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

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ABSTRACT

Electrical conductivity and thermogravimetric measurements were made on Ta_2O_5 -doped nonstoichiometric cerium dioxide (i.e. $\text{Ce}_{1-y}\text{Ta}_y\text{O}_{2-x}$) as a function of temperature and oxygen partial pressure. Over a limited range of temperature and nonstoichiometry the isothermal dependence of the electrical conductivity on nonstoichiometry may be described by an equation of the form

$$\sigma = A + Bx$$

Parameter A is the electronic conductivity associated with the electronic defects produced by doping CeO_2 with Ta_2O_5 . The electronic conductivity resulting from the nonstoichiometric defect reaction

is equal to the second term in the above equation (i.e. Bx).

An improved electrochemical cell technique was developed 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.

The ionic conductivity may be described by the following relation

$$\sigma_i = B[y+x]e\mu_{\text{V}_{\text{O}}^{\bullet\bullet}} \exp(-E_i/kT)$$

and the electronic conductivity by the following isothermal expressions

$$\sigma_e \propto P_{\text{O}_2}^{-1/4}$$

and

$$\sigma_e \propto x \quad ; \quad x < 3 \times 10^{-2}$$

These results are consistent with defect models involving doubly ionized oxygen vacancies.

An empirical expression (i.e. $\Delta \bar{H}_{O_2} \propto y/2$ or $z/4$) was obtained relating the dependence of $\Delta \bar{H}_{O_2}$ on the dopant concentration of lower valent foreign cations (e.g. $y/2$ for $Ce_{1-y}M_yO_{2-y-x}$ and $z/4$ for $Ce_{1-z}M'_zO_{2-z/2-x}$ where $M = Ca, Sr$ and $M' = Y, La$).

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) if 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.¹⁻¹⁸

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. ThO_2 , Y_2O_3 and Ta_2O_5) 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 $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$, (3) the nonstoichiometric defect structure, and (4) the mobility of electrons and oxygen vacancies in doped CeO_{2-x} .

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

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} .^{13,14,17,18} Cerium dioxide was selected as the host oxide in these doping experiments because it exhibits a large nonstoichiometric region,^{13,19} an extensive solubility for foreign cations²⁰ and extensive studies have been performed on the thermodynamic^{9,13} and electrical^{3,9,10} behavior of "pure" CeO_{2-x} .

Based on studies of x-ray and neutron diffraction,¹⁶ thermodynamic,¹² electrical conductivity¹³ 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.⁷ Thus, the solution of CaO in nonstoichiometric cerium dioxide may be represented by the formula $\text{Ce}_{1-y}\text{Ca}_y\text{O}_{2-y-x}$. As described in the last progress report¹⁴ a study was initiated on SrO -doped CeO_2 to determine the effect of a large cation ($\text{Sr}^{+2}:1.14\text{\AA}$)¹⁶ with the same valence as Ca^{+2} on the electrical behavior.

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.¹⁷ 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 study²⁰ 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

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

$$\mu = \mu_0 e^{-Q/kT} \quad (2)$$

In the current study specimens of CeO_2 doped with ThO_2 were prepared by cold pressing and sintering a powder of ThO_2 and CeO_2 obtained by a chemical precipitation technique.²⁰ 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_0 varies linearly with dopant concentration between CeO_2 and ThO_2 .¹⁷

The electrical conductivity of sintered specimens of ThO_2 -doped nonstoichiometric cerium dioxide (10 and 20 mole % ThO_2) was measured as a function of temperature (i.e. 800° to 1100°C) and oxygen pressure (1 to 10^{-19} atm).

Typical behavior of the isothermal dependence of the conductivity on oxygen pressure is shown in Fig. 1 for a 10 mole % doped CeO_2 specimen. For comparative purposes the conductivity of a "pure" CeO_2 specimen is represented by a dashed line in Fig. 1.

A qualitative explanation of the observed electrical conductivity data may be given in terms of two regions as follows:

Region I At low temperatures and high oxygen partial pressures (i.e. near stoichiometric conditions), the conductivity of the ThO_2 doped specimen is essentially independent of oxygen partial

Figure 1 Isothermal plot of $\log \sigma$ vs $\log P_{O_2}$ for a specimen of CeO_2 doped with 10 mole % ThO_2 .

pressure. The σ is also much larger than that of "pure" CeO_2 . Since this region is in the near stoichiometric condition, the σ is most likely controlled by impurities in this region.

