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Grain Size Dependence of Ionic Conductivity of Polycrystalline Doped Ceria

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Conductivities of polycrystalline ceria doped with several rare earth oxides were measured by AC admittance and DC four probe method. The conductivities were separated into grain and grain boundary contributions using the complex admittance technique as well as grain size dependence of conductivity. The grain size dependence of polycrystalline conductivity, which can be adequately described by the so-called brick layer model, appears to give a more reliable measure of the grain conductivity compared to the complex admittance method. Polycrystalline resistivity (1/conductivity) increases linearly with the reciprocal of grain size The intercept of resistivity vs. inverse grain size plot gives a measure of the grain resistivity and the slope gives a measure of the grain boundary resistivity. It was also noted that errors involved in the analysis of experimental data may be different between the complex admittance method and the impedance method. A greater resolution of the spectra was found in the complex admittance method, insofar as the present work is concerned, suggesting that the commonly used equivalent circuit may require re-evaluation.

Key words: Solid oxide fuel cel, Electrolyte, Ceria, Ionic conductivity, Microstructure, Grain size, Grain boundary

1. Introduction

In polycrystalline ceramic materials, grain boundary effect plays an important role in determining ionic conductivity.[1-4] The influence of the grain boundary effect increases with decreasing temperature. Based on the other studies carried out by D.Y. Wang, K.L. Kliewer *et al.*,[5-8] it has been reported that the grain boundary effect may be governed by (1) dopant size and concentration which affect the site accessibility of impurities related to the strain energy configuration in grain boundaries, (2) impurity or phase segregation which may lead to a lower charge carrier concentration, and (3) static space charge distribution along the grain boundaries. The grain boundary effect can be investigated by studying the effect of a grain size on ionic conductivity because (1) a direct measurement of 'microscopic'[9] grain boundary conductivity is impossible unless the grain bounary thickness is known and (2) the grain boundary thickness varies depending upon grain boundary configuration.[10] A few literature which discuss a 'macroscopic' grain boundary conductivity can be found.[11] However, it was calculated by multiplying the grain boundary resistance obtained from and impedance plot using bulk geometry, that is, cross-sectional area and the thickness of the sample. In that case, it is not suitable to generalize the ionic conduction behavior with the 'macroscopic' grain boundary conductivity as long as the conductivity varies depending upon the grain boundary thickness for a given sample.

The objective of this paper was to investigate the relationship between conductivity (resistivity) and grain size of doped ceria electrolytes. The polycrystalline and grain conductivities will be measured as a function of dopant type, concentration, and grain size using the AC admittance method. Because a direct measurement of 'microscopic'[9] grain boundary conductivity is impossible unless the grain boundary thickness is known, the main focus was on the measurement of polycrystalline and grain conductivities. For studies on the grain size dependence of ionic resistivity and the analysis of activation energies, the so-called brick layer model was empolyed which treats a microstructure by explicitly accounting for the grain boundary conductivity. Grain cconductivity obtained by the two approaches was compared.

II. Experimental Procedure

For the study of grain size dependence of conductivity, samples containing 5 and 13 mol.% of Dy_2O_3 and Er_2O_3 were fabricated using a conventional ceramic process. The samples were heat-treated over a range of temperatures between 1600°C and 1850°C for up to 6 hours to obtain a range of grain sizes. Subsequently, the samples were further annealed at 1500°C for additional 12 hours. This annealing was to ensure that, as far as possible, the only difference between samples within a given set were due to the differences in grain sizes, and not due to any differences in the grain boundary characteristics due to differences in heat treatment temperatures. For example, the objective was to ensure that the degree of

segregation of the dopant at grain boundaries or effects related to space charge distribution were similar. The samples were polished down to a 1 μm finish using diamond plate and thermally etched to reveal the grain boundaries at 1500°C for 1 hour. The grain sizes were measured using the linear intercept method[12] on optical micrographs taken on a Normarski optical microscope. The thermal treatment procedure used resulted in samples with at least 5 to 7 different grain sizes of each doped ceria were made for this part of the study. The AC conductivity was measured between 5 Hz to 13 MHz by a two probe AC complex admittance technique using an AC impedance analyzer (HP4192A).

