"The Electrical Conductivity of CaO-doped
Nonstoichiometric Ce_{1-y}O₂ from 700° to 1500°C"¹

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ABSTRACT

The electrical conductivity of sintered specimens of CaO-doped CeO₂ (0.1 - 7.0 mole %) was measured over the temperature range 700° - 1500°C and from 1 to 10⁻²² atm of oxygen. All specimens of CaO-doped CeO₂ exhibited mixed conduction. Predominantly ionic conductivity was observed at low temperatures and high oxygen partial pressures. Conversely, high temperatures and lower oxygen partial pressures were dominated by electronic conductivity. In the CaO content, temperature and oxygen pressure region investigated, the electronic conductivity has been rationalized in terms of a defect model involving nonstoichiometric defects (ionized cerium interstitials and localized electrons) and impurity generated defects (doubly ionized oxygen vacancies). Good agreement has been obtained between the theoretically derived relation

$$\sigma = \sigma_{oe} (1 - \bar{\xi}a) + A(\%CaO)\exp(-E_i/kT)$$

and the electrical conductivity data. Where, the electronic conductivity of nonstoichiometric "pure" CeO₂ is σ_{oe} and $(1 - \bar{\xi}a)$ is a correction for

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CaO-doping. The quantity, $\bar{\xi}$, is related to a geometrical blocking factor associated with the site fraction of Ca^{+2} ions on normal Ce^{+4} ion sites,

a. The second term in the above expression for σ represents the ionic conductivity which is proportional to the oxygen vacancy concentration and mole % CaO.

INTRODUCTION

Only a limited number of studies¹⁻⁴ have been reported on the electrical conductivity of CaO-doped nonstoichiometric cerium dioxide. Kevane et al² measured the electrical conductivity as a function of temperature (250° - 1500°C), oxygen pressure (1 - 10⁻⁴ atm) and CaO content (0.03 - 0.86 % Ca). They reported mixed conduction electronic and ionic. The electronic conductivity was predominately n-type at elevated temperatures; at lower temperatures p-type behavior was observed. A recent electrical conductivity study of solid electrolytes in air by Meyer and Marincek⁴ indicates that a 15 mole % CaO-doped CeO₂ specimen is highly ionic. Ionic transference measurements in air by Yushina and Pal'guev⁵ confirm the ionic nature of CeO₂ doped with 5-15 mole % CaO in the temperature range 700° - 1100°C.

The solubility of CaO in CeO₂ based on an x-ray study has been reported to be 15 mole % CaO at 1600°C.⁶ Although no thermodynamic study on CaO-doped CeO₂ has been reported, the range of oxygen pressure which the fluorite structure is stable should be large since Ce_{1+y}O₂ is thermodynamically stable⁷⁻⁹ over a wide range of P_{O₂} and temperature. For example, the fluorite structure of Ce_{1+y}O₂ is stable to values of P_{O₂} as low as 10⁻²⁰ atm at 1023°C.

The above conductivity studies have been made over only a rather limited range of oxygen pressures and CaO content. The results of a recent electrical conductivity study¹⁰ on Ce_{1+y}O₂ over a wide range of oxygen pressures (1 to 10⁻²¹ atm) and temperatures (800° - 1500°C) have been interpreted in terms of a nonstoichiometric defect model involving triply and quadruply ionized cerium interstitials and localized electrons.

This defect model was based on a comparison of the oxygen pressure and temperature dependence of the electrical conductivity and a theoretically derived expression for the conductivity using the law of mass action.

The purpose of this study was to (1) measure the electrical conductivity over a wide range of temperature, oxygen pressure and CaO content and (2) to characterize the electronic and ionic conductivity by a comparison of the data with proposed defect models for CaO-doping and oxygen nonstoichiometry.

