C00-1441-26

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

Progress Report

Robert N. Blumenthal

College of Engineering
Marquette University
Milwaukee, Wisconsin

January 1, 1974 - December 31, 1974

PREPARED FOR THE U. S. ATOMIC ENERGY COMMISSION
UNDER CONTRACT NO. AT(11-1)-1441

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

LB

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

Electrical conductivity and thermogravimetric measurements were made on SrO-doped nonstoichiometric cerium dioxide (i.e. $\text{Ce}_{1-y}\text{Sr}_y\text{O}_{2-y-x}$) as a function of temperature ($\sim 700^\circ$ to 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 $y \gg x$ (i.e. at low temperatures and high oxygen pressures) the following equation was obtained

$$\sigma_i \approx 4.5 \pm 0.5 [\text{m/o SrO}] \exp^{-0.58\text{eV}/kT}$$

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 σ_e varies linearly with x and the electronic mobility decreases with increasing SrO content.

An electrochemical cell technique was used to measure the ionic transference number of CeO_{2-x} doped with 10 mole % CaO (i.e. $\text{Ce}_{1-y}\text{Ca}_y\text{O}_{2-y-x}$) as a function of temperature and P_{O_2} . The transference data, $t_i = t_i(P_{\text{O}_2}, T)_{y=0.1}$, was combined with the electrical conductivity and thermodynamic data to obtain the dependence of the electronic and ionic conductivities on composition and temperature.

At high oxygen pressures the electronic conductivity is p-type and the electrical conductivity is predominantly ionic. The ionic conductivity in this region is controlled by the dopant concentration (i.e. $y \gg x$). As the partial pressure of oxygen decreases σ_e exhibits a minimum and at

very low oxygen pressures conduction is predominantly electronic (n-type).

In the composition region $10^{-3} < x < 10^{-2}$, $\sigma_i \propto x$.

The electronic conductivity of the CaO-doped CeO_2 specimen exhibits a similar dependence on x as "pure" CeO_2 , except the magnitude of σ_e is lower and at smaller values of x the electronic conductivity exhibits a nonlinear dependence on x .

Thermogravimetric measurements were performed on specimens of CeO_2 doped with 1 and 7 mole % SrO , 14 mole % La_2O_3 and 14 mole % Y_2O_3 as a function of P_{O_2} and T . From this data the deviation from stoichiometry $x = x(T, P_{\text{O}_2})$ was determined. The thermodynamic quantities $\Delta \bar{H}_{\text{O}_2}$ and $\Delta \bar{S}_{\text{O}_2}$ were calculated in the region $0.001 \leq x \leq 0.2$ and found to be independent of temperature. In the composition region near stoichiometry the variation of $\Delta \bar{S}_{\text{O}_2}$ with $\log x$ is consistent with the same nonstoichiometric defect model as proposed for "pure" and CaO-doped CeO_2 .

"This report was prepared as an account of Government-sponsored work. Neither the United States, nor the Atomic Energy Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

As used in the above, 'person acting on behalf of the Commission' includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor."

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 is 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 will also be made on doped-nonstoichiometric oxides to determine the effect of the defects produced by doping on the nonstoichiometric defect structure and the transport properties of these defects. In this investigation the thermodynamic and electrical properties

of "pure" and doped nonstoichiometric oxides will be measured as a function of oxygen nonstoichiometry, temperature, type (e.g. valence, ionic radius of the dopant ion) and concentration of the dopant. The analysis of the data should permit the calculation of the energies of formation of the various defect reactions which contribute to the defect structure. In addition, from the determination of the thermodynamic quantities $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$, it should be possible to determine the range of composition where i) the law of mass action is applicable and ii) a more complex statistical thermodynamic treatment is necessary to explain the equilibrium relations between defects in the nonstoichiometric oxides investigated. 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, such data has been rather sparse in the literature.

The thermodynamic and electrical property study initiated on "pure" and doped nonstoichiometric cerium dioxide has been continued. The literature on the x-ray, thermodynamic and electrical property studies on nonstoichiometric CeO_{2-x} and CaO-doped CeO_2 has been reviewed previously.¹⁻¹³ The following is a brief summary of some of the results of previous studies in this laboratory on the electrical and thermodynamic behavior of "pure" and CaO-doped nonstoichiometric cerium dioxide.

In a recent thermodynamic study,^{4,12} thermogravimetric measurements were performed on nonstoichiometric CeO_{2-x} in the temperature range 700° to 1500°C and from oxygen pressures of 10^{-1} to 10^{-26} atm. From this data the deviation from stoichiometry $x = x(T, P_{O_2})$ was determined. The thermodynamic quantities $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ were calculated from this data and found to be independent of temperature. In the composition region $0.001 < x < 0.01$,

the variation of $\Delta \bar{S}_{O_2}$ with x is consistent with the defect reaction

involving randomly distributed doubly ionized oxygen vacancies, $V_{O}^{\bullet\bullet}$, and electrons localized on a cerium ion at a normal cerium site, $Ce_{Ce}^{\bullet}$. The experimental $P_{O_2}^{-1/5}$ dependence of x and σ was rationalized on the basis of the above defect model and the observation that $\Delta \bar{H}_{O_2}$ (≈ 10 eV) exhibits a slight dependence on x . Thus the application of the law of mass action is invalid in this composition range because $\Delta \bar{H}_{O_2}$ is a function of x . At large deviations from stoichiometry $\Delta \bar{H}_{O_2}$ changes rapidly with x , the nonstoichiometric behavior in this region appears to be more strongly dependent on defect interaction.

Two recent studies have provided convincing evidence that the predominant nonstoichiometric defects in CeO_2 are oxygen vacancies; Steele and Floyd¹⁴ by measurements of oxygen self diffusion from 850° to 1150°C and Faber¹⁵ by x-ray and neutron diffraction measurements from 800° to 1000°C.