III. Results and Discussion

3.1 Brick Layer Model

A simplified microstructure of polycrystalline ceria electrolytes can be considered as consisting of cubic grains with grain size, d and a grain boundary with thickness, δ(δ<<d), as shown in Fig. 1(a). Assuming that the simplified microstructure is equivalent to the network of grain resistance and grain boundary resistance, a repeating unit of the microstructure is then made up of two parts as shown in Fig. 1(b):

[1] Grain with a resistance of:

$$R_g = \rho_g \frac{d}{d^2} = \frac{\rho_g}{d} \tag{1}$$

[2] Grain boundaries where all cubic faces of the grain are surrounded by the grain bounary with thickness $\frac{\delta}{2}$. Then, there are two grain boundary contributions depending upon the type of oxygen vacancy conduction:

case (a): Conduction through grain boundaries only, or,

case (b): Conduction through grains and grain boundaries alternatively.

The cases (a) and (b) are illustrated in Fig. 1(b). In case (a), the grain boundary resistance, which is defined by R_{gb}', becomes:

$$R_{gb}' = \rho gb \left(\frac{d}{4\left(\frac{\delta}{2}\right)d} \right) = \frac{\rho_{gb}}{2\delta} \tag{2}$$

and in case (b), the grain boundary resistance, which is defined by R_{gb}'', becomes:

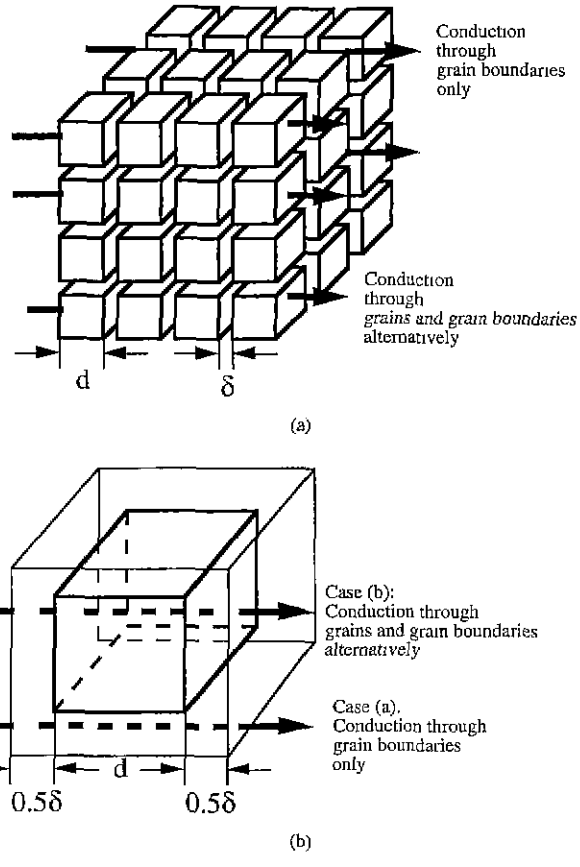

Fig. 1. A simplified microstructure of ceria electrolytes and a corresponding equivalent circuit for the description of brick layer model. (a) A simplified microstructure with grain size, d and grain boundary thickness δ and (b) a repeating unit.

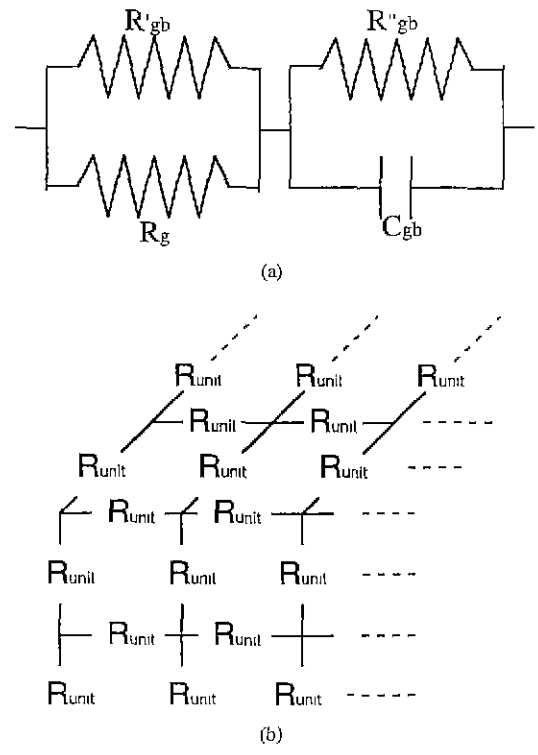

Fig. 2. Equivalent circuitus for the description of brick layer model. (a) An equivalent circuit for the repeating unit where R_g is grain resistance, R_{gb}' is grain boundary resistance where an oxygen ion passes through the grain boundary only (Case (a)) and R_{gb}'' is grain boundary resistance where the oxygen ion passes through gram and grain boundary alternatively (Case (b)) and (d) an equivalent circuit for the simplified microstructure of ceria electrolytes.

$$R_{gb}'' = \rho_{gb}\left(\frac{\delta}{d^2}\right) \tag{3}$$

Then, such repeating unit is composed of R_{gb}' and R_g in parallel and R_{gb}'' in series with the first two. Then, an equivalent circuit which represents the repeating unit can be proposed as given in Fig. 2(a). Therefore, net resistance of the repeating unit, R_{unit} becomes:

$$R_{unit} = \frac{1}{\frac{1}{R_{gb}'}+\frac{1}{R_g}} + R_{gb}'' = \frac{R_g R_{gb}'}{R_{gb}'+R_g} + R_{gb}''$$
$$= \frac{(\frac{\rho_g}{d})(\frac{\rho_{gb}}{2\delta})}{\frac{\rho_{gb}}{2\delta}+\frac{\rho_g}{d}} + \rho_{gb}(\frac{\delta}{d^2}) = \frac{\rho_g\rho_{gb}}{d\rho_{gb}+2\delta\rho_g} + \frac{\rho_{gb}\delta}{d^2} \tag{4}$$

In one unit length, there are $\frac{1}{d}$ units (in fact, $\frac{1}{\delta+\delta}$ but $d>>\delta$) and in one unit cross-sectional area, there are $\frac{1}{d^2}$ units. then, an equivalent circuit which represents the simplified microstructure may be proposed as illustrated in Fig. 2(b). For a given unit length, there are $\frac{1}{d}$ series units and $\frac{1}{d^2}$ parallel units of R_{unit}, in the equivalent circuit (Fig. 2(b)). Therefore, per unit length and unit cross-sectional area, the total resistance of the simplified microstructure, R_{total} will be,

$$R_{total} = \frac{R_{unit}(\frac{1}{d})}{(\frac{1}{d^2})} = dR_{unit} = \rho_{total} \tag{5}$$

wher ρ_{total} is total resistivity. Since the total resistance, R_{total}, was calculated at a given unit length and unit cross-sectional area, it is the same as the total resistivity, ρ_{total}, and should be equal to polycrystalline resistivity measured in the experiment. Therefore,

$$\rho_{total} = \frac{d\rho_{gb}\rho_g}{d\rho_{gb}+2\delta\rho_g} + \frac{\rho_{gb}\delta}{d} \tag{6}$$

or,

$$\frac{1}{\sigma_t} = \frac{\frac{d}{\sigma_{gb}\sigma_g}}{\frac{d}{\sigma_{gb}}+\frac{2\delta}{\sigma_g}} + \frac{\delta}{d\sigma_{gb}} \tag{7}$$

$$\therefore\ \sigma_t = \frac{\sigma_{gb}d(2\delta\sigma_{gb}+d\sigma_g)}{\sigma_{gb}(d^2+2\delta^2)+\delta d\sigma_g} \tag{8}$$

If we let $\rho_{gb}>>\rho_g$, then Eq. [6] simplifies to,

$$\rho_{total} \cong \rho_g + \frac{\delta}{d}\rho_{gb} \tag{9}$$

Eq. [9] shows that the ionic resistivity is linearly proportional to inverse of grain size.

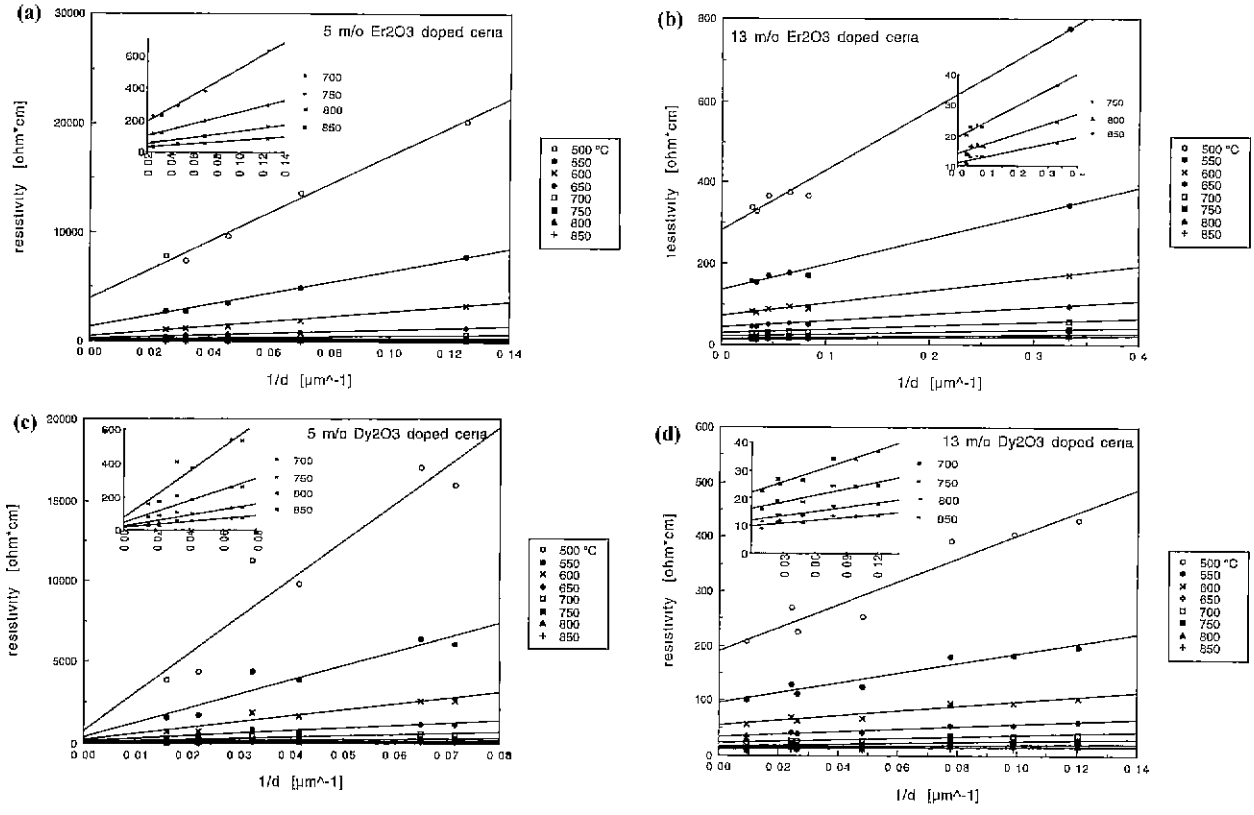

Fig. 3. Resistivity polts as a function on inverse gain size 15 mol.% Er_2iO_3-doped ceria. (a)

3.2 Grain Size Dependence of Ionic Conductivity

Experimentally, it is not possible to directly measure the 'microscopic' grain boundary conductivity, $\sigma_{gb}=\frac{1}{\rho_{gb}}$ where ρ_{gb} is *the microscopic grain boundary resistivity*, since the grain boundary thickness and order of magnitude of grain boundary conductivity, which is calculated by multiplying the grain boundary resistance obtained from an impedance plot using the bulk geometry, can also be found in the literature.[10,11] Such a parameter, however, depends upon the grain size and thus is a representative of the particular sample and not a material parameter. A more fundamental parmeter is $\frac{\delta}{\sigma_{gb}}$ or $\delta\rho_{gb}$, assuming it can be readily determined, since this is independent of the grain size.

Figs. 3(a) through 3(d) show polycrystalline resistivity (ρ) as a function of inverse grain size (1/d) for 5 and 13 mol.% Dy_2O_3 and Er_2O_3-doped samples over a range of temperatures. Insets in each figure show plots with an expanded 'y' scale for clarity since, at high temperatures, the grain boundary contribution to the resistivity is small. It is seen that ρ vs. 1/d can be adequately represented by a straight line the slope of the line decreases with increasing temperature. the figures also show that the slopes for samples with 5 mol.% dopant are much larger than those for 13 mol.% dopant, being consistent with the generally accepted notion that the grain boundary contribution to the polycrystalline resistivity decreases with increasing dopant concentration. For 5 mol.% Er_2O_3 doped ceria with a relatively large grain boundary effect, the conductivity increases (resistivity decreases) by about an order of magnitude when the grain size increases from 8 μm to 39 μm (about 5 times ($\frac{39}{8}\cong 4.9$) increase in the size). By contrast, for 13 mol.% Er_2O_3 doped ceria with a relatively small grain boundary effect, the conductivity increased less than 1/2 order of magnitude even when the grain size increased from 3 μm to 35 μm (almost 12 times ($\frac{35}{3}\cong 11.7$) increase in the grain size). Similar results were obtained on Dy_2O_3 doped ceria as shown in Figs. 3(c) and 3(d). For 5 mol.% Dy_2O_3 doped ceria, the polycrystalline conductivity increased almost one order of magnitude as the grain size increased from 14 μm to 63 μm ($\frac{63}{14}=4.5$). However, for samples containing 13 mol.% Dy_2O_3, the conductivity increased less than 1/2 order of magnitude as the grain size increased 13 times ($\frac{104}{8}=13.0$). The grain size dependence of conductivity can be described in terms of the brick layer model which assumes that grain boundaries offer a greater resistance to ion transport compared to the grains.