THEORY

Based on the results of the previous electrical conductivity and transference studies, CaO-doped $\text{Ce}_{1+y}\text{O}_2$ exhibits mixed electronic and ionic conduction.¹⁻⁵ Thus, the total electrical conductivity, σ , may be represented as a sum of the electronic conductivity, σ_e , and the ionic conductivity, σ_i . According to the phase rule both σ_e and σ_i should be functions of the variables temperature, oxygen partial pressure and CaO content. Expressions for σ_e and σ_i as a function of these variables were derived using simple defect models as described below.

1. Defect Models for Electronic Conduction

The simplest method of obtaining an expression for the electronic conductivity of CaO-doped $\text{Ce}_{1+y}\text{O}_2$ was to modify the expression which has been derived previously for the electronic conductivity, σ_{oe} , of "pure" $\text{Ce}_{1+y}\text{O}_2$.¹⁰ Equations for σ_{oe} have been derived based on a nonstoichiometric defect model involving triply and quadruply ionized cerium interstitials and localized electrons. Over a wide range of oxygen pressures and temperature (e.g. $1 < P_{\text{O}_2} < 10^{-7}$ atm at 1500°C and $1 < P_{\text{O}_2} < 10^{-12}$ atm at 1200°C) the following defect reaction was assumed to predominate.

where V_i is a vacant interstitial site, Ce_{Ce} and O_o are cerium and oxygen ions, respectively, in their normal lattice sites, $\text{Ce}_i^{\cdot\cdot\cdot\cdot}$ is a quadruply ionized cerium interstitial, and Ce_{Ce}' is an electron localized at a cerium ion on a normal cerium site. Applying the law of mass action yields

$$K = \frac{[Ce_i^{\bullet\bullet\bullet\bullet}][Ce_{Ce}']^4 P_{O_2}}{[V_i^x][Ce_{Ce}^x]^5 [O_o^x]^2} \quad (2)$$

where K is the mass action constant and the bracketed terms represent the number of a given species divided by the number of sites available for that species.

Since the oxygen sublattice is unaffected by the interstitial defect, $[O_o^x] = 1$. The concentration of normal cerium sites, however, should be corrected for the occupancy of some sites by localized electrons. Kofstad and Hed¹¹ have also proposed that an ionized interstitial may block the six neighboring normal cerium ions from electron occupation. The number of interstitial sites in $Ce_{1+y}O_2$ is equal to the number of normal cation sites. Thus

$$[Ce_{Ce}^x] = 1 - [Ce_{Ce}'] - 6(1 - \alpha)[Ce_i^{\bullet\bullet\bullet\bullet}] \quad (3)$$

where α is the relative probability of a neighboring Ce_{Ce} site being occupied by an electron.

In addition, each ionized cerium interstitial may block the 12 nearest neighboring interstitial sites from occupation because of coulombic repulsion. Thus

$$[V_i^x] = 1 - [Ce_i^{\bullet\bullet\bullet\bullet}] - 12(1 - \beta)[Ce_i^{\bullet\bullet\bullet\bullet}] \quad (4)$$

Assuming the predominant atomic defect is $Ce_i^{\bullet\bullet\bullet\bullet}$ then $y = [Ce_i^{\bullet\bullet\bullet\bullet}]$ and the electroneutrality relation is $[Ce_{Ce}'] = 4[Ce_i^{\bullet\bullet\bullet\bullet}]$. For this case $[Ce_{Ce}']$ may be related to P_{O_2} by the following expression¹⁰

$$K = \frac{[Ce_{Ce}']^5 P_{O_2}}{[4 - [Ce_{Ce}'] (13 - 12\beta)][1 - [Ce_{Ce}'] (10 - 6\alpha)/4]^5} \quad (5)$$

and for CaO-doped $\text{Ce}_{1+y}\text{O}_2$ the corresponding relation can be shown¹² to be

