upon as a large number of randomly oriented microcrystals fused together, and Koops (1951) has suggested characterizing the sample by the use of the equivalent circuit shown in Fig. 3-b where  $R_1$ ,  $R_2$ ,  $C_1$ , and  $C_2$  are constants. The merit of this circuit lies in the fact that one may be able to lump all the grain boundary properties qualitatively into the top parallel R-C circuit and all the bulk properties of the grains into the lower circuit, thereby giving these four constants some physical meaning.

Setting the circuit shown in 3-b equivalent to the circuit shown in 3-a, one can obtain expressions for the measured  $R$  and  $C$  in terms of the four constants and frequency and see how these fit the experimental curves. Algebraic manipulations of the expressions shows that if the four-constant circuit of 3-b is equivalent to circuit 3-a then the quantity  $[R(f_1)C(f_1) - R(f_2)C(f_2)]/[R(f_1) - R(f_2)]$  must be a constant for all frequency pairs. Here  $R(f_1)$  and  $C(f_1)$  denote the experimental values of  $R$  and  $C$  evaluated at frequency  $f_1$  from Figs. 4 and 5. From the experimental data it was found for these ceramic samples that the above ratio deviated at most 15% over the measured frequency range indicating that circuit 3-b provides a reasonable, although not exact, equivalency to the experimental results.

It is evident that more complicated equivalent circuits could provide an improved fit since the number of adjustable parameters would be increased. At the present stage of the study, however, it is felt that no useful purpose would be served by increasing the equivalent-circuit complexity since this would tend only to make the physical interpretation of the individual parameters increasingly obscure.

In conclusion it can be said that the experimentally observed dispersion of dielectric constant and resistivity in stannic oxide ceramics can be plausibly explained by the presence of grain-boundary capacitances and resistances in association with the normal capacitances and resistances of the microcrystals themselves. Extensions of this preliminary study must take into account the presence of actual voids in the specimens and make use of additional experimental techniques to explore their intricate microstructure.

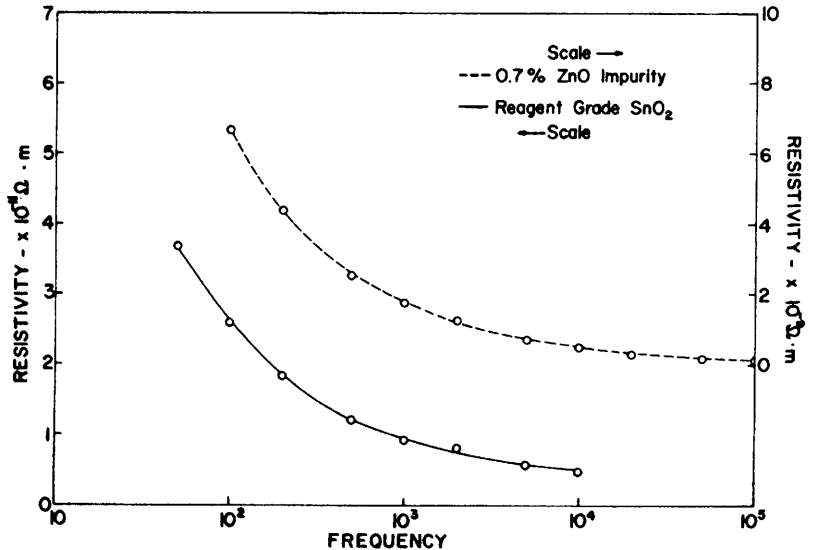


Fig. 5. Dispersion of resistivity in specimens.

## LITERATURE CITED

- Goodman and Gregg. 1960. The production of active solids by thermal decomposition. Part XI. The heat treatment of precipitated stannic oxide. *J. Chem. Soc.* 1960: 1162-67.
- Kohnke, E. E. 1962. Electrical and optical properties of natural stannic oxide crystals. *J. Phys. Chem. Solids* 23: 1557-62.
- Koops, C. G. 1951. On the dispersion of resistivity and dielectric constant of some semiconductors at audiofrequencies. *Phys. Rev.* 83: 121-4.
- Wyckoff, R. W. G. 1951. *Crystal Structure*. Interscience, New York.
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