Employing an electrochemical cell technique ionic transference measurements were made in this laboratory on sintered specimens of nonstoichiometric CeO_{2-x} as a function of temperature (600° - 1000°C) and oxygen pressure (1 to 10^{-22} atm).¹⁰ In the composition region $10^{-3} < x < 0.2$ between 700° and 1000°C, t_i was less than 0.08 with an average value of about 0.05. The electrical conduction in this region was reported to be predominantly electronic and controlled by the nonstoichiometric defects, $V_{O}^{\bullet\bullet}$ and $Ce_{Ce}^{\bullet}$.

In a recent study the electrical conductivity of sintered specimens of nonstoichiometric CeO_{2-x} was measured as a function of temperature (750° - 1500°C) and oxygen pressure (1 to 10^{-26} atm).⁹ The isothermal compositional

dependence of the electrical conductivity of CeO_{2-x} was determined by combining the above thermodynamic data,^{4,12} $x = x(P_{\text{O}_2}, T)$, with the appropriate conductivity data, $\sigma = \sigma(T, P_{\text{O}_2})$. The compositional and temperature dependence of the electrical conductivity was represented by the expression

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

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

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

$$n_{\text{Ce}'_{\text{Ce}}} = \frac{8x}{a_o^3} \quad (3)$$

where $n_{\text{Ce}'_{\text{Ce}}}$ is the number of Ce'_{Ce} per cm^3 , a_o is the lattice parameter and (b) the electron mobility

$$\mu = 5.2(10^{-2})e^{-Q/kT} \text{ (cm}^2\text{/volt-sec)} \quad (4)$$

where the activation energy, Q , for electronic transport is given by the expression

$$Q = 0.158 + x. \quad (5)$$

It was postulated that the decrease in mobility, which is a result of the increase in Q with x , is related to the observed increase in a_o with x .^{9,11} The linear dependence of $n_{\text{Ce}'_{\text{Ce}}}$ on x , Eq. (3), suggests that the nonstoichiometric defect reaction, Eq. (1), proposed on the basis of the above thermodynamic study for the composition region $10^{-3} < x < 10^{-2}$ is in all probability valid over the composition region $10^{-3} < x < 10^{-1}$.

Although there have been several defect structure analyses based on the thermodynamic and/or electrical properties of "pure" nonstoichiometric

oxides and doped-stoichiometric oxides, there have been very few of these types of analyses on doped-nonstoichiometric oxide systems. In order to help provide a better understanding of defect behavior in doped-nonstoichiometric oxide systems we have initiated a comprehensive study 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} . Cerium dioxide was selected as the host oxide in these doping experiments because it exhibits a large nonstoichiometric region,^{4,12} an extensive solubility for foreign cations¹⁶ and as discussed above extensive studies have been performed on the thermodynamic and electrical behavior of "pure" CeO_{2-x} . Based on these studies the predominant defects in nonstoichiometric CeO_2 have been shown to be doubly ionized oxygen vacancies and electrons localized on normal cerium atoms (Eq. 1).

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.⁷ Thus, the solution of CaO in nonstoichiometric cerium dioxide may be represented by the formula $\text{Ce}_{1-y}\text{Ca}_y\text{O}_{2-y-x}$. In a recent study⁷ in this laboratory the electrical conductivity (0.1 to 16 mole %) CaO doped cerium dioxide specimens has been measured as a function of P_{O_2} (i.e. 1 to 10^{-22} atm) and temperature (i.e. 700° to 1500°C).

Two limiting case regions were observed. At low temperatures and high oxygen pressures, the conductivity is predominantly ionic. In this region the conductivity is independent of P_{O_2} and between approximately 1 and 8 m/o CaO is proportional to mole per cent CaO. The following equation for ionic conductivity

$$\sigma_i = 6.0 \pm .05 [\text{m/o CaO}] \exp^{-0.62/kT} \quad (6)$$

was obtained by fitting the conductivity data in this region to an expression derived on the basis of an oxygen vacancy model. At high temperatures and low oxygen partial pressures and for lower CaO content the conductivity is predominantly electronic.

Thermogravimetric measurements were also performed in this laboratory on CaO-doped nonstoichiometric cerium dioxide (i.e. $\text{Ce}_{1-y}\text{Ca}_y\text{O}_{2-y-x}$) in the temperature range $800^\circ - 1500^\circ\text{C}$ and from oxygen pressures of 10^{-1} to 10^{-21} atm.¹³ From this data the deviation from stoichiometry $x = x(T, P_{\text{O}_2})_y$ was determined for values of $y = 0.01, 0.07, 0.10$ and 0.14 . The thermodynamic quantities $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$ were calculated in the region $0.001 \leq x \leq 0.2$ and found to be independent of temperature with the exception of the 14 mole % CaO at large deviations from stoichiometry.

In the composition region near stoichiometry (i.e. for x between approximately 10^{-3} and 10^{-2}), the variation of $\Delta\bar{S}_{\text{O}_2}$ with x was consistent with a defect model, Eq. (1), involving randomly distributed doubly ionized oxygen vacancies and electrons localized on normal cerium sites. The experimental observation that $x \propto P_{\text{O}_2}^{-1/4}$ was rationalized on the basis of the above defect model for the case where $y > x$.

At large deviations from stoichiometry the dependence of $x = x(T, P_{\text{O}_2})_y$ is similar to the nonstoichiometric behavior of "pure" CeO_{2-x} when $y = 0.01$ or 0.07 . The dependence of $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$ on x was also similar. However, for $y = 0.10$ and 0.14 the nonstoichiometric behavior and the dependence of $\Delta\bar{H}_{\text{O}_2}$ on x differs significantly from the behavior of "pure" CeO_{2-x} .

In the current investigation, the thermodynamic and electrical property study initiated on doped nonstoichiometric CeO_{2-x} was continued. Electrical conductivity and ionic transference measurements initiated on CaO-doped CeO_2 as a function of temperature, oxygen pressure and CaO

content were continued. Electrical conductivity and thermodynamic measurements were also made as a function of temperature, oxygen pressure and dopant concentration on CeO_2 doped with other oxides (e.g. SrO , La_2O_3 , Y_2O_3 , ThO_2 , etc.) which have cations with different valences and ionic radii. The results of these studies will be used to determine the effect of ionic radii, valence and concentration of the dopant cation on (1) nonstoichiometric behavior, (2) the thermodynamic quantities $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$, (3) the nonstoichiometric defect structure, and (4) the mobility of electron and oxygen vacancies in doped CeO_{2-x} .

RESULTS AND DISCUSSION

A. Electrical Property Studies on "Pure" and Doped-CeO_{2-x}

In the last progress report,⁶ a study was initiated to determine the effect of valence and ionic radii of the dopant cation on the behavior of the electrical conductivity. As discussed above a comprehensive study has been made on the electrical conductivity of CaO-doped CeO₂.⁷ 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).¹⁶ The dependence of the lattice parameter on CaO content has been reported to be 0.0004Å/mole % CaO.¹⁶ Thus the lattice parameter increased only slightly with the addition of CaO. As described in the previous report⁶ a study was initiated on SrO-doped CeO₂ to determine the effect of a large cation (Sr⁺²:1.14Å)¹⁶ with the same valence as Ca⁺² on the electrical behavior. In the current study conductivity measurements were made on SrO-doped CeO₂ (0.1, 1, 3 and 7 mole per cent) as a function of temperature (700° - 1500°C) and oxygen partial pressure (1 - 10⁻²² atm).

The temperature and compositional dependence of the electrical conductivity of Ce_{1-y}Sr_yO_{2-y-x} (i.e. $\sigma = f(T, x)_y$) was obtained using a combined analysis of the equilibrium $\sigma = \sigma(P_{O_2}, T)_y$ and $x = x(P_{O_2}, T)_y$ data¹³ obtained from a recent thermogravimetric study in our laboratory. The results of this combined study are described in a paper submitted for publication and in AEC Report C00-1441-25 and may be summarized as follows.

Assuming limiting case defect models the ionic, σ_i , and electronic, σ_e , conductivities were calculated from the electrical conductivity and thermodynamic data.

In the region where $y \gg x$ (i.e. at low temperatures and high oxygen pressures) the conductivity is independent of P_{O_2} and up to approximately

3 mole % SrO is proportional to mole % SrO. The following equation for ionic conductivity

$$\sigma_i = 4.5 \pm 0.5 [\text{m/o SrO}] \exp^{(-0.58 \text{ eV/kT})} \quad (7)$$

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 the same nonstoichiometric defect reaction that occurs in "pure" CeO_{2-x} .

where the doubly ionized oxygen vacancies and electrons localized on normal cerium sites were randomly distributed.

The electronic conductivity was calculated by subtracting σ_i from the total conductivity. The calculated electronic conductivity of $\text{Ce}_{1-y}\text{Sr}_y\text{O}_{2-y-x}$ exhibited essentially the same dependence on x as "pure" CeO_{2-x} .⁹ Thus the nonstoichiometric composition and temperature dependence of σ_e may be represented by the same type of expression as used for "pure" CeO_{2-x} .⁹

$$\sigma_e = A[x] e^{-Q/kT} \quad (8)$$

For "pure" CeO_{2-x} the concentration of electrons, $n_{\text{Ce}_{\text{Ce}}'}$, is proportional to x (Eq. 3) and the activation energy for electronic transport, Q , exhibits a linear dependence on x (Eq. 5). The electronic mobility of SrO-doped CeO_2 was observed to decrease with SrO content. Because of the limiting case models used to calculate σ_e and since only two SrO compositions, 1 and 7

mole %, were available for this analysis, no attempt was made to quantitatively determine the dependence of the electronic mobility on SrO content.

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.⁶ In this study ThO_2 was selected as a dopant because: (a) the ionic radius of Th^{+4} is larger than Ce^{+4} and (b) ThO_2 has the same fluorite crystal structure as CeO_2 (an x-ray study¹⁷ has shown that ThO_2 and CeO_2 are completely soluble in one another), (c) 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

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

$$\mu = \mu_0 e^{-Q/kT} \quad (9)$$

In the last progress report⁶ the preliminary results of the temperature dependence of the conductivity in oxygen indicated that the conductivity decreases with increasing ThO_2 content. The specimens used in the preliminary study were obtained by solid state sintering which yielded specimens with quite low densities (i.e. approximately 50% of theoretical).

In the current study specimens of CeO_2 doped with 10, 20, 30 and 40 mole % ThO_2 were prepared by cold pressing and sintering a powder of ThO_2 and CeO_2 obtained by a chemical precipitation technique.¹⁷ The density of these specimens were about 92% of theoretical density.

Lattice parameter measurements on these specimens were in agreement with

a previous study where it was shown that a_o varies linearly with dopant concentration between CeO_2 and ThO_2 .¹⁷

The preliminary results obtained in this study are shown in Fig. 1, where $\log \sigma$ vs $1/T$ is plotted for atmospheres of "pure" oxygen and a mixture of $CO-CO_2$ ($CO/CO_2 = .1$). For comparative purposes σ data on "pure" CeO_{2-x} is also plotted in Fig. 1. The conductivity is observed to decrease with increasing ThO_2 content at high temperatures in "pure" oxygen and over the entire temperature region ($800^\circ - 1500^\circ C$) in the $CO-CO_2$ mixture.