Thus, in a polycrystalline material, the ion transport in grain boundary regions parallel to the grain boundaries can be neglected in comparison to the grain conduction. The polycrystalline conductivity then can simply be given as a sum of resistances to transport through the grains and across the grain boundaries. In terms of microstructural parameters such as the grain size, d, and the grain boundary thickness, δ, the polycrystalline resistivity is given by [13,14]

$$\rho=\rho_g+\frac{\lambda\delta}{d}\rho_{gb} \qquad (10)$$

where ρ and λ are respectively (polycrystalline) resistivity and a geometrical (microstructural) parameter. Such an equation was earlier used to describe relationship between resistivity and microstructure in β" alumina.[13,14] Eq. (10) implies that the intercept of ρ vs. $\frac{1}{d}$ is the grain resistivity, ρ_g, while the slope is proportional to ρ_{gb}, with the proportionality constant of $\lambda\delta$. The geometric parameter, λ, can be evaluated based on the knowledge of microstructure. However, the grain boundary thickness, δ, is neither easily determined experimentally nor calculated theoretically. The reason is that the actual δ may or may not have any relation with the physically distinct grain boundary region. Fortunately, it can be reasonably expected that over the temperature range of conductivity measurements, δ will be a constant. Thus, the temperature dependence of the slope can be unequivocally attributed to the temperature dependence of ρ_{gb} assuming that should be valid as long as the grain shape does not change with size.

Figs. 4(a) through 4(d) are Arrhenius plots of the polycrystalline and grain conductivities for 5 mol.% and 13 mol.% Er_2O_3-doped and Dy_2O_3-doped samples, as measured using the complex admittance technique. The slopes and the intercepts from Figs. 3(a) through 3(d) are also plotted on the same figures; namely; $\log_{10}\left(\frac{T}{\text{intercept}}\right)$ and $\log_{10}\left(\frac{T}{\text{slope}}\right)$ vs. $\frac{10^4}{T}$. Note that, in each case, $\log_{10}\left(\frac{T}{\text{slope}}\right)$ trace, which is essentially $\log_{10}\left(\frac{T}{\lambda\delta\rho_{gb}}\right)$, is lower than $\log_{10}\left(\frac{T}{\text{intercept}}\right)$, which is essentially $\log_{10}\left(\frac{T}{\rho_g}\right)$, showing that grain boundaries are more resistive than grains. An examination of Figs. 4(a) through 4(d), however, shows that the grain conductivity estimated from the grain size dependence of conductivity (resistivity) is considerably lower than that determined from the second intercept of complex admittance plots. Further, it was also observed that grain conductivities determined by the complex admittance method were themselves dependent upon the grain size. Additionally, it was observed that, regardless of the dopant concentration (5% or 13%), the grain con-