$$K = \frac{[\text{Ce}'_{\text{Ce}}]_{\text{P}}^5}{[4 - [\text{Ce}'_{\text{Ce}}](13 - 12\beta)][(1 - \xi a) - (10 + a - 6\alpha)[\text{Ce}'_{\text{Ce}}]/4]^5 [1 - a/2 - (a/8)[\text{Ce}'_{\text{Ce}}]]^2} \quad (6)$$

where a is the site fraction of Ca'' on $\text{Ce}^{\text{x}}_{\text{Ce}}$ sites and ξ is the relative probability of a neighboring $\text{Ce}^{\text{x}}_{\text{Ce}}$ site around a Ca''_{Ce} site being occupied by an electron. The physical basis for this is that since Ca''_{Ce} has a negative effective charge when it replaces cerium atoms there should be a coulombic interaction between Ca''_{Ce} and Ce'_{Ce} which would tend to block near neighbor $\text{Ce}^{\text{x}}_{\text{Ce}}$ atoms from accepting localized electrons. In the model for CaO-doping the CaO is assumed to produce oxygen vacancies. Thus, as shown in Eq. (6), only the concentration of $[\text{O}^{\text{x}}_{\text{O}}]$ and $[\text{Ce}^{\text{x}}_{\text{Ce}}]$ in Eq. (2) should be effected directly by CaO-doping.

Using Eq. (6) it can be shown¹² that $[\text{Ce}'_{\text{Ce}}]$ should be controlled primarily by the temperature and oxygen pressure. The CaO-doping should be a second order effect which may be represented by the following expression

$$[\text{Ce}'_{\text{Ce}}]_{\text{CaO-doped}} = [\text{Ce}'_{\text{Ce}}]_{\text{"pure" Ce}_{1+y}\text{O}_2} [1 - \xi a] \quad (7)$$

The mobility of electrons may also be affected by CaO-doping. The proposed compositional dependence of the electron mobility may be approximated by the expression¹²

$$\mu_e = (1 - \xi a) \mu_{oe} \quad (8)$$

where μ_{oe} is the electron mobility¹³ for "pure" $\text{Ce}_{1+y}\text{O}_2$.

Thus if the above defect model is correct the conductivity of CaO-doped $\text{Ce}_{1+y}\text{O}_2$ may be approximated by relation

$$\sigma_e \cong \sigma_{oe} (1 - \xi a)^2 \cong \sigma_{oe} (1 - \bar{\xi} a) \quad (9)$$

In the region where $4[Ce_i^{''''}] = [Ce']$ is valid the oxygen pressure dependence of σ_{oe} has been represented¹⁰ by the relation

$$\sigma_{oe}^5 = (E - E_1 \sigma_{oe}) P_{O_2}^{-1} \quad (10)$$

where E and E_1 are parameters which contain the mass action constant K from Eq. (2) and the mobility μ_{oe} of the localized electrons. Near stoichiometry Eq. (10) may be approximated by the

$$\sigma_{oe} = E P_{O_2}^{-1/5} \quad (11)$$

Eq. (11) may be easily derived by assuming the concentrations in the denominator of Eq. (5) are equal to 1. This assumption is valid near stoichiometry.

Thus, one way of testing Eq. (9) is to compare the oxygen pressure dependence of the conductivity of the "pure" $Ce_{1+y}O_2$ and Ca-doped $Ce_{1+y}O_2$. Eq. (9) predicts that these conductivities should have the same P_{O_2} dependence and, σ_e should decrease with increasing concentration of CaO.