Region II At high temperatures and particularly at low oxygen pressures, the σ of the ThO_2 -doped specimens exhibits a similar P_{O_2} dependence as "pure" CeO_2 . The magnitude of the σ however is smaller for the ThO_2 -doped specimen.

As discussed in the thermodynamic section the P_{O_2} dependence of the ThO_2 -doped CeO_2 specimen

$$\sigma \propto P_{\text{O}_2}^{-1/4} \quad (x < 0.01) \quad (3)$$

is consistent with the behavior observed for CeO_2 doped with lower valent cations (e.g. Ca, Sr, Y, La).¹⁷ Thus the impurities referred to in Region I are most likely lower valent cations. This sample is now being analyzed to check the above interpretation. It should be noted that the ThO_2 -doped CeO_2 specimens prepared by the aforementioned chemical precipitation technique²⁰ are brownish in color, an indication that defects produced by impurities are present.

If the impurities are lower valent cation, then the σ in Region I is probably controlled by ionic conduction because σ is independent of P_{O_2} in this region. The σ in Region II probably exhibits both electronic and ionic conduction. The electronic conductivity increases with decreasing P_{O_2} and is probably the predominant conduction mechanism at lower P_{O_2} . The above interpretation could be checked by measuring the ionic transference number as a function of P_{O_2} . However, before continuing a comprehensive study on ThO_2 -doped CeO_2 we will first obtain chemical analysis on these specimens. Since the above specimens were prepared by a

chemical precipitation technique, it appears likely that the impurities are introduced from the starting materials (i.e. $(\text{NH}_4)\text{Ce}(\text{NO}_3)_6$ and $\text{Th}(\text{NO}_3)_4$). The above compounds of Ce and Th are not commercially available in the same purity as their oxide powders.

We will also compare the electrical conductivity and thermodynamic behavior obtained on the above chemically prepared specimens with those obtained on samples prepared by dry mixing high purity CeO_2 and ThO_2 powders and sintering. It would be expected that the higher purity samples would give different results.

As discussed above 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 $\Delta\bar{H}_{\text{O}_2}$, we initiated a combined electrical conductivity and thermodynamic study on Ta_2O_5 doped cerium dioxide. 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.

In this preliminary investigation the electrical conductivity of a sintered specimen of cerium dioxide doped with 1 mole % Ta_2O_5 was measured as a function of temperature ($800^\circ - 1300^\circ\text{C}$) and oxygen partial pressure ($1 - 10^{-22}$ atm). These results are shown in Fig. 2 as isothermal plots of $\log \sigma$ vs $\log P_{\text{O}_2}$ at 100° intervals between 800° and 1300°C . For comparative purposes the conductivity of a "pure" CeO_2 specimen is shown as a solid line in Fig. 2.

A qualitative explanation of the observed electrical conductivity data may be given in terms of two regions as follows:

Figure 2 Comparison of Isothermal plot of $\log \sigma$ vs $\log P_{O_2}$ for "pure" nonstoichiometric cerium dioxide and 1 m/o Ta_2O_5 -doped CeO_2 sintered specimen.

- Region I At low temperatures and high oxygen partial pressures (i.e. near stoichiometric conditions) the conductivity of the Ta_2O_5 doped specimen is independent of oxygen partial pressure. The σ is also much larger than that of pure CeO_2 . These observations are consistent with a conduction process which is primarily electronic and where the electron carrier concentration is controlled by the dopant concentration of Ta_2O_5 .
- Region II At higher temperatures and lower oxygen partial pressures (i.e. at larger departures from stoichiometry) the P_{O_2} dependence of the conductivity varies with both temperature and P_{O_2} . The conduction process in this region is also predominantly electronic. The concentration of electrons, however, appears to depend on both the Ta_2O_5 dopant concentration as well as the departure from stoichiometry.

No attempt was made to analyze the P_{O_2} dependence of the σ using the law of mass action because of the complicated dependence of σ on P_{O_2} . As discussed in the thermodynamic section an investigation of the nonstoichiometric behavior of CeO_2 doped with 1 mole % Ta_2O_5 was undertaken to determine the dependence of x on P_{O_2} . The results of this study showed that any mass action type analysis would be invalidated because $\Delta\bar{H}_{\text{O}_2}$ was a function of x over the entire range of x investigated. To circumvent this problem we employed a method of analysis similar to that used on "pure" CeO_{2-x} .⁹ The isothermal compositional dependence of the electrical conductivity of 1 mