COO-1441-28

A STUDY OF THE DEFECT STRUCTURE OF "PURE" AND DOPED NONSTOICHIOMETRIC CeO_2

Final Report
for Period January 1, 1965-May 31, 1977

Robert N. Blumenthal

College of Engineering
Marquette University
Milwaukee, Wisconsin 53233

MASTER

November 1977

Prepared For
THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT NO. E(11-1)-1441

REA

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

ABSTRACT

The purpose of this research program was to determine the defect structure (i.e. the type and concentration of atomic and electronic defects and the equilibrium relationships between these defects and the external variables such as temperature and oxygen pressure) and transport properties of defects in nonstoichiometric oxides from their electrical and thermodynamic behavior. Similar studies were also made on doped-nonstoichiometric oxides to determine the effect of the ionic radii, valence and concentration of the dopant cation on the nonstoichiometric defect structure and the transport properties of these defects. Studies of this kind also provide information about the magnitude, temperature and compositional dependence of the mobility of both electronic and ionic charge carriers in "pure" and doped-nonstoichiometric oxides at elevated temperatures, such data has been rather sparse in the literature.

The thermodynamic and electrical property study on "pure" and doped-nonstoichiometric CeO_{2-x} is reviewed. The combined study of the electrical conductivity, ionic transference, and thermodynamic measurements initiated on CaO-doped CeO_2 as a function of temperature, oxygen pressure and CaO content is discussed. The results of similar measurements on CeO_2 doped with other oxides (e.g. ThO_2, Ta_2O_5, etc.) which have cations with different valences and ionic radii are also discussed. The primary objective of these studies was to determine the effect of ionic radii, valence and concentration of the dopant cation on (1) the nonstoichiometric behavior, (2) the thermodynamic quantities $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$, (3) the nonstoichiometric defect structure, (4) the electronic and ionic conductivities, and (5) the mobility of electrons and oxygen vacancies in doped CeO_{2-x}.

INTRODUCTION

Applications and potential applications of metal oxides in science and technology have increased significantly in recent years. For example, fluorite solid solutions of zirconia and thoria have been incorporated in a variety of galvanic cells to measure basic thermodynamic and kinetic data. Examples of technological applications of oxides include: oxide fuel elements for nuclear reactors, oxide electrolytes for batteries and fuel cells, electrodes in magnetohydrodynamic power generators, high-temperature electrochemical devices for monitoring the oxygen content of liquid metal and gases, air-fuel ratio monitors for internal combustion engines based on the electrical conductivity of metal oxide sensors which respond to the concentration of O_2 in the exhaust gas, high temperature oxide insulators, oxide catalysis, and high dielectric capacitors.

The utilization of oxide systems in the above applications depends primarily on their unique properties. Since the properties of oxides are controlled to a great extent by the type and concentration of defects, optimization of these properties for a particular application requires that the defect structure be well characterized.

The purpose of this research program was to determine the defect structure (i.e. the type and concentration of atomic and electronic defects and the equilibrium relationships between these defects and the external variables such as temperature and oxygen pressure) and transport properties of defects in nonstoichiometric oxides from their electrical and thermodynamic behavior. Similar studies were also made on doped-nonstoichiometric oxides to determine the effect of the ionic radii, valence and concentration of the dopant cation on the nonstoichiometric defect structure and the transport properties of these defects. Studies of this kind also provide information about the magnitude, temperature and compositional dependence of the mobility of both electronic and ionic charge carriers in "pure" and doped-nonstoichiometric oxides at elevated temperatures, such data has been rather sparse in the literature.

The thermodynamic and electrical property study on "pure" and doped-nonstoichiometric CeO_{2-x} will be reviewed.[1-11] The combined study of the electrical conductivity, ionic transference, and thermodynamic measurements initiated on CaO-doped CeO_2 as a function of temperature, oxygen pressure and CaO content will be discussed.[9,10] The results of similar measurements on CeO_2 doped with other oxides (e.g. ThO_2, Ta_2O_5, etc.) which have cations with different valences and ionic radii will also be discussed.[11,12] The primary objective of these studies was to determine the effect of ionic radii, valence and concentration of the dopant cation on (1) the nonstoichiometric behavior, (2) the thermodynamic quantities $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$, (3) the nonstoichiometric defect structure, (4) the electronic and ionic conductivities, and (5) the mobility of electrons and oxygen vacancies in doped CeO_{2-x}.

