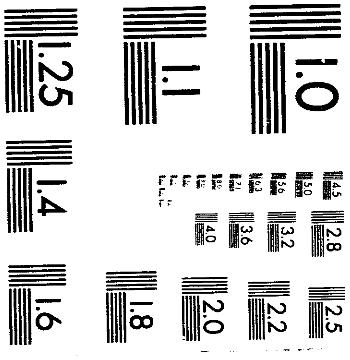
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CONDUCTIVITY MEASUREMENTS OF CERIA-BASED SOLID ELECTROLYTES USING AC IMPEDANCE

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CONDUCTIVITY MEASUREMENTS OF CERIA-BASED SOLID ELECTROLYTES USING AC IMPEDANCE

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ABSTRACT

The ionic conductivities of cerium oxide samples doped separately with oxides of the entire lanthanide series (except promethium) and yttrium were measured using AC impedance. A wide variation in conductivities was observed, from 1×10^{-2} S cm^{-1} for $Ce_{0.8}Sm_{0.2}O_{1.9}$ to 2×10^{-4} S cm^{-1} for undoped ceria at 600 °C. Many of these ceria systems exhibited ionic conductivities higher than those of zirconia systems, making ceria a logical choice for certain low temperature applications. A correlation was found between the ionic radii of the dopant and the corresponding ionic conductivities, with ceria doped with Gd_2O_3, Sm_2O_3 and Y_2O_3 exhibiting the highest values. In addition, the relative contributions of the grain boundaries and grain interiors to the overall resistance was measured. The ceria/samaria and ceria/gadolinia systems showed a different response than the ceria/yttria system with regard to the effect of sintering time on the relative contributions.

INTRODUCTION

Solid electrolytes (1-4) have received increasing attention in recent years due to their excellent suitability as ionically conductive materials in high temperature systems. For those applications requiring conduction by oxide ion vacancies, such as H_2/O_2 fuel cells or oxygen sensors, yttria stabilized ZrO_2 with the cubic flourite structure has been the most extensively investigated (1-5). The vacancies introduced in the crystal lattice by the dopant allow ionic conduction to occur when the activation energy for oxide ion movement in the lattice is exceeded. In doped zirconia, the temperature required for significant ionic conduction is approximately 600 °C, although some response is observed at lower temperatures (6). Work with other phases of zirconia has reported functional temperatures as low as 200 °C (7), and this may provide a new area of interest.

Other flourite-type oxide ion conductors are known (1-4), among them is doped cerium oxide. Previous research on doped ceria systems (8-12) has investigated the conductivity obtained with dopants such as Y_2O_3, CaO and rare earth oxides. Many of these doped ceria materials have conductivities at lower temperatures surpassing that of similar zirconia systems. However, the tendency for Ce(IV) to be reduced to Ce(III) at higher temperatures and low oxygen partial pressures limits the lower limit for pO_2 under which conduction is predominately ionic. In addition to this, the difficulties encountered in the fabrication of ceria systems have led to a relative paucity of conductivity data on ceria. In applications operating at intermediate temperatures (300-400 °C) and under conditions of relatively high oxygen partial pressure, ceria stands out as a promising material.

We have investigated the structure and the ionic conductivity of ceria doped with the rare earth elements. Because the ionic radius of ceria is compatible with that of many of the rare earths, a large number of dopants cations could be studied (yttrium and the entire lanthanide series, except promethium). AC impedance techniques were used to obtain the conductivity data, and in many cases the relative contributions of the crystal grains and the grain boundaries to the overall resistance could be separated. Dopant cation size, and crystal lattice structure is believed to be a major factor in the ionic conductivity of solid electrolytes. For this reason, oxides of all of the rare earth elements were investigated as dopants.