The conductivity of the CeO_2 specimen doped with 40 mole % ThO_2 is about 1/3 of the value of σ for "pure" CeO_{2-x} . However, in 100% O_2 at lower temperatures the conductivity does not appear to be as well behaved. The presence of ionic conduction in this region may be responsible for this behavior.

The conductivity studies on ThO_2 -doped CeO_2 (i.e. $Ce_{1-y}Th_yO_{2-x}$) will be continued to determine $\sigma = \sigma(T, P_{O_2})_y$. As discussed in the thermodynamic section, a thermogravimetric study on $Ce_{1-y}Th_yO_{2-x}$ will also be undertaken to determine $x = x(T, P_{O_2})_y$. Transference measurements will also be made on $Ce_{1-y}Th_yO_{2-x}$ to determine $t_i = t_i(P_{O_2}, T)_y$. The temperature and compositional dependence of σ_i and σ_e will then be obtained from a combined analysis of this data.

The compositional dependence of the electronic conductivity will be compared with the model proposed for "pure" CeO_{2-x} .^{8,9} Since the effect of increasing y is to increase the lattice parameter,¹⁷ it should be possible to test the postulate that the activation energy for electronic transport increases with increasing lattice dilatation from the dependence

Figure 1 Comparative plot of $\log \sigma$ vs $1/T$ for "pure" CeO_2 and CeO_2 doped with 10, 20, 30 and 40 mole % ThO_2 in 100% O_2 and CO-CO_2 mixture.

of Q on y .⁹ If this postulate is true then μ_e will decrease with increasing ThO_2 content.

If the electronic conductivity can be suppressed by the addition of ThO_2 it may be possible to produce a ternary electrolyte (e.g. $\text{CeO}_2\text{-ThO}_2\text{-CaO}$) where $t_i \approx 1$ at low oxygen pressures. Since CaO -doped CeO_2 exhibits a significant amount of electronic conductivity at low oxygen pressures, this would represent a significant improvement in t_i (see section on transference measurements). It should be noted that the mobility of oxygen vacancies in the CeO_2 host lattice is an order of magnitude greater than in CaO -doped ZrO_2 , which would imply that for the same vacancy concentration σ_i for CaO -doped CeO_2 is about an order of magnitude greater than CaO -doped ZrO_2 . Thus the development of a ternary electrolyte based on a CeO_2 system where $t_i \approx 1$ may have potential application in fuel cells at elevated temperatures.

B. Thermodynamic Studies on Doped-CeO_{2-x}

1. Transference measurements on doped-CeO_{2-x}.

As discussed in recent progress reports^{5,6} a combined analysis of electrical conductivity, ionic transference and thermodynamic data on CaO-doped CeO₂ dioxide was employed to 1) provide information on the compositional dependence (i.e. both CaO and oxygen content) on the mobility and diffusion coefficient of oxygen vacancies; 2) characterize the electronic conductivity of CaO-doped CeO₂ by modifying the proposed oxygen vacancy nonstoichiometric defect model for "pure" CeO_{2-x}.^{9,10,12}

An electrochemical cell of the type

was used to measure t_i of CaO-doped CeO₂ as a function of T and P_{O_2} . The experimental measuring system was modified so that a continuous variation in the partial pressure of oxygen at each electrode could be achieved. With the modified system the following procedure was used to determine t_i . Depending on the value of P_{O_2} desired, a tank mixture of either Ar-O₂ or CO-CO₂ was used to fix the value of P_{O_2} at electrode I. The P'_{O_2} at electrode II was controlled by mixing gas from another tank with the same gas mixture as used at electrode I. The oxygen partial pressure at each electrode was then measured using an oxygen gauge.¹⁸ Note that since the value of P_{O_2} at electrode I is fixed and the P'_{O_2} at electrode II can be varied continuously (i.e. $P'_{O_2} >$ or $< P_{O_2}$) the sign of the emf, E , may be negative or positive. With this technique t_i was calculated from the slope of a plot of emf versus $\log P_{O_2}$ and the expression

$$\left(\frac{dE}{d \ln P_{O_2}} \right)_{\text{at } P_{O_2} = P_{O_2}^{II}} = \frac{kT}{4e} (t_1)_{\text{at } P_{O_2} = P_{O_2}^{II}} \quad (10)$$

The advantages of this technique are: (1) the value of t_1 may be determined uniquely for each value of P_{O_2} , (2) polarization effects can be minimized since only small differences in P_{O_2} are used at each electrode.

In the current study ionic transference measurements were made on sintered specimens of CeO_{2-x} doped with 10 mole % CaO using this technique. The results of these measurements are shown in Fig. 2 as isothermal plots of t_1 vs $\log P_{O_2}$.

There are two oxygen pressure regions separated by a gap which widens with decreasing temperature. The data at higher oxygen pressures were obtained with O_2 -Ar mixtures while those at lower oxygen pressures were obtained with CO - CO_2 mixtures. Oxygen pressures in the gap are unobtainable with these gas mixtures at a total pressure of one atmosphere. Dashed lines have been drawn in Fig. 2 in an attempt to show how the transition in t_1 from high to low oxygen pressures might look.

For purposes of discussion the P_{O_2} dependence of t_1 may be described in terms of two oxygen pressure regions:

Region 1: At high oxygen partial pressures (i.e. $1 - 10^{-4}$ atm obtained with O_2 -Ar mixtures) the electrical conductivity is predominantly ionic.

Region 2: At low oxygen partial pressures t_1 decreases with decreasing P_{O_2} . At the lowest P_{O_2} investigated t_1 is small and the electrical conduction in this region is predominantly electronic.

The ionic transference data, $t_1 = t_1(P_{O_2}, T)_{y=0.1}$, was combined with the total electrical conductivity, $\sigma = \sigma(P_{O_2}, T)_{y=0.1}$, to obtain both the ionic and electronic conductivities as a function of P_{O_2} and T for $y = 0.1$.