NONSTOICHIOMETRIC "PURE" CERIUM DIOXIDE

Nonstoichiometric cerium oxide, CeO_{2-x}, is a metal excess, n-type semiconductor. The earlier studies of the defect structure of CeO_{2-x} inferred from the observed oxygen partial pressure dependence of the electrical conductivity and the oxygen nonstoichiometry x have not been in unanimous agreement. Many of these studies have interpreted the experimental results using mass-action law treatments involving either cerium interstitials, oxygen vacancies or both in various states of ionization as being the predominant nonstoichiometric defect.[1,3-5,13,14]

The recent thermodynamic study on CeO_{2-x} by Panlener et al. has contributed much to the clear understanding of the nonstoichiometric defect structure.[7] The range of nonstoichiometry covered was $0.001 \leq x \leq 0.3$. The thermodynamic quantities $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ (i.e. the relative partial molal enthalpy and entropy) were found to be independent of temperature. In the composition range $0.001 < x < 0.01$, $\Delta\bar{H}_{O_2}$ exhibits a slight dependence on x; however the variation of $\Delta\bar{S}_{O_2}$ is consistent with the defect reaction represented by Eq. (1) involving randomly distributed doubly ionized oxygen vacancies and electrons localized on cerium atoms.

$$2Ce_{Ce} + 2O_{O} = 1/2O_2(g) + V_{O}^{\bullet\bullet} + 2Ce'_{Ce} \qquad (1)$$

In this composition region, the oxygen partial pressure dependence of x, $x \sim P_{O_2}^{-1/5}$, is attributed to the variation of $\Delta\bar{H}_{O_2}$ with nonstoichiometry. The previous defect model analysis utilizing the law of mass action approach is invalid because of the requirement of constant $\Delta\bar{H}_{O_2}$ (i.e. $\Delta\bar{H}_{O_2} \neq f(x)$).

In the composition region $x > 0.01$ defect interactions become important and $x \sim P_{O_2}^{-1/n}$ where $n > 5$ increases with decreasing P_{O_2}.

Other experimental evidence for the presence of oxygen vacancies as nonstoichiometric defects are: (i) oxygen self diffusion measurements by Steele and Floyd;[15] (ii) high temperature x-ray and neutron diffraction studies of Faber.[16]

The combination of thermodynamic and electrical conductivity studies by Blumenthal and Sharma[5] has resulted in the first complete characterization of the electronic conductivity of CeO_{2-x}. The isothermal electronic conductivity, σ_e, dependence on composition may be represented by the following expression

$$\sigma_e = 410[x]e^{-(0.158+x)/kT}(\text{ohm-cm})^{-1} \qquad (2)$$

over the temperature range 750° to 1500°C and from $x = 0.001$ to $x = 0.1$.

Equation (2) was rationalized in terms of the following simple relations for (a) the electron carrier concentration

$$n_{Ce'_{Ce}} = 8x/a_o^{\,3} \qquad (3)$$

where $n_{Ce'_{Ce}}$ is the number of Ce'_{Ce} per cubic centimeter and a_o is the lattice parameter, and (b) the electron mobility

$$\mu_e = 5.2(10^{-2})e^{-(0.158+x)/kT}(\text{cm}^2/\text{V-sec}) \qquad (4)$$

In a recent study in this laboratory an electrochemical cell technique was used to measure the ionic transference number of sintered specimens of "pure" nonstoichiometric CeO_{2-x} as a function of temperature and oxygen partial pressure.[6] The results were described in terms of a high and low oxygen pressure region. The ionic transference number, t_i, is controlled by impurities in the high oxygen region (i.e. $1 > P_{O_2} > 10^{-3}$ atm). In the low oxygen pressure region the ionic transference number is small (e.g. above

700°C, $t_i < 0.08$). The electrical conduction in this region is controlled by the nonstoichiometric defects and is predominantly electronic. Using the value of $t_i \simeq 0.05$ an estimate of the diffusion coefficient for doubly ionized oxygen vacancies, $D_{V_O^{\cdot\cdot}} \simeq 3.5 \times 10^{-5}$ cm^2/sec at 1000°C was calculated by combining thermodynamic and conductivity data with the Nernst-Einstein relation.