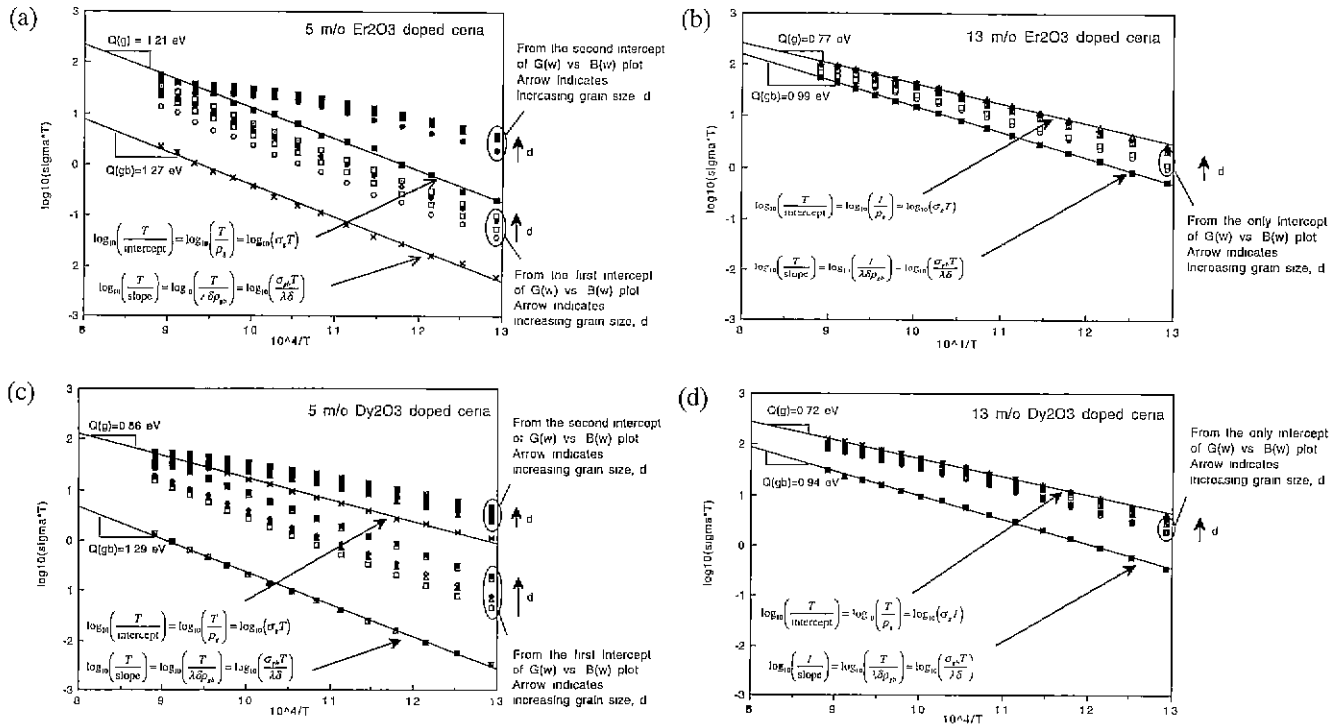

Fig. 4. Arrhenius plots polycrystalline and grain conductivity and plots of $\log_{10}\left(\frac{T}{\text{slope}}\right)$ and $\log_{10}\left(\frac{T}{\text{intercept}}\right)$ vs. for (a) 5 mol.% Er_2O_3 -doped ceria, (b) 13 mol.% Er_2O_3-doped ceria, (c) 5 mol.% Dy_2O_3-doped ceria and (d) 13 mol.% Dy_2O_3-doped ceria.

ductivity determined by complex admittance was essentially the same for a given dopant type (Dy_2O_3 or Er_2O_3). The latter two observations are contrary to expectations, thus raising a question regarding the interpretation of the second intercept of complex admittance plots in the context of the present data.

By contrast, the grain conductivity determined from the grain size dependence of resistivity exhibited the expected behavior. First, the straight line dependence of ρ vs. 1/d implies a unique grain size independent of grain conductivity (σ_g) or resistivity (ρ_g). Second, the grain conductivities depend upon the dopant concentration, as expected. In general, grain conductivity is given by

$$\sigma_g = 2e\mu_{V_o} N_v [V_o^{\cdot\cdot}] \tag{11}$$

where e is the electronic charge, μ_{V_o} is the oxygen vacancy mobility, N_v is the number of oxygen ion sites per unit volume, and $[V_o^{\cdot\cdot}]$ is the fractional oxygen vacancy concentration. The fractional vacancy concentration is related to the dopant concentration by