Figure 2 Isothermal plot of the ionic transference number versus $\log P_{O_2}$ for CeO_2 doped with 10 mole % CaO .

Plots of $\log \sigma_i$ vs P_{O_2} and $\log \sigma_e$ vs $\log P_{O_2}$ are shown in Figs. 3 and 4, respectively, for CeO_2 doped with 10 mole % CaO . Dashed lines have also been drawn in Figs. 3 and 4 in an attempt to show how the transition in t_i from high to low oxygen pressures might look.

At higher oxygen pressures ($1 - 10^{-4}$ atm) the ionic conductivity decreases slightly with decreasing P_{O_2} as shown in Fig. 3. This behavior may be explained on the basis of a fixed concentration of mobile charge-compensating oxygen vacancies arising from substitutional incorporation of calcium ions on cerium sites. At lower oxygen pressures, obtained with $CO-CO_2$ mixtures, σ_i increases with decreasing oxygen pressure.

The simplest model for ionic conduction in CaO -doped CeO_2 is to assume that the ionic conduction occurs by the migration of oxygen vacancies with only one state of ionization, $V_O^{\bullet\bullet}$. For this case the σ_i may be represented by an expression of the type

$$\sigma_i = 2B[V_O^{\bullet\bullet}]e\mu_{V_O^{\bullet\bullet}} \quad (11)$$

where the bracketed term represents the number of a given species divided by the number of sites available for that species, B is a parameter which relates the concentration in site fraction to number/cubic centimeter, e is the charge on an electron, and $\mu_{V_O^{\bullet\bullet}}$ is the mobility of doubly ionized oxygen vacancies. If all of the oxygen vacancies are isolated point defects and randomly distributed,¹³

$$[V_O^{\bullet\bullet}] = \frac{y+x}{2} \quad (12)$$

In addition, if $\mu_{V_O^{\bullet\bullet}}$ is assumed to be a function of temperature only

$$\mu_{V_O^{\bullet\bullet}} = \mu_{V_O^{\bullet\bullet}}' \exp(-E_i/kT) \quad (13)$$

Figure 3 Isothermal plot of $\log \sigma_i$ vs $\log P_{\text{O}_2}$ for CeO_2 doped with 10 mole % CaO .

Figure 4 Isothermal plot of $\log \sigma_e$ vs $\log P_{O_2}$ for CeO_2 doped with 10 mole % CaO .

Combining Eqs. (11), (12) and (13) the relation for ionic conductivity is

$$\sigma_i = B[y+x]e\mu_{V_O}^i \exp(-E_i/kT) \quad (14)$$

The isothermal dependence of the ionic conductivity of $\text{Ce}_{1-y}\text{Ca}_y\text{O}_{2-y-x}$ on x was determined by combining thermodynamic data, $x = x(P_{O_2}, T)_y$ with the appropriate ionic conductivity data, $\sigma_i = \sigma_i(P_{O_2}, T)_y$. The combined analysis of this data for the case where $y = 0.1$ is shown in Fig. 5 as an isothermal plot of σ_i vs x at 800° , 900° and 1000°C . It is interesting to note that σ_i is proportional to x as predicted by Eq. (14) between approximately $10^{-3} < x < 10^{-2}$. At large values of x , the nonlinear behavior of σ_i suggests that $\mu_{V_O}^i$ decreases with increasing x .

The dependence of E_i on x in Eq. (14) was determined from plots of $\log \sigma_i$ vs $1/T$ for different vacancy concentrations. In the high oxygen pressure region where $y \gg x$ a value of 0.68 eV was calculated for E_i . This value of E_i is 0.06 eV larger than reported in a previous publication where it was assumed that $t_i = 1$ in this oxygen pressure region.⁷ In the composition region $10^{-3} < x < 10^{-2}$, $E_i = 0.75$ eV. Although on the basis of the information available at this time it is difficult to fully explain the apparent minimum in σ_i that occurs between the high and the low oxygen region (Fig. 3), it is possible that it may be associated with the observed increase in E_i .

As shown in Fig. 4 the electronic conductivity exhibits a minimum in the oxygen pressure region 1 to 10^{-4} atm. In contrast to the high oxygen pressure region where the electrical conductivity is predominantly ionic the conduction in the low pressure region is predominantly electronic. The minimum in the electronic conductivity has been attributed to a p to n transition. The holes most likely arise from interaction between

Figure 5 Isothermal plot of σ_i vs x at 800°, 900° and 1000°C for CeO_2 doped with 10 mole % CaO .

oxygen vacancies and the oxygen in the surrounding atmosphere as follows

This type of defect reaction was used to explain hole conduction in "pure" CeO_{2-x} by VanHandel¹⁰ and in Y_2O_3 doped- ThO_2 by Bauerle.¹⁹

The compositional and temperature dependence of the electronic conductivity of $\text{Ce}_{1-y}\text{Ca}_y\text{O}_{2-y-x}$ (i.e. $\sigma_e = \sigma_e(x, T)_y$ for $y = 0.10$) was determined by drawing smooth curves through the isotherms of $\log \sigma_e$ vs $\log P_{\text{O}_2}$ and $\log x$ vs $\log P_{\text{O}_2}$ data and selecting values of σ and x which correspond to the same values of P_{O_2} and T for $y = 0.1$. The results of this combined analysis are shown in Fig. 6 where isotherms of $\log \sigma_e$ are plotted as a function of $\log x$ for fixed values of y (i.e. $y = 0.10$). For comparative purposes the results of a recent study⁹ on "pure" CeO_{2-x} are also shown in Fig. 6.