DOPED NONSTOICHIOMETRIC CERIUM DIOXIDE

In our previous progress reports and recent publications we have described in detail a comprehensive study initiated in our laboratory to determine the effect of ionic radius, valence and concentration of foreign cations on the thermodynamic and electrical behavior of doped CeO_{2-x}.[8,9,11,12] Cerium dioxide was selected as the host oxide in these doping experiments because it exhibits a large nonstoichiometric region,[7,17] an extensive solubility for foreign cations[18] and extensive studies have been performed on the thermodynamic[7,17] and electrical[3-6] behavior of "pure" CeO_{2-x}.

Based on studies of x-ray and neutron diffraction,[16] thermodynamic,[7] electrical conductivity[3-6] and oxygen diffusion,[15] the predominant defects in nonstoichiometric CeO_2 are doubly ionized oxygen vacancies and electrons localized on normal cerium atoms.

The doping experiments on CeO_{2-x} were initiated using CaO because the calcium ion has an ionic radius similar to a cerium ion and the addition of CaO to CeO_2 results in the formation of oxygen vacancies.[8] Thus, the solution of CaO in nonstoichiometric cerium dioxide may be represented by the formula $Ce_{1-y}Ca_yO_{2-y-x}$.

In a recent study the electrical conductivity of CaO-doped CeO_2 (0.1 to 16 mole percent CaO) was measured as a function of P_{O_2} (1 to 10^{-22} atm) and temperature (700° to 1500°C).[8] All compositions exhibited mixed conduction and two limiting case regions were observed. The isothermal electrical conductivity at low temperatures and high oxygen partial pressures is independent of P_{O_2}; the electrical conduction in this region is predominantly ionic and is directly proportional to the CaO content up to about 8 mole % CaO. The following expression was obtained

$$\sigma_i = [6.0 \pm 0.5][\text{mole \% CaO}]e^{-0.62/kT} \qquad (5)$$

relating the ionic conductivity to the mole % CaO and temperature in this oxygen pressure and temperature region. At very low oxygen pressures and high temperatures the conduction is primarily electronic. In this region the magnitude and P_{O_2} dependence of σ is similar to "pure" CeO_{2-x}. At intermediate oxygen pressures the conduction is mixed (i.e. both electronic and ionic conduction is important).

As in the case of the defect structure analysis of "pure" CeO_2, the same problems associated with the mass action law approach and the compositional dependence of the charge carrier mobility are also present in the analysis of doped CeO_2 (e.g. a) negligible interaction of defects (i.e. $\Delta\bar{H}_{O_2} \neq f(x)$), b) random distribution of defects, c) Boltzmann statistics instead of Fermi Dirac statistics).[19]

Recently, an extensive thermodynamic investigation has been done on CaO-doped CeO_2, $Ce_{1-y}Ca_yO_{2-y-x}$.[9] The results indicate that the thermodynamic behavior of CeO_2 doped with aliovalent cations with valence less than four are more readily suitable for mass action law treatments than the corresponding behavior of "pure" CeO_2. For example, the oxygen nonstoichiometry x in the formula $Ce_{1-y}Ca_yO_{2-y-x}$ is proportional to $P_{O_2}^{-1/4}$ over an appreciable range of P_{O_2}. The relative partial molal enthalpy, $\Delta\bar{H}_{O_2}$, is also constant in this same composition region. The dependence of $\Delta\bar{S}_{O_2}$ on x is consistent with the defect reaction described in Eq. (1).

Reddy recently measured the ionic transference numbers, t_i, of CaO-doped CeO_2 samples, using an oxygen concentration cell from 700° to 1000°C and from 1 to 10^{-22} atm of oxygen.[10,12] The transference data $t_i = t_i(P_{O_2},T)_y$ was combined with the appropriate electrical conductivity data, $\sigma = \sigma(P_{O_2},T)_y$

to obtain the following type of data for the ionic, σ_i, and electronic, σ_e, conductivities:

$$\sigma_i = \sigma_i(T,P_{O_2})_y \tag{6}$$

$$\sigma_e = \sigma_e(T,P_{O_2})_y \tag{7}$$

$$\sigma_i = \sigma_i(T,x)_y \tag{8}$$

$$\sigma_e = \sigma_e(T,x)_y \tag{9}$$

The results obtained to date may be summarized as follows:

a) Under isothermal conditions

$$\sigma_i \propto x \tag{10}$$

which is consistent with the dependence of σ_i on x predicted by the following expression

$$\sigma_i \cong B/T[y+x]e\mu'_{V_O^{\cdot\cdot}}.\exp(-E_i/kT) \tag{11}$$

For the case where $x >> x$ (i.e. at high oxygen pressures) Eq. (11) simplifies to the following expression

$$\sigma_i \cong B/T[y]e\mu'_{V_O^{\cdot\cdot}}.\exp(-E_i/kT) \tag{12}$$

The derivation of Eqs. (11) and (12) is based on a defect model involving doubly ionized oxygen vacancies.