EXPERIMENTAL

Several different sources of polycrystalline ceria were used; results given in this work were obtained by using precipitated powders (Rhone-Poulenc). Ceria mixed with the appropriate quantities of the rare earth oxides was ball milled in a Spex mixing mill with a tungsten carbide mixing ball for several minutes, and then mixed further in a Turbula mixing mill for one-half hour. One gram of the powders was pressed (without any binder) at 140 MPa into pellets (approx. 1/2" x 1/4" before sintering) and then sintered at 1550 to 1600 °C in air. The "soak" time at the upper temperature varied from several minutes to several days. The density of the resultant pellets was in all cases greater than 95% of theoretical density. X-ray diffraction patterns measured with Cu kα radiation indicated that the lattice structure corresponded to the cubic flourite structure expected for ceria. Ceria samples doped with Lu_2O_3, Yb_2O_3, Tm_2O_3, Eu_2O_3 Nd_2O_3 and La_2O_3 did exhibit the presence of a second phase, which is evidence of incomplete dissolution.

Both faces of the disks (approx. 1 cm x 2 mm) were polished using 600 grit emery paper, and either Ag or Pt electrodes were deposited on the smooth faces. Ag electrodes were fabricated by painting the face with Ag paste and firing at 600 °C for several hours. Pt was deposited by using a paste or through DC magnetron sputtering. The electrodes (both Ag and Pt) applied by the paste method were several microns thick, while the sputtered Pt electrodes were 1 ±0.1 μm thick.

AC impedance spectra were measured in air with a Princeton Applied Research model 273 potentiostat and a Solartron model 1255 frequency response analyzer using PAR M383 software. The samples were heated during the measurement in a home-built muffle furnace, and the thermocouple was placed right next to the sample so as to minimize temperature errors. The frequency range measured was 100 kHz to 1.0 Hz, and in many cases down to 0.01 Hz. The magnitude of the AC signal imposed on the sample was limited to 2 mV, in order to minimize any disturbance from equilibrium either to the ceria sample or to the electrode/air interface.

RESULTS AND DISCUSSION

Sample Sintering

The particle size of the ceria powders had a strong influence on the behavior of the pressed pellets during sintering. It was observed that larger sized particles (>1 µm) did not sinter well, even at temperatures up to 1650 °C. After repeated attempts, it was found that pure ceria powders prepared by precipitation (≈ 0.1 µm particle size) worked quite well with samples approaching full densification after as little as two or three hours at 1400 °C.

In most cases, the addition of dopants did not affect the sintering, with most forming mechanically durable pellets. However, ceria pellets doped with Yb_2O_3, Eu_2O_3, Nd_2O_3 or La_2O_3 remained very fragile and tended to crumble on the edges, even though the measured densities were near the theoretical value. Of all of the dopants examined, these four cations are the most different in ionic radii from cerium, and it is not surprising that their size is incompatible with the ceria host lattice. As mentioned above, the x-ray crystal spectra of ceria samples doped with these oxides exhibited the presence of a second phase.

Electrical Conductivity Measurements

Overview. The technique of AC impedance is well suited to the measurement of electrical conductivities (13-15). In addition to the overall conductivity, one can also obtain information about electrode processes, and in the case of polycrystalline samples, the separate contributions of the crystal grains and grain boundaries to the overall resistance can be studied. In the present study, while our primary goal has been to measure the overall ionic conductivity, some attempt has been made to separate the relative contributions of grain boundary and grain interior resistance.

It was assumed that the electronic contribution to the overall conductivity was negligible, i.e., $t_{ionic} = 1$. This assumption is reasonable since all measurements were done in air, and at temperatures less than 1000 °C. Previous research indicates that although Ce(IV) can be reduced to Ce(III), this reduction occurs only in reducing atmospheres and especially at higher temperatures (8,16). No evidence for electronic conduction was seen in the present study, except when the sample was exposed to a very reducing atmosphere, or was intentionally biased with a large voltage across the electrode (>1 V).