Although the combined data is available at 50°C increments between 800° and 1050°C, only data at 800° and 1000°C are shown in this figure to simplify the presentation of the data. The smallest value of x for each isotherm is determined by the constraint that the error in x be less than 2%.⁹

The electronic conductivity of the CeO_2 specimen doped with 10 mole % CaO exhibits a similar dependence on x as "pure" CeO_2 (Eq. 2), except the magnitude of the electronic conductivity is lower and at smaller values of x the electronic conductivity exhibits a nonlinear dependence on x for the CaO -doped specimen.

Since conduction by electrons in CeO_{2-x} is assumed to occur by a hopping type process (i.e. an exchange of an electron between $\text{Ce}_{\text{Ce}}^{\text{I}}$ and

Figure 6 Comparative isothermal plot of $\log \sigma_e$ vs $\log x$ for "pure" CeO_{2-x} and CeO_2 doped with 10 mole % CaO .

Ce_{Ce}^x), as a first order approximation it would be expected that for

$$\mu_e \propto (1-y) \quad (15)$$

when $y > x$. According to Eq. (15), σ_e should decrease by 10%. As shown in Fig. 6 the observed decrease in σ_e is larger than predicted by Eq. (15). The nonlinear dependence of σ_e on x for the CaO doped CeO_2 specimen in the region near stoichiometry may be attributed to the presence of some p-type conduction. In order to obtain a more quantitative determination of the dependence of the electronic conductivity and the mobility of electrons and holes and the band gap energy on CaO content requires the combined analysis of electrical conductivity, ionic transference data and thermodynamic data on samples with several different dopant concentrations.

Additional ionic transference measurements will be made as a function of P_{O_2} and T on samples of CeO_2 doped with 1 and 7 mole % CaO, because the electrical conductivity⁷ and thermodynamic¹³ data is already available for these compositions.

2. Thermogravimetric Measurements on Doped Nonstoichiometric CeO_{2-x}

In the last progress report⁶ the results of a thermodynamic study on CaO-doped CeO_2 was described. Thermogravimetric measurements were performed on CaO-doped nonstoichiometric cerium dioxide (i.e. $\text{Ce}_{1-y}\text{Ca}_y\text{O}_{2-y-x}$) in the temperature range $750^\circ - 1500^\circ\text{C}$ and from oxygen pressures of 10^{-1} to 10^{-22} atm. From this data the deviation from stoichiometry $x = x(T, P_{\text{O}_2})_y$ was determined for values of $y = 0.01, 0.07$ and 0.14 . The thermodynamic quantities $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$ were calculated in the region $0.001 \leq x \leq 0.2$ and found to be independent of temperature.

In the composition region near stoichiometry $\Delta\bar{H}_{O_2}$ exhibits only a slight dependence on x for the 1 and 7 mole % CaO samples (i.e. less than 0.2 eV variation between $x = 10^{-3}$ and $x = 10^{-2}$). For the 14 mole % CaO sample $\Delta\bar{H}_{O_2}$ is independent of x between $x = 10^{-3}$ and $x = 3 \times 10^{-2}$.

At large deviations from stoichiometry the dependence of $\Delta\bar{H}_{O_2}$ on x appears to be independent of CaO content up to at least 7 mole %. However, $\Delta\bar{H}_{O_2}$ for the 10 and 14 mole % CaO-doped specimens exhibits a different dependence on x .

Discussion of the dependence of $\Delta\bar{S}_{O_2}$ on x and y was directed towards two different regions of x . In the near stoichiometric region there is good agreement between the measured and calculated dependence of $\Delta\bar{S}_{O_2}$ on x for $y = 0.01, 0.07$ and 0.14 . The calculated values of $\Delta\bar{S}_{O_2}$ were obtained from the expression¹³

$$\begin{aligned} -\Delta\bar{S}_{O_2} = S_{O_2}^0 + 2\Delta S_{+}^V - 2R \ln \left[\frac{x+y}{2} \right] - 4R \ln[2x] + 4R \ln[1-y-2x] \\ + 2R \ln \left[1 - \frac{x+y}{2} \right] \end{aligned} \quad (16)$$

Thus, in this composition region, it appears that the variation of $\Delta\bar{S}_{O_2}$ with x is consistent with a random distribution of doubly ionized oxygen vacancies, $V_O^{\bullet\bullet}$, and electrons localized on cerium sites, Ce_{Ce}' .

At larger deviations from stoichiometry the dependence of $\Delta\bar{S}_{O_2}$ on x is similar for "pure" CeO_{2-x} and the 1 and 7 mole % CaO specimens. In this composition region the calculated dependence of $\Delta\bar{S}_{O_2}$ on x deviates from the measured dependence. This is the same region where $\Delta\bar{H}_{O_2}$ exhibits a significant dependence on x . This behavior is interpreted as due to an increase in the defect-host interaction and undoubtedly the onset of defect-defect interaction.

In the above study CaO was selected as dopant because the ionic radius of the calcium ion (Ca^{+2} :1.09Å) is very similar to cerium ion (Ce^{+4} :1.07Å).¹⁶ In the current study a similar thermodynamic investigation was initiated on CeO_2 doped with other cations (e.g. Sr^{+2} , La^{+3} and Y^{+3}) which have different valences and ionic radii. This study was initiated to help determine the effect of the ionic radii, valence and concentration of the dopant cation on (1) the nonstoichiometric behavior of doped CeO_{2-x} , (2) the thermodynamic quantities $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$, and (3) the nonstoichiometric defect structure. As described above the results of these studies will also be combined with the corresponding results from the electrical conductivity and ionic transference studies to help characterize the electrical conductivity and to obtain information about the mobility of electrons, holes and oxygen vacancies in doped CeO_{2-x} .

In the current study the thermodynamic behavior of SrO-doped CeO_2 was investigated. SrO was selected as a dopant to determine the effect of a larger cation (Sr^{+2} :1.14Å)¹⁶ with the same valence as Ca^{+2} on the thermodynamic and electrical behavior of doped nonstoichiometric cerium dioxide. The results of this study have been described in detail in AEC Report OOO-1441-25 and in a paper recently submitted for publication. These results will be summarized as follows.

Thermogravimetric measurements were made on SrO-doped nonstoichiometric cerium dioxide specimens (1 and 7 mole % SrO) as a function of temperature (800° - 1500°C) and oxygen pressure (0.1 to 10^{-21} atm). From this data the deviation from stoichiometry $x = x(T, P_{\text{O}_2})_y$ was determined for values of $y = 0.01$ and 0.07 .

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

$$x \propto P_{O_2}^{-1/4} \quad (17)$$

Increasing the SrO content increases the range of nonstoichiometry for Eq. (17) applies. It is interesting to note that this behavior was also observed for CaO-doped CeO_2 .¹³

The thermodynamic quantities $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ were calculated in the region $0.001 < x < 0.2$ and found to be independent of temperature for the 1 mole % SrO-doped CeO_2 specimen. No attempt was made to calculate $\Delta\bar{H}_{O_2}$ or $\Delta\bar{S}_{O_2}$ for the 7 mole % SrO-doped CeO_2 specimen because of the experimental problems encountered with the 7 mole % SrO-doped CeO_2 specimen below 1000°C and the limited number of isotherms available at higher temperatures.

In the composition region near stoichiometry (i.e. for approximately $10^{-3} < x < 10^{-2}$) $\Delta\bar{H}_{O_2}$ exhibits only a slight dependence on x . It is interesting to note that in this composition region the value of $\Delta\bar{H}_{O_2}$ is larger for the 1 mole % SrO than for "pure" CeO_{2-x} . The variation of $\Delta\bar{S}_{O_2}$ with x was consistent with the nonstoichiometric defect model that was used to explain the nonstoichiometric behavior of "pure" and CaO-doped CeO_{2-x} .^{12,13} (Eqs. 1 and 16).

At large deviations from stoichiometry the nonstoichiometric behavior, $x = x(T, P_{O_2})$ and the dependence of $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ on x of $Ce_{0.99}Sr_{0.01}O_{2.99-x}$ is similar to "pure" CeO_{2-x} .

The thermodynamic study on SrO-doped CeO_2 was terminated because of the problems associated with determining $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ for the sample doped with higher SrO contents (e.g. CeO_2 doped with 7 mole % SrO).

To circumvent the problems associated with limited solubility of SrO in CeO_2 , a preliminary thermodynamic study was initiated on CeO_2 doped with La_2O_3 and Y_2O_3 . These oxides were selected for the following reasons:

- (1) extensive solubility in CeO_2 ,¹⁶ (2) the cations have a valence of +3, (3) the lattice parameter increases with La_2O_3 and decreases with Y_2O_3 .¹⁶

Thermogravimetric measurements were performed on specimens of CeO_2 doped with 14 mole % La_2O_3 and with 14 mole % Y_2O_3 , as a function of temperature ($800^\circ - 1500^\circ\text{C}$) oxygen partial pressure (.1 to 10^{-21} atm). From this data the deviation from stoichiometry $x = x(T, P_{\text{O}_2})_z$ was determined for values of $z = 0.246$ for $\text{Ce}_{1-z}\text{La}_z\text{O}_{2-1/2z-x}$ and $\text{Ce}_{1-z}\text{Y}_z\text{O}_{2-1/2z-x}$. The thermodynamic quantities $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$ were calculated in the region $0.001 \leq x \leq 0.2$ and found to be independent of temperature.

In the composition region near stoichiometry (i.e. for x between approximately 10^{-3} and 10^{-2}), the variation of $\Delta\bar{S}_{\text{O}_2}$ with $\log x$ is consistent with the same nonstoichiometric defect model as proposed for "pure" and CaO -doped CeO_2 ^{12,13} (see Eqs. 1 and 16). In this same nonstoichiometric region $\Delta\bar{H}_{\text{O}_2}$ is independent of x .

One of the objectives of this study was to determine the effects of ionic radius, valence and concentration of the dopant on $\Delta\bar{H}_{\text{O}_2}$. Although there is insufficient thermodynamic data at this time for a quantitative determination of each of these effects on $\Delta\bar{H}_{\text{O}_2}$, it is interesting to observe as shown in Fig. 7 the dependence of $\Delta\bar{H}_{\text{O}_2}$ on the site fraction of charge compensating oxygen vacancies formed by the dopant (e.g. $y/2$ for $\text{Ce}_{1-y}\text{Ca}_y\text{O}_{2-y-x}$ and $z/4$ for $\text{Ce}_{1-z}\text{La}_z\text{O}_{2-1/2z-x}$). The values of $\Delta\bar{H}_{\text{O}_2}$ used in Fig. 7 were determined in the near stoichiometry region, see Region I in Fig. 8, where $\Delta\bar{H}_{\text{O}_2}$ exhibits either a small dependence or is independent of x . As discussed above this is the composition region where the variation of $\Delta\bar{S}_{\text{O}_2}$ with $\log x$ is consistent with the nonstoichiometric defect model proposed for "pure" CeO_2 and CeO_2 doped with CaO , SrO , La_2O_3 and Y_2O_3 .

Figure 7 $\Delta\bar{H}_{\text{O}_2}$ vs site fraction of charge compensating oxygen vacancies formed by dopant

Figure 8 Comparison plot of $\Delta \bar{H}_{O_2}$ vs $\log x$ for "pure" CaO -, La_2O_3 -, and Y_2O_3 -doped CeO_{2-x}

Although the exact dependence of $\Delta\bar{H}_{O_2}$ on the site fraction of charge compensation oxygen vacancies cannot be ascertained, it appears that $\Delta\bar{H}_{O_2}$ increases monotonically with $y/2$ or $z/4$.

Additional thermodynamic studies will be made on CeO_2 doped with La_2O_3 , Y_2O_3 and ThO_2 to determine the relative effects of ionic radius and valence on $\Delta\bar{H}_{O_2}$. Studies on CeO_2 doped with ThO_2 will be particularly useful because direct information concerning the effect of the ionic radius of the foreign cation on $\Delta\bar{H}_{O_2}$ may be obtained without the formation of charge compensating defects.

Thermodynamic data obtained from the above type of studies should provide a better understanding of the effect of the ionic radii, valence and concentration of the dopant on (1) the nonstoichiometric behavior, (2) the thermodynamic quantities $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$, and (3) the nonstoichiometric defect structure. This understanding can then provide a framework in which the basic assumptions of the simple defect model^{12,13} for $\Delta\bar{S}_{O_2}$ in "pure" and doped- CeO_{2-x} may be relaxed so that an extended defect model incorporating the variation of $\Delta\bar{H}_{O_2}$ with dopant addition and nonstoichiometry may be developed.

RELATED RESEARCH STUDIES

The materials science research program on metal oxides at Marquette University is a broadly based program which includes the following areas of research:

1. Preparation of ceramic and single crystals of metal oxides.
2. Defect structure studies.
3. Electronic and atomic transport studies.
4. Dielectric behavior.
5. Mechanical behavior.
6. Optical behavior.

Several faculty members in the College of Engineering are involved in this program.

The work sponsored by the Atomic Energy Commission under Contract AT(11-1)-1441 with Marquette University is concerned primarily with determining the defect structure and transport properties of defects in "pure" and doped nonstoichiometric cerium dioxide. These studies are complemented by other research studies in the metal oxide program at Marquette University. Three of these studies which are directly related to the AEC sponsored work will be discussed briefly below.

1. A vapor transport technique has been developed in this laboratory for growing single crystals of CeO_2 .²⁰ This research was originally sponsored by the Advanced Research Projects Agency, however, it is now supported by Marquette University. The availability of single crystals of CeO_2 is particularly important for measurements on the transport properties of defects in CeO_2 . Single crystals have recently been furnished to Dr. Frederiske of the National Bureau of Standards for measurements of the optical behavior of CeO_2 . They have an interest in

CeO_2 -mixed oxide systems because of their potential application for MHD electrodes.

2. A high temperature x-ray and neutron diffraction study on the isothermal dependence of the intensity of the diffraction peaks on nonstoichiometry in CeO_{2-x} has recently been completed. The analysis of this data confirms the presence of oxygen vacancies as the predominate nonstoichiometric defect in CeO_{2-x} . The neutron diffraction study on CeO_{2-x} was conducted at Argonne National Laboratory by Dr. John Faber, a recent Ph.D. graduate in the materials science program at Marquette, and Dr. M. H. Mueller of Argonne National Laboratory. An interest has been expressed by Dr. Faber, who currently holds a post-doctoral position at Argonne National Laboratory, in the possibility of a room temperature neutron diffraction study on CeO_2 specimens doped with aliovalent ions that produce charge compensating oxygen vacancies. If this study were undertaken we would furnish Dr. Faber with some of the specimens used in our combined study of the electrical behavior of doped CeO_2 .

3. A high temperature x-ray, dilatometric and gas pycnometric study on CeO_{2-x} was recently completed in the laboratory. A combined analysis of these data (i.e. $\Delta a/a$, $\Delta l/l$ and $\Delta v/v$ as a function of x) confirms the presence of oxygen vacancies as the predominant nonstoichiometric defect in CeO_{2-x} . However, it does appear that the number of unit cells increases with increasing x to $\text{CeO}_{1.9}$ and then decreases with x , which implies that some cerium vacancies are also formed. An independent test of this interpretation could be obtained by measuring the tracer diffusion coefficient of cerium atoms as a function of nonstoichiometry. The feasibility of making this type of study is currently under discussion with Dr. W. K. Chen at Argonne National Laboratory.

REFERENCES

1. R. N. Blumenthal, Technical Report, C00-1441-6 (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, Technical Report, C00-1441-18 (1972).
5. R. N. Blumenthal, Technical Report, C00-1441-19 (1972).
6. R. N. Blumenthal, Technical Report, C00-1441-23 (1972).
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. R. N. Blumenthal and R. K. Sharma, to be published in the J. Solid State Chem.
10. G. H. VanHandel and R. N. Blumenthal, J. Electrochem. Soc., 121, 1198 (1974).
11. J. R. Sims, Jr., Ph.D. Dissertation, Marquette University, Milwaukee, Wisconsin, 1973.
12. R. J. Panlener, R. N. Blumenthal and J. E. Garnier, to be published in J. Phys. Chem. Solids.
13. J. E. Garnier, R. N. Blumenthal and R. J. Panlener, to be published in J. Phys. Chem. Solids.
14. B. C. H. Steele and J. M. Floyd, Proc. Brit. Ceram. Soc., 19, 55 (1971).
15. J. Faber, Ph.D. Dissertation, Marquette University, Milwaukee, Wisconsin, 1973.
16. H. H. Mobius, Z. Chem., 4, 81 (1964).
17. H. J. Whitfield, D. Roman and A. P. Palmer, J. Inorg. Nucl. Chem., 28, 2817 (1966).
18. R. N. Blumenthal, Technical Report, C00-1441-9 (1969).
19. J. E. Bauerle, J. Chem. Phys., 45, 4162 (1966).
20. W. M. Hirthe, R. N. Blumenthal and M. A. Seitz, Technical Progress Report No. 3, Advanced Research Projects Agency (1970).