2. Defect Model for Ionic Conductivity

According to Kevane et al.² and Lay¹⁴ doping CeO_2 with CaO produces oxygen vacancies. A study in this laboratory¹⁵ comparing pycnometric density and calculated values of the density based on lattice parameter data substantiates the oxygen vacancy model for specimens with CaO contents between 0.1 and 7.0 mole %. The simplest model for ionic conduction assumes that the only mechanism responsible for ionic conduction in CaO-doped CeO_2 is the migration of oxygen vacancies with only one state of

ionization, V''_O . The ionic conductivity, σ_i , may then be represented by the expression

$$\sigma_i = B[V''_O]e\mu_{V''_O} \quad (12)$$

If the oxygen vacancies are isolated point defects randomly distributed then

$$[V''_O] = B_1(\text{mole } \% \text{ CaO}) \quad (13)$$

and if $\mu_{V''_O}$ is a function of temperature only then

$$\mu_{V''_O} = \mu'_{V''_O} \exp(-E_i/kT) \quad (14)$$

Combining Eqs. (12, 13 and 14) the following relation for ionic conductivity was obtained

$$\sigma_i = A(\text{mole } \% \text{ CaO})\exp(-E_i/kT) \quad (15)$$

where

$$A = BB_1\mu'_{V''_O} e \quad (16)$$

Eq. (15) may be tested in a region where the ionic conduction predominates (i.e. $\sigma \approx \sigma_i$) by observing if σ is directly proportional to the CaO content in this region. In this limiting case region σ should also be independent of P_{O_2} .

EXPERIMENTAL

Conductivity specimens of CeO_2 doped with CaO (0.1 to 7.0 mole % CaO) were prepared by dry mixing the appropriate proportions of CeO_2 and CaCO_3 powder. The chemical analysis of CeO_2 and CaCO_3 powders are shown in Tables I and II, respectively. These mixtures were calcined for 12 hours at 1000°C in air. The calcined material was ground in an alumina mortar and pestle into a powder with an approximate particle size of 20 micron or less. These powders were then pressed into bars 2 in. x 1/4 in. x 1/4 in. with a pressure of 20,000 psi. The bars were placed in an alumina boat and completely covered with CaO doped CeO_2 powder of the same composition to avoid loss of CaO during sintering. A molybdenum wound resistance furnace was used to sinter the bars at 1650°C for 3-1/2 hrs in an argon atmosphere. Conductivity specimens were cut from the sintered bars to an average length of 2 cm. The nominal calcia content, density and the results of the chemical analysis of these specimens are shown in Table III. The nominal calcia content specimens, 0.3, 2.0, 5.0 and 7.0 mole % CaO , agree with the results of the x-ray fluorescence and the atomic absorption analysis within the reported experimental error of these analyses $\pm 10\%$. With the exception of the 1 mole % CaO specimen, the nominal values of mole % CaO of all specimens were within the reported experimental accuracy of the x-ray fluorescence and atomic absorption analysis. Thus, in this study the nominal mole % CaO values will be used to identify the calcia content of each specimen.

The electrical conductivity measurements of $\text{Ce}_{1+y}\text{O}_2$ as a function of P_{O_2} in the temperature range $800^\circ - 1500^\circ\text{C}$ were made in a molybdenum wound resistance furnace. A standard four-probe d-c technique was

employed for the electrical conductivity measurements. The experimental apparatus employed was essentially the same as that described in an earlier publication.¹⁶

Oxygen partial pressures were achieved by means of two methods. For pressures from 1 to 10^{-4} atm, premixed and analyzed O_2 -Ar mixtures at 1 atm total pressure were used in the study. Controlled oxygen partial pressures in the low-pressure region were obtained by introducing known mixtures of CO and CO_2 at 1 atm total pressure. The well-known free energy values for the CO/ CO_2 reaction were then used to calculate the oxygen partial pressure. A linear flow rate of 0.7 cm/sec was maintained for all gas mixtures used in this investigation to avoid errors arising from thermal diffusion.¹⁷ However, no flow dependence was noted if this flow rate was increased or decreased within 50% of this value. Electrical conductivity measurements were taken at various temperatures between 700° and 1500°C for a fixed gas mixture for both increasing and decreasing temperature. Data were taken in 200°C increments, starting at 700°C and proceeding to 1500°C while heating. During cooling from 1400° to 800°C data was recorded at 200°C intervals. Since the composition of calcia doped nonstoichiometric ceria has a unique value for each CaO content, oxygen partial pressure and temperature, the above technique insured the measurement of equilibrium conductivity because the nonstoichiometric equilibrium state was approached from both higher and lower compositions of oxygen.