b) Under isothermal conditions

$$\sigma_e \propto P_{O_2}^{-1/4} \tag{13}$$

and

$$\sigma_e \propto x \tag{14}$$

for $x < 3 \times 10^{-2}$. These results are consistent with defect models involving doubly ionized oxygen vacancies.

In the above study, CaO was selected as a dopant because the ionic radius of the calcium ion (Ca^{+2} : 1.09Å) is very similar to the cerium ion (Ce^{+4} : 1.07Å).[18] To determine the effect of a larger cation with the same valence as Ca^{+2}, an electrical conductivity and thermodynamic study[11] was made on SrO-doped nonstoichiometric cerium dioxide (i.e., $Ce_{1-y}Sr_yO_{2-y-x}$) as a function of temperature (∿ 700 - 1500°C) and oxygen partial pressure (∿ 1 to 10^{-21} atm). Assuming limiting case defect models the ionic, σ_i, and electronic, σ_e, conductivities were calculated from this data.

In the region where $y >> x$ (i.e., at low temperatures and high oxygen pressures) the conductivity is independent of P_{O_2} and up to approximately 3 mole % SrO, it is proportional to mole % SrO. The equation for ionic conductivity,

$$\sigma_i \simeq [4.5 \pm 0.5][\text{m/o SrO}]\exp(-0.58/kT) \ , \tag{15}$$

was obtained by fitting the conductivity data in this region to an expression derived on the basis of an oxygen vacancy model.

In the composition region between approximately $x = 10^{-3}$ and $x = 10^{-2}$, both the thermodynamic behavior and the electrical conductivity was shown to be consistent with a defect model involving randomly distributed doubly ionized oxygen vacancies and electrons localized on normal cerium sites. In this region the electronic conductivity varies linearly with x and the electronic mobility decreases with increasing SrO content.

An approximation expression for the diffusion coefficient of oxygen vacancies, $D_{V_O^{\cdot\cdot}}$, in SrO-doped CeO_2

$$D_{V_O^{\cdot\cdot}} \simeq 2.8 \times 10^{-3} \exp-(0.58/kT) \qquad (16)$$

was determined in this study from the above data and the Nernst-Einstein relation. It is interesting to note that $D_{V_O^{\cdot\cdot}}$ for SrO-doped CeO_2 is about 20% greater than $D_{V_O^{\cdot\cdot}}$ for CaO-doped CeO_2 at 800°C, whereas at 1000°C both values of $D_{V_O^{\cdot\cdot}}$ are about equal.[8]

A recent study of oxygen self-diffusion[15] in yttria doped ceria at $P_{O_2} = 1$ atm in the temperature range 850 - 1150°C indicates that the activation energy, approximately 20 kcal/mole, is essentially independent of yttria composition (i.e., for z between 0 and 0.2 in the formula $Ce_{1-2z}Y_{2z}O_{2-z}$). The activation energy obtained in this study (∿ 13 kcal/mole) for diffusion of oxygen vacancies produced by SrO is about 1 kcal less than observed in a similar study[8] on CaO-doped CeO_2 and about 7 kcal less than the value reported for self-diffusion of oxygen in $Ce_{1-2z}Y_{2z}O_{2-z}$.

In our previous progress reports and recent publications we have described in detail a comprehensive study initiated in our laboratory to determine the effect of the ionic radii, valence and concentration of foreign cations on (1) the nonstoichiometric behavior of doped CeO_{2-x}, (2) the thermodynamic quantities, $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$, and (3) the nonstoichiometric defect structure of doped CeO_{2-x}.[9,11,12]

Our earlier reported thermodynamic studies on doped-CeO_{2-x} have been limited primarily to foreign cations with a lower valence than cerium (i.e., Ca, Sr, Y and La).[12] It has been shown that doping CeO_2 with these lower valent cations produces oxygen vacancies.[8,11] Thus the solution of MO or M'_2O_3 in nonstoichiometric cerium dioxide may be represented by the formulae $Ce_{1-y}M_yO_{2-y-x}$ and $Ce_{1-z}M'_zO_{2-z/2-x}$ respectively where M = Ca, Sr and M' = Y, La. In the composition region near stoichiometry (i.e., for x between approximately 10^{-3} and 10^{-2}). For these lower valent dopants the variation of $\Delta\overline{S}_{O_2}$ with x was found to be consistent with a defect model involving randomly distributed doubly ionized oxygen vacancies and electrons localized on normal cerium sites.[9] The range of nonstoichiometry with which this defect model fits the experimental results increases with increasing dopant concentration.[9] In this same nonstoichiometric region $\Delta\overline{H}_{O_2}$ exhibits a very small dependence on x for the lower dopant concentration (e.g. $y < 0.045$ for $Ce_{1-y}Ca_yO_{2-y-x}$) and for the higher dopant concentration $\Delta\overline{H}_{O_2}$ is essentially independent of x.

In the last progress report[12] an attempt was made to relate the dependence of $\Delta\overline{H}_{O_2}$ on the dopant concentration for the lower valent foreign cation (e.g. y/2 for $Ce_{1-y}Ca_yO_{2-y-x}$ and z/4 for $Ce_{1-z}La_zO_{2-z/2-x}$). The values of $\Delta\overline{H}_{O_2}$ used were determined in the near stoichiometric region (i.e. where $\Delta\overline{H}_{O_2}$ exhibits either a small dependence or is independent of x). As discussed in previous publications[9,11] and reports,[12] this is the same region of nonstoichiometry where the variation of $\Delta\overline{S}_{O_2}$ with log x is consistent with the nonstoichiometric defect model proposed for "pure" CeO_2 and CeO_2 doped with either CaO, SrO, La_2O_3 or Y_2O_3. From plots of $\Delta\overline{H}_{O_2}$ versus y/2 and z/4 it was observed that the dependence of $\Delta\overline{H}_{O_2}$ on the oxygen vacancy concentration appears to be linear within a band of approximately ± 0.2 eV.[12] It also appears that the dependence of $\Delta\overline{H}_{O_2}$ on the ionic radius is very small.

Although we do not have any quantitative explanation for these results, it is interesting to speculate about the possible causes for the observed behavior. For example, to a first order approximation the increase in $\Delta\overline{H}_{O_2}$ with y/2 or z/4 may be related to a decrease in the coulombic attraction resulting from the decreased average charge of the ions (i.e. substitution of lower valent cations and the presence of oxygen vacancies would reduce the average charge of the cations and anions in CeO_2 doped with lower valent oxides).

A recent study in this laboratory has also been initiated on the electrical conductivity of ThO_2-doped CeO_2 as a function of P_{O_2} and temperature.[12] In this study ThO_2 was selected as a dopant because: (1) the ionic radius of Th^{+4} is larger than Ce^{+4} and (2) ThO_2 has the same fluorite crystal structure as CeO_2 (an x-ray study has shown that ThO_2 and CeO_2 are completely soluble in one another), (3) the thorium ion has the same valence as a cerium ion. Thus, ThO_2 should be an excellent dopant for determining the effect of lattice dilatation on the (a) energy of formation of the nonstoichiometric defects reaction

$$2Ce^{x} + O^{x} = V_{O}^{\cdot\cdot} + 2Ce_{Ce}' + 1/2\ O_2(g) \qquad (1)$$

and (b) the energy of motion for the electrons, Q, in the expression

$$\mu = \mu_o e^{-Q/kT} \quad . \qquad (17)$$

As described in the progress report[12] thermogravimetric measurements were made on ThO_2-doped nonstoichiometric cerium dioxide specimens (10 mole % ThO_2) as a function of temperature and oxygen pressure. From this data the deviation from stoichiometry $x = x(T,P_{O_2})_y$ was determined for value of $y = 0.10$.

At small deviations from stoichiometry (i.e. for x less than approximately 0.01) the nonstoichiometric behavior is best characterized by the relation

$$x \propto P_{O_2}^{-1/4} \qquad (18)$$

As discussed in the electrical properties section the electrical conductivity of ThO_2 doped CeO_2 samples was effected by the presence of impurities.[12] The nonstoichiometric dependence, x, on P_{O_2} given by Eq. (18) is consistent with the behavior observed for CeO_2 doped with lower valent cations (e.g. Ca, Sr, Y, La).[12] Thus it appears that the lower valent impurities are effecting the nonstoichiometric behavior of ThO_2 doped CeO_2. This sample is now being analyzed to check the above interpretation.

It is interesting to note that $\Delta\overline{H}_{O_2}$ is independent of x in the region near stoichiometry.[12] In this same composition region the magnitude of $\Delta\overline{H}_{O_2}$ increases about 1 eV relative to the value reported for "pure" CeO_{2-x}.[12] However, it is difficult to attribute the above changes in $\Delta\overline{H}_{O_2}$ solely to the presence of ThO_2 because the thermodynamic behavior may also be influenced by the presence of lower valent cation impurities.

The effect of the lattice parameter on $\Delta\overline{H}_{O_2}$ appears to be more of a second order effect because the above change in $\Delta\overline{H}_{O_2}$ is much smaller than would be expected based on the large increase in the lattice parameter resulting from the presence of 10 mole % ThO_2.

All of the previous studies on doped CeO_2 have been limited to foreign cation with the same or lower valence than cerium. None of these dopants produce charge compensating electronic defects. Thus, in an attempt to determine the relative importance of the valence of substitutional foreign ions and electronic defects on $\Delta\overline{H}_{O_2}$, a combined electrical conductivity and thermodynamic study on Ta_2O_5 doped cerium dioxide was initiated.[12] A higher valent dopant Ta_2O_5 was selected because it produces charge compensating electronic defects rather than oxygen vacancies as is the case for lower valent cations.

Thermogravimetric and electrical conductivity measurements were made on Ta_2O_5-doped nonstoichiometric cerium dioxide (i.e. $Ce_{1-y}Ta_yO_{2-x}$) as a function of temperature (800-1300°C) and oxygen partial pressure ($1-10^{-22}$ atm).[20] From the thermodynamic data the deviation from stoichiometry $x = x(T,P_{O_2})_y$ was determined from values of y = 0.00199, 0.00598, 0.00995, 0.01489 and 0.0198. The thermodynamic quantities $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ were calculated in the region $0.003 \leq x \leq 0.2$ and found to be independent of temperature.

In the composition region near stoichiometry, $\Delta\bar{H}_{O_2}$ for Ta_2O_5 doped samples decreases with x. The range of this dependence increases with increasing Ta_2O_5 content. In this composition range, relative partial molal enthalpy, $\Delta\bar{H}_{O_2}$ for "pure" CeO_2 increases with x. At large deviations from stoichiometry the dependence of $\Delta\bar{H}_{O_2}$ for Ta_2O_5 doped specimen is similar to "pure" CeO_2, i.e. it increases with x. Since the relative partial molal enthalpy, $\Delta\bar{H}_{O_2}$ for doped samples exhibits a strong and complicated dependence on x, the variation of $\Delta\bar{S}_{O_2}$ is not consistent with the equations based on randomly distributed defect models.

In the region where y >> x (i.e. at low temperature and high oxygen pressures) the conductivity is independent of P_{O_2} and exhibits a maximum near 0.75 mole % Ta_2O_5. In the same region of nonstoichiometry and between 0.3 and 1.0 mole % Ta_2O_5, the activation energy, Q, increases with dopant concentration. At intermediate oxygen pressures, the conductivity does not exhibit a single P_{O_2} dependence except with increasing Ta_2O_5 content the P_{O_2} dependence decreases. However in the same region of oxygen partial pressures, the conductivity of "pure" CeO_{2-x} is proportional to $P_{O_2}^{-1/5}$.

From the electrical conductivity and thermodynamic data, the isothermal compositional dependence of the electrical conductivity of Ta_2O_5 doped CeO_2 was determined. Over the temperature range 800 - 1300°C, from $y = 0.00199$ to $y = 0.0198$ and $x = 0.002$ to $x = 0.16$, the compositional and temperature dependence of the electrical conductivity may be represented by the expression

$$\sigma = (177.3 + 19600y)(1-2y-2x)(y+2x) \exp\left[\frac{-[(0.167 + 9.57y) + (0.676 - 21.4y)x]}{kT}\right]$$

where activation energy of electron motion is a function of both dopant concentration and nonstoichiometry.[20]