If the relaxations of the electrical dipoles associated with the grain boundaries, grain interiors, and electrode interfaces have sufficiently different time constants, the resistances associated with each of these processes can be resolved in an AC impedance spectrum. At higher temperatures, a single arc corresponding to the electrode interfacial processes was observed. As the temperature at which the spectra was measured was decreased, the dipole relaxation processes slowed and first grain boundary and then grain interior processes were observed. The actual experimental observation was the presence of an arc corresponding to the electrode process, followed by the appearance of another semicircle corresponding to grain boundary electrical relaxations, and finally a complete semicircle associated with the relaxations of the crystal interiors. In Figure 1 is shown a "Nyquist" plot of the impedance data for $Ce_{0.8}Sm_{0.2}O_{1.9}$. The right x-intercept of each of the semicircles corresponds to the resistive component for each of the processes mentioned above. This plot is qualitatively very similar to that obtained previously obtained for $Zr_{0.88}Y_{0.12}O_{1.94}$ (13) and is one of only a few such studies for ceria (8,11,12,17,18).

In general, it was possible to obtain relatively clean impedance spectra at temperatures down to about 200 °C. However, the doped ceria samples having the lowest conductivity values yielded very noisy spectra, and their spectra became meaningless below about 400 °C. All subsequent measurements on these particular samples were done at temperatures of 400 °C and above.

Rare Earth Doped Ceria. From the Nyquist plots of the AC impedance data, conductivity values can be calculated for the doped ceria samples over a wide temperature range. The x-intercept in common between the electrode arc and the electrolyte arc(s) gives the desired value, and these data are shown in Figure 2. All of these samples were fabricated using Ag electrodes; no difference was observed in the measured conductivity values when Pt electrodes were used, although the electrode arc did show some effects. The temperature limit for the samples with Ag electrodes was set at 900 °C because higher temperatures resulted in electrode degradation. The conductivities exhibit Arrhenius behavior at lower temperatures, with a slight curvature noted at temperatures above approximately 800 °C. It is believed that this deviation from linearity is caused by the degradation of the Ag electrodes since Pt electrodes did not show this effect.

In addition, the conductivity plot for $Ce_{0.8}Pr_{0.2}O_{1.9}$ appeared to be composed of two lines of unequal slope, an effect much more pronounced than the one mentioned above. It is likely that this break in the slope is related to an oxidation state change of the Pr(III) dopant. Before sintering, the sample was green (indicative of Pr(III)). After sintering, the color changed to black (indicative of Pr(IV)). The exact distribution of valence states is not known and the conductivity values may be somewhat misleading.

As seen in Figure 2, the conductivity values cover a wide range and in all cases the ionic conductivity of doped ceria is higher than that of pure ceria. The latter had a measured conductivity of 2×10^{-4} S cm^{-1} at 600 °C. The ceria samples which did not sinter well (those doped with Yb_2O_3, Eu_2O_3, Nd_2O_3 and La_2O_3) were not included in the figure because it was felt that these data were unreliable. The values in Figure 2 are in general agreement with those found in the literature (8-10). In the most favorable cases, doped ceria exhibits almost an order of magnitude higher conductivity at significantly lower temperatures than does doped zirconia. The conductivity of $Zr_{0.84}Y_{0.16}O_{1.92}$ at 600 °C was measured at 2×10^{-3} S cm^{-1}, as compared to the value of about 10^{-2} S cm^{-1} for ceria doped with yttria, samaria, or gadolinia.

Yttria Doped Ceria. As noted earlier, yttria is a common dopant for zirconia and also has been used to increase ionic conductivity with ceria systems (8-10) as well. For these reasons, yttria was studied in greater detail than the other rare earth dopants. In Figure 3 is shown the conductivity data for the ceria-yttria system, where the dopant level of Y_2O_3 was varied between 0 (pure ceria) and 20 mole %. These data were obtained in exactly the same fashion as the other rare earth systems investigated in this study.

As the dopant level of Y_2O_3 increases, the ionic conductivity increases until it reaches a maximum at a doping level of 8 mole % Y_2O_3, a figure which has been reported previously (2) to yield the optimum conductivity. The peak is attributable to the number of oxygen vacancies, and thus the oxide ion conduction, increasing until a point is reached where the deleterious effect of additional distortions and imperfections causes a decrease in conductivity.