Some difficulty was experienced in obtaining equilibrium conductivity values below 900°C in Ar- O_2 mixtures. To circumvent this problem isothermal conductivity measurements were made in Ar- O_2 mixtures for decreasing oxygen pressures. For this method the criteria for equilibrium was independence of the measured values of the conductivity with time.

RESULTS AND DISCUSSION

The electrical conductivity of sintered specimens of calcia-doped nonstoichiometric cerium dioxide (0.1 to 7.0 mole % CaO) was measured as a function of temperature (i.e. 700° to 1500°C) and oxygen pressure (1 to 10^{-21} atm). Typical behavior of the conductivity as a function of the reciprocal absolute temperature in Ar- O_2 and CO- CO_2 mixtures is illustrated in Fig. 1 for a nonstoichiometric cerium dioxide specimen doped with 1.0 mole % CaO. The measured values of the conductivity, σ_{meas} , for the sintered specimen have been corrected for porosity using the relation¹⁸

$$\sigma_c = \sigma_{\text{meas}} \frac{\rho_{\text{theor}}}{\rho_{\text{meas}}} \quad (17)$$

where ρ_{theor} is the theoretical density and ρ_{meas} is the bulk density of the sintered specimen. For all of the CaO doped specimens two distinct types of behavior are observable as shown in Fig. 1. At low temperature and high oxygen pressures (i.e. Ar- O_2 mixtures), the conductivity is independent of oxygen partial pressure and exponentially dependent on temperature. At high temperature and lower oxygen pressures, the conductivity exhibits n-type behavior (i.e. conductivity increases with decreasing oxygen pressures). According to Eq. (15) the oxygen independent behavior indicates the presence of predominantly ionic conductivity.

Based on the simple defect models proposed in the theory section the ionic conductivity should be proportional to mole % CaO and independent of P_{O_2} ; whereas the electronic conductivity of Ca-doped CeO_2 should exhibit a dependence on P_{O_2} similar to "pure" $Ce_{1+y}O_2$. Isothermal plots of $\log \sigma$ vs $\log P_{O_2}$ were made for each of the CaO-doped specimens to test these

simple models.¹² A typical plot for a 1 mole % CaO specimen is shown in Fig. 2. For comparative purposes the conductivity for a "pure" CeO_2 specimen is also shown in Fig. 2.

For purposes of convenience of discussion, the conductivity data may be described in terms of 3 regions. A qualitative explanation of the observed electrical conductivity data in terms of these three regions is described as follows:

Region I At high temperatures and particularly at low oxygen pressures, the σ of the CaO-doped specimen exhibits essentially the same P_{O_2} dependence as "pure" CeO_2 except that the magnitude of σ is slightly smaller. The conductivity in this region appears to be predominantly electronic (i.e. $\sigma \sim \sigma_e > \sigma_i$) and is probably controlled by the same nonstoichiometric defects as in "pure" $\text{Ce}_{1+y}\text{O}_2$.

Region II For higher oxygen partial pressures and lower temperatures, the conductivity of the CaO-doped specimen appears to be independent of oxygen partial pressure. The σ for this specimen is also much larger than that of "pure" CeO_2 . Since σ_i is to a first order approximation independent of the oxygen pressure, this observation is consistent with a conduction process which is primarily ionic (i.e. $\sigma \sim \sigma_i > \sigma_e$).

Region III For all oxygen pressures and temperatures intermediate to regions I and II, the conductivity appears to be mixed. That is composed of ionic and electronic conduction where σ_e and σ_i are of the same order of magnitude.