REFERENCES

1. R. N. Blumenthal and J. E. Laubach, "Anisotropy in Single-Crystal Refractory Compounds", Vol. 2, p. 137, Plenum Press, New York (1968).
2. R. N. Blumenthal and R. J. Panlener, J. Phys. Chem. Solids, 31, 1190 (1970).
3. R. N. Blumenthal, P. W. Lee and R. J. Panlener, J. Electrochem. Soc., 118, 123 (1971).
4. R. N. Blumenthal and R. L. Hofmaier, J. Electrochem. Soc., 121, 126 (1974).
5. R. N. Blumenthal and R. K. Sharma, J. Solid State Chem., 13, 360 (1975).
6. G. H. VanHandel and R. N. Blumenthal, J. Electrochem. Soc., 121, 1198 (1974).
7. R. J. Panlener, R. N. Blumenthal and J. E. Garnier, J. Phys. Chem. Solids, 36, 1213 (1975).
8. R. N. Blumenthal, F. S. Brugner and J. E. Garnier, J. Electrochem. Soc., 120, 1230 (1973).
9. J. E. Garnier, R. N. Blumenthal, R. J. Panlener and R. K. Sharma, J. Phys. Chem. Solids, 37, 369 (1976).
10. S. Reddy, Ph.D. Dissertation, Marquette University, Milwaukee, WI, 1977.
11. R. N. Blumenthal and J. E. Garnier, J. Solid State Chem., 16, 21 (1976).
12. R. N. Blumenthal, Technical Report, COO-1441-27 (1975).
13. E. H. Greener, J. M. Wimmer and W. M. Hirthe, "Rare Earth Research II," (Karl S. Vorres, Ed.), p. 539, Gordon and Breach, New York (1964).
14. C. J. Kevane, Phys. Rev., 133, A1431 (1964).
15. B. C. H. Steele and J. M. Floyd, Proc. Brit. Ceram. Soc., 19, 55 (1971).
16. J. Faber, Ph.D. Dissertation, Marquette University, Milwaukee, Wisconsin, 1973.
17. D. J. M. Bevan and J. Kordis, J. Inorg. Nucl. Chem., 26, 1509 (1964).
18. H. H. Mobius, Z. Chem., 4, 81 (1964).
19. R. N. Blumenthal, J. Solid State Chem., 12, 307 (1975).
20. R. K. Sharma, Ph.D. Dissertation, Marquette University, Milwaukee, WI, 1977.

LIST OF PUBLICATIONS ISSUED DURING THE CONTRACT PERIOD

January 1, 1965 to May 31, 1977

1. R. N. Blumenthal, J. Coburn, J. Baukus and W. M. Hirthe, J. Phys. Chem. Solids, 27, 643 (1966).
2. R. N. Blumenthal and B. A. Pinz, J. Appl. Phys., 38, 2376 (1967).
3. R. N. Blumenthal and J. E. Laubach, "Anisotropy in Single Crystal Refractory Compounds", Vol. 2, p. 137, Plenum Press, New York (1968).
4. R. N. Blumenthal and R. J. Panlener, J. Phys. Chem. Solids, 31, 1190 (1970).
5. F. S. Brugner and R. N. Blumenthal, J. Am. Ceram. Soc., 54, 57 (1971).
6. R. N. Blumenthal, P. W. Lee and R. J. Panlener, J. Electrochem. Soc., 118, 123 (1971).
7. R. N. Blumenthal, F. S. Brugner and J. E. Garnier, J. Electrochem. Soc., 120, 1230 (1973).
8. R. N. Blumenthal and R. L. Hofmaier, J. Electrochem. Soc., 121, 126 (1974).
9. G. J. VanHandel and R. N. Blumenthal, J. Electrochem. Soc., 121, 1198 (1974).
10. R. N. Blumenthal and R. K. Sharma, J. Solid State Chem., 13, 360 (1975).
11. R. J. Panlener, R. N. Blumenthal and J. E. Garnier, J. Phys. Chem. Solids, 36, 1213 (1975).
12. R. N. Blumenthal, J. Solid State Chem., 12, 307 (1975).
13. J. E. Garnier, R. N. Blumenthal, R. J. Panlener and R. K. Sharma, J. Phys. Chem. Solids, 37, 369 (1976).
14. R. N. Blumenthal and J. E. Garnier, J. Solid State Chem., 16, 21 (1976).