$$[V_o] = \frac{1}{2}[RE'] \tag{12}$$

where [RE'] is the fractional trivalent rare earth dopant concentration. The oxygen vacancy mobility may depend upon the dopant concentration, especially at lower temperatures where vacancy-dopant complexes may form. At elevated temperatures, however, the dependence of μ_{V_o} on $[V_o^{\cdot\cdot}]$ is expected to be weak. Thus, as a first approximation, it might be expected that the ratio of grain conductivities for the different dopant concentrations will be about the same as the ratio of dopant concentrations, or alternatively, the ratio of grain resistivities will be in inverse proportion to the ratio of dopant concentrations. For Er_2O_3-doped ceria, the $\frac{\rho_g(5\%)}{\rho_g(13\%)}$ varied between ~1.76 (at 800°C) to ~13.66 (at 500°C); and for Dy_2O_3-doped ceria, the ratio $\frac{\rho_g(5\%)}{\rho_g(13\%)}$ varied between ~2.05 (at 800°C) to ~3.76 (at 500°C). If the mobilities are assumed to be composition-independent and if there is no defect complex formation, the expected ratio, $\frac{\rho_g(5\%)}{\rho_g(13\%)}$, would have been $\frac{13}{5}$ or 2.6. Presumably, the mobilities are composition-dependent, and some vacancy complexes do form, especially at low temperatures. The present work shows that grain conductivities obtained from the grain size dependence of polycrystalline conductivity (resistivity) qualitatively obey the expected compositional dependence.

It was observed that grain boundary resistance also depends upon the composition, and in fact, an even greater variation in grain boundary resistance is observed compared to the grain resistance. Since it is possible to separate ρ_{gb} and δ, and in general λ may also be com-

position-dependent (provided mictrostructural characteristics are composition-dependent), the measured grain boundary resistance reflects a product of these three parameters. It was observed that $\frac{(\lambda\delta\rho_{gb}(5\%))}{\lambda\delta\rho_{gb}(13\%))}$ varied between ~24.6 (at 800°C) and ~89.7 (at 500°C) for Er_2O_3-doped samples, and between ~22.2 (at 800°C) and ~109.9 (at 500°C) for Dy_2O_3-doped samples. Greater variation in the grain bounary effect is presumably due to variation in both ρ_{gb} and δ with composition.

The grain size dependence of conductivity (resistivity) in polycrystalline solid electrolytes has been investigated by many researchers. Ioffe *et al.*[7] investigated the effect of grain size on conductivity of Y_2O_3 polycrystalline ceramics. Samples of grain size between ~0.2 and ~1.8 μm were fabricated by sintering over a range of temperatures between 1430 and 2000°C. The samples, however, were not equilibrated at a fixed temperature unlike in the present work. As a result, there may well have been differences in grain boundary characteristics among samples. Nevertheless, the authors observed an increases in conductivity, σ, with increasing size, d. However, σ was plotted vs. d, instead ρ vs. 1/d as in the present case. For this reason, Ioffe *et al.* observed a nonlinear dependence of σ with d, consistent with the inverse of Eq. [9]. They observed that grain conductivity, as determined from complex impedance plots, was independent of grain size, being consistent with Eq. [9]. Grain conductivity in their work, however, was not estimated from grain size dependence of polycrystalline conductivity.

IV. Conclusions

(1) Grain boundary conductivity was evaluated by using the so-called brick layer model. It was estimated to be more than 3 orders of magnitude lower than grain conductivity. In such a case, the grain boundary resistivity becomes a dominant factor determining the resistivity of polycrystalline ceria.

(2) The conductivity of doped ceria was found to be a function of both the composition and grain size. The grain size dependence of resistivity could be adequately described by the so-called brick layer model. A plot of polycrystalline resistivity, ρ vs. inverse grain size, 1/d was linear. The intercept was identified with grain resistivity, ρ_g, while the slope with $\lambda\delta\rho_{gb}$; i.e., a product of the geometrical parameter, λ, the grain boundary thickness. δ, and the grain boundary resistivity, ρ_{gb}. However, as λ and δ are expected to be constant over the temperature range of measurements, the temperature dependence of $\lambda\delta\rho_{gb}$ essentially yields the temperature dependence of ρ_{gb}. It was observed that both the grain resistivity, ρ_g, and grain boundary resistivity, ρ_{gb}, decreased with increasing dopant concentration.

(3) It was observed that, despite a well-defined semicircular arc in most samples, grain conductivity deduced from the complex admittance plots was not in good agreement with values obtained from the grain size dependence of polycrystalline conductivity. A possible reason is the inadequacy of the simplified equivalent circuit used to describe the behavior of polycrystalline materials investigated in the present work. Also, the present work suggests that a realistic measure of grain conductivity can be obtained by an investigation of the grain size dependence of polycrystalline conductivity (resistivity).

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