According to the proposed nonstoichiometric defect model for electronic conductivity, Eq. (9), the conductivity should decrease with increasing CaO content. However, based on the defect model for CaO doping the ionic conductivity is directly proportional to the CaO content. As a test of the appropriateness of these models, isothermal plots were made of $\log \sigma_c$ vs $\log$ mole % CaO for all of the Ar- O_2 and CO-CO $_2$ gas mixtures used in this study.¹² A typical plot of $\log \sigma_c$ vs $\log$ mole % CaO which illustrates these results are shown in Fig. 3 for the case where $P_{O_2} = 1$ atm. Again three distinct regions of behavior may be observed. In region I (i.e. $\sigma \sim \sigma_e$) the conductivity is seen to decrease slightly with CaO addition. For region II (i.e. $\sigma \sim \sigma_i$) the slope of $\log \sigma$ vs $\log$ % CaO is approximately one except at low CaO contents where curvature in the line is observed. Region III appears to be a region of mixed conduction. Since a curvature of $\log \sigma_c$ vs $\log$ % CaO was observed in region II, a plot of σ_c vs mole % CaO, Fig. 4, for the data in this region was used to test the proportionality of σ on the CaO content required by Eq. (15). These results are illustrated in Fig. 4 at $P_{O_2} = 1$ atm for the temperature range 700° - 1100°C and for CaO contents between 1 and 7 mole %. A direct proportionality was observed for these data. The curvature shown in Fig. 3 at low CaO content was probably due to impurities in CeO $_2$. The conductivity for "pure" CeO $_2$ has been reported to be influenced by impurities in this temperature and oxygen pressure region. Thus, it appears that approximately 1 mole % CaO is required to produce a sufficient number of defects to completely swamp out the effect of impurities in "pure" CeO $_2$.

In order to attempt a quantitative test of the proposed models for electronic and ionic conductivity Eqs. (9) and (15) respectively it was first necessary to obtain the parameters which characterize these equations.

These parameters were determined from the dependence of σ on P_{O_2} , temperature and mole % CaO in the limiting case regions (i.e. where either electronic or ionic conductivity predominates). For example, the parameter E_i in Eq. (15) was obtained from the plot shown in Fig. 5 of $\log \sigma_c$ vs $1/T$ at $P_{O_2} = 1$ atm for several different compositions. The data used in Fig. 5 was obtained from Fig. 4 where σ_c was shown to be proportional to mole % CaO. The average value of E_i determined from a least square analysis was 0.61 ± 0.03 eV for compositions from 1.0 to 7.0 mole % CaO. The following values of $A = 4.0$ was then determined by curve fitting the expression

$$\sigma_i = A[\% \text{ CaO}] \exp(-.61/kT) \quad (18)$$

to the data shown in Fig. 5. Thus, if the proposed defect model for ionic conductivity is correct and ionic conductivity predominates in region II, then σ_i may be characterized by the relation

$$\sigma_i = 4.0[\text{mole } \% \text{ CaO}] \exp(.61/kT) \quad (19)$$

The procedure for characterizing the electronic conductivity in CaO-doped $\text{Ce}_{1+y}\text{O}_2$ was to use the conductivity data of "pure" $\text{Ce}_{1+y}\text{O}_2$ for σ_{oe} in Eq. (9) and to consider $\bar{\xi}$ as an adjustable parameter. A quantitative test of the proposed defect models for electronic and ionic conductivity was made by curve fitting the expression

$$\sigma = \sigma_{oe}[1 - \bar{\xi}a] + 4[\text{mole } \% \text{ CaO}] \exp(.61/kT) \quad (20)$$

to the P_{O_2} and temperature dependence of the conductivity data for specimens with 1 and 7 mole % CaO. The value of $\bar{\xi}$ for a given CaO content was determined from the best fit of the conductivity data.

The results of this curve fitting technique is shown as a solid line in Figs. 6 and 7 where $\log \sigma_c$ is plotted vs $\log P_{O_2}$ for 1 and 7 mole % CaO, respectively. For 1 and 7 mole % CaO the value of $\bar{\xi}$ used was 43 and 8, respectively.

Although the proposed defect model appears to provide a good fit of the conductivity data there are a few problems with this model. For example, there is no simple physical model to explain how $\bar{\xi}$ should vary with CaO content. Another problem is illustrated in Fig. 6 of the plot of $\log \sigma_c$ vs $\log P_{O_2}$ for the 1 mole % CaO specimen. At lower temperatures 700° - 900°C and oxygen pressures the actual conductivity data exhibits a greater dependence on P_{O_2} than the simple model predicts. Since this region is characterized by predominantly electronic conductivity this observation would imply that the proposed model for electronic conductivity in this region is overly simplified.

A more subtle problem is the assumption that predominantly ionic conductivity occurs in the region of temperature and P_{O_2} where the total conductivity is observed to be independent of P_{O_2} . If this region of P_{O_2} and temperature occurs where the electronic conductivity is a minimum (i.e. in the transition region between n and p-type conductivity), then the electronic conductivity should be slightly dependent on P_{O_2} and the total conductivity might appear as if it were independent of P_{O_2} . Thus it is also possible that some p-type behavior may exist at lower temperatures (e.g. 700° - 900°C) and higher oxygen pressures (e.g. $1 - 10^{-4}$ atm).

Additional studies that would aid in providing a better understanding of electrical conduction in CaO-doped $Ce_{1+y}O_2$ are:

1. Thermodynamic measurements of the oxygen content as a function of temperature and oxygen pressure. This type of data would

allow one to test the model for dependence of the electronic carrier concentration $[Ce'_{Ce}]$ on P_{O_2} and temperature without the complication of considering the effects of CaO on the electronic mobility.

2. Transference measurements as a function of temperature, P_{O_2} and CaO content when combined with the corresponding σ data should allow the determination of the temperature, P_{O_2} and CaO content dependence of the electronic and ionic conductivity.

This type of data will indicate if p-type conductivity is present at low temperatures and high P_{O_2} . It would also permit a test of the simple model for ionic conductivity which assumes that σ_i is independent of P_{O_2} .

An equation for the diffusion coefficient of oxygen vacancies, $D_{V''_O}$, in CaO-doped CeO_2 was also determined in this study.¹² The expression

$$D_{V''_O} = 1.4 \times 10^{-1} (kT) \exp(-.61/kT) \quad (21)$$

was calculated by combining Eqs. (13 and 19) with the Nernst-Einstein relation. It is interesting to note that mobility of oxygen vacancies in CaO-doped CeO_2 is larger than in CaO-doped ZrO_2 .¹⁹

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Table I.

Mass Spectrographic Analysis of CeO_2 (ppmw)

Element ¹	American Potash and Chemical Corporation CeO_2 (code 217.91)
Ca	200
F	30
Fe	10
K	600
Li	20
Mg	10
Na	300
P	200
Pb	10
S	100
Si	20
Th	40
Ti	20
Zr	10

¹ Seventy-three elements were present, most in traces; only major impurities are listed.

Table II

Impurity Analysis of Fisher F.W. 100.091
Certified Reagent CaCO_3

Impurity ¹	Percentage
SO_4	0.009
Ba	0.001
Cl	0.0005
Fe	0.0005
Pb	0.001
Sr	0.0
Mg	0.005
K	0.00

¹0.004% insoluble in HCl and 0.001% insoluble in NH_3OH

Table III

Chemical Analysis of the CaO Content of
the Conductivity Specimens used in this Investigation

Nominal Mole % CaO	XRF ¹ Mole % CaO	AAS ² Mole % CaO
1.00	1.43	----
2.00	1.82	2.06
5.00	4.93	5.10
7.00	7.30	7.10

¹X-ray Fluorescence

²Atomic Absorption Spectrometry