Conductivity versus Dopant Size. The size of the dopant cation is an important factor in the overall conductivity, and it is not surprising that the conductivity could be optimized with certain dopants (8-10). From the data shown in Figures 2 and 3, a plot of the conductivity versus dopant radius (19) can be constructed (Figure 4). The conductivity of doped ceria generally increases as the dopant ionic radius increases until a maximum is reached with samarium, at which point the conductivity appears to decrease with further increase in dopant radius. This decrease may be artificial because, as mentioned above, the sample doped with praseodymium oxide showed uncertainty in the valence state distribution. The general trend seen in Figure 4 was seen at temperatures from 400 to 800 °C, and in all cases ceria doped with the oxides of yttrium, samarium or gadolinium exhibited the highest conductivity, while those of lutetium, thulium, erbium, holmium and dysprosium showed much lower conductivities. Further conclusions are speculative as other factors are no doubt involved.

Sintering Effects

In an effort to understand the influence of the sintering time on the conductivity behavior, several samples were prepared under different conditions. Pellets pressed from Ce/Gd oxide or Ce/Sm oxide powders were sintered with soak times ranging from 0 to 24 hours. Impedance spectra were run at lower temperatures in order to determine the relative contribution of grain interior versus grain boundary resistances to the overall resistance. Under optimum conditions, separate arcs corresponding to these two processes appear, and the assignment of resistance values is straightforward.

The results are shown in Table I. For $Ce_{0.8}Gd_{0.2}O_{1.9}$, the resistances associated with both the grain interiors and grain boundaries decrease as the sintering time is increased. However, the fraction of the total resistance which is due to the crystal grain interiors increases with longer sintering times. The same trend in seen with the $Ce_{0.8}Sm_{0.2}O_{1.9}$ system, although the grain interior resistance did not show an equivalent trend by decreasing with longer sintering times.

In both samples, grain interior resistance accounted for about one-third of the total resistance at the shortest sintering times, and approached two-thirds of the resistance after 24 hours. The observation that the "grain boundary effect" decreases with longer sintering times is in disagreement with results from previous work (18), where it was noted that in the ceria/yttria system, grain boundary effects were reduced with shorter sintering times. Likewise, overall conductivity values decreased with longer sintering times whereas our values increased.

In an effort to understand this discrepancy, we also performed AC impedance analyses of the ceria/yttria system. A typical result is shown in Figure 5. For this system, grain boundary effects are a very large contribution to the overall resistance, and it was noted that longer sintering times did indeed increase the grain boundary arc (middle arc of Figure 5). Qualitatively, these results are identical to the earlier work by Wong and Nowick (18). We are currently unable to explain the differences seen in the ceria/yttria system versus the ceria/samaria and ceria/gadolinia systems.

CONCLUSIONS

The addition of rare earth oxide dopants to ceria results in changes in the ionic conductivity resulting from the introduction of oxide ion vacancies in the crystal lattice. The nature of the dopant cation had a large effect on the electrical conductivity of the samples; the increase in oxygen vacancies causes an increase in the ionic conductivity in all cases. A rough correlation was found between the radius of the dopant cation and the measured conductivities and, in agreement with previous results, yttria, samaria, and gadolinia yielded the highest conductivities.

In several aspects of this research, it appears that the distinction between grain boundary vs grain interior reistance is a very important one. Further examination of this topic in the samples with the highest overall conductivity showed differing results. Longer sintering times increased the grain boundary effect in the ceria/yttria system, but decreased it for the ceria/gadolinia and ceria/samaria systems. Further research is needed to explain these observations completely.

With regard to the ionic conductivity, doped ceria appears to be a promising alternative to doped zirconia for several applications at intermediate temperatures. Due to its higher conductivity, ceria can function in applications at lower temperature under conditions of relatively high oxygen partial pressure. In order to test the suitability of a ceria-based oxygen sensor for automotive applications, we have constructed a prototype amperometric sensor having a diffusion barrier to establish a linear response (20,21). Preliminary results are encouraging, and the sensor exhibits the expected linear response at temperatures as low as 400 °C.

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Figure 1. AC impedance spectrum of $Ce_{0.8}Sm_{0.2}O_{1.9}$ at 200 °C. Frequencies shown are in Hertz.

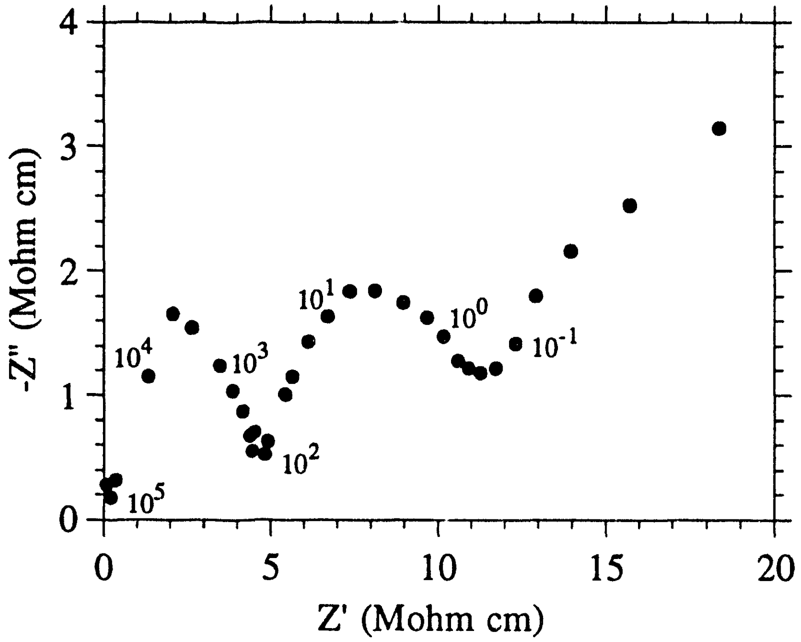

Figure 2. (A) Ionic conductivity of ceria doped with 10 mole % Sm_2O_3, Gd_2O_3, Pr_2O_3, Tb_2O_3 or Er_2O_3.
(B) Ionic conductivity of ceria doped with 10 mole% Tm_2O_3, Lu_2O_3, Ho_2O_3, or Dy_2O_3

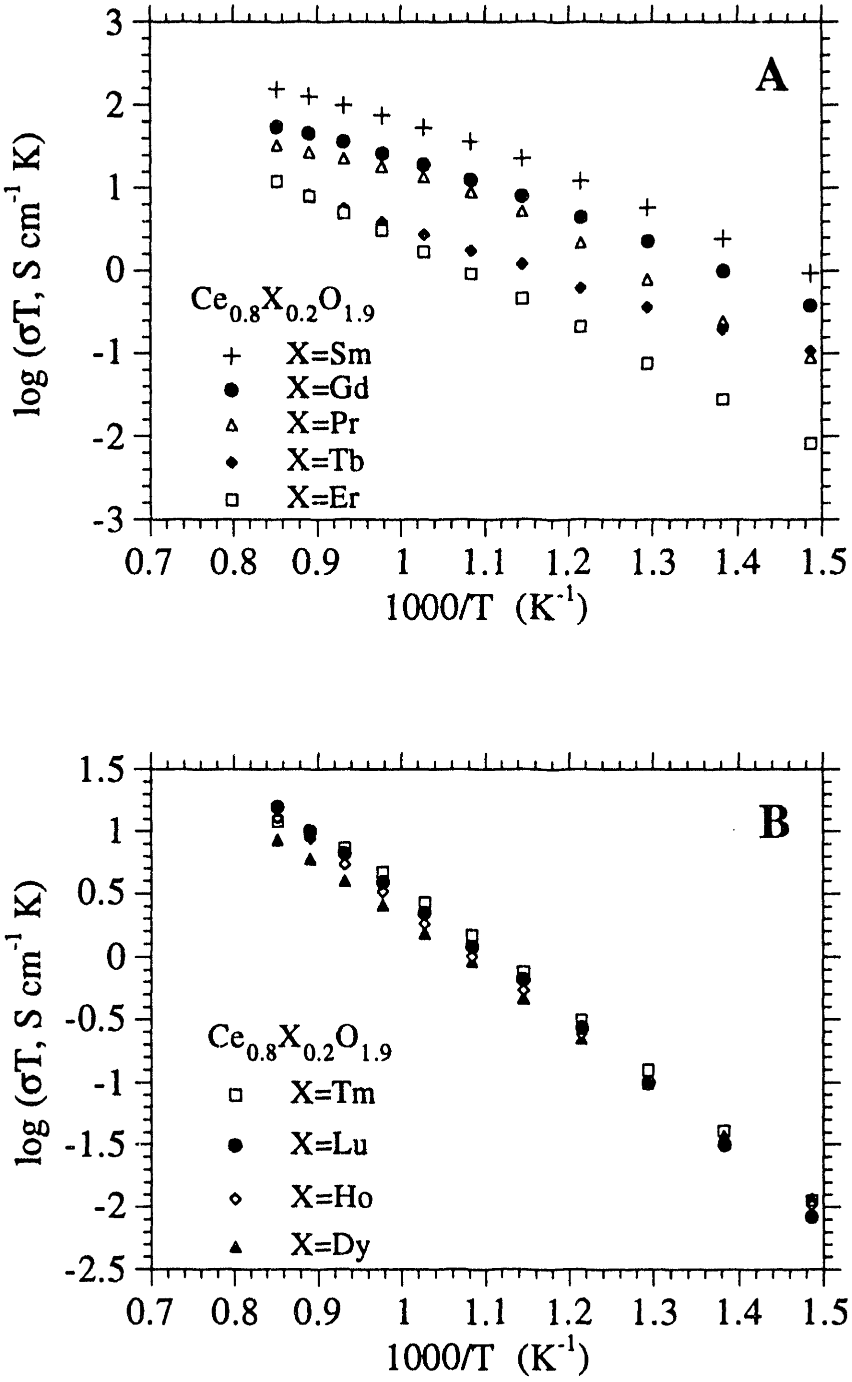

Figure 3. Effect of dopant level on conductivity of ceria/yttria system.

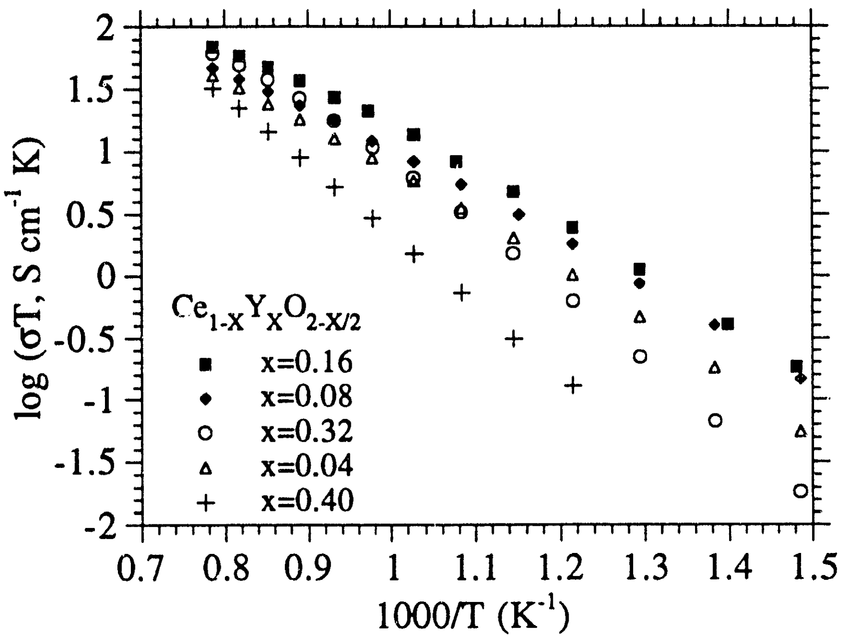

Figure 4. Conductivity of doped ceria at 400 °C versus ionic radius of dopant cation.

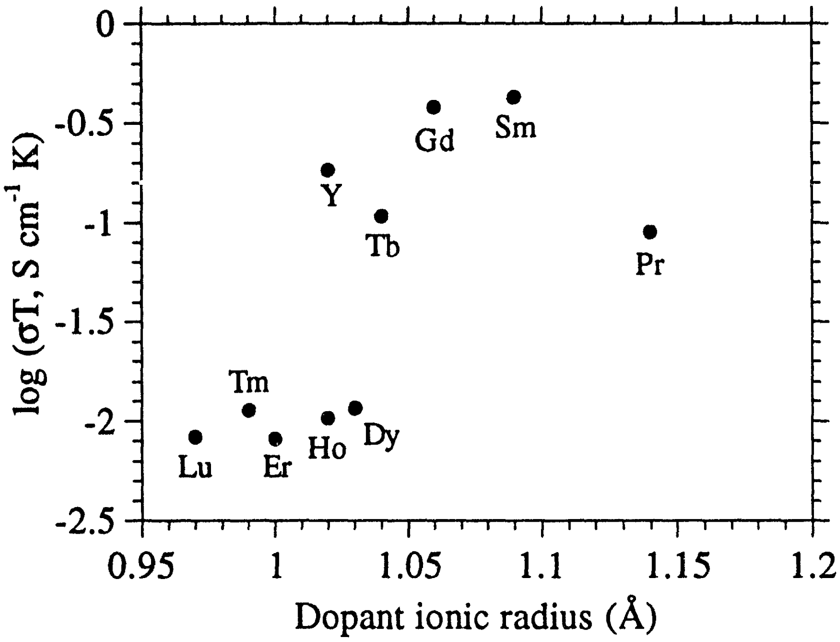

Figure 5. AC impedance spectrum of $Ce_{0.84}Y_{0.16}O_{1.92}$ at 220 °C.

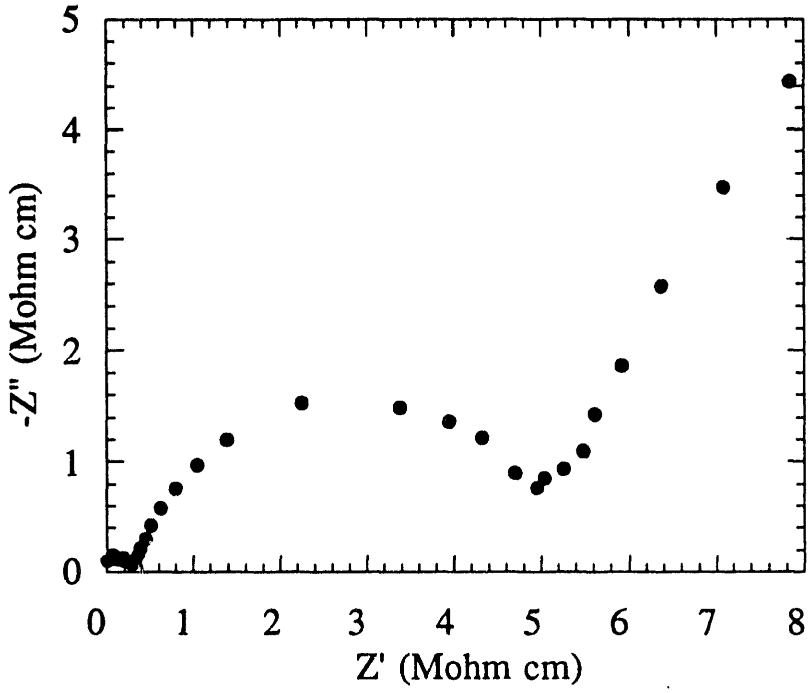

Table I. Effect of sintering time on grain interior and grain boundary resistances of doped ceria at 200 °C as measured by AC impedance.

Sintering Time (hours)	Resistance$_{g.i.}$ (Mohm cm)	Resistance$_{g.b.}$ (Mohm cm)	$R_{g.i.}/R_{g.i.} + R_{g.b.}$
$Ce_{0.8}Gd_{0.2}O_{1.9}$			
0	1.5	2.3	0.41
2	0.65	0.65	0.50
24	0.55	0.30	0.65
$Ce_{0.8}Sm_{0.2}O_{1.9}$			
0	0.38	0.78	0.33
2	0.45	0.75	0.38
8	0.35	0.33	0.51
24	0.38	0.29	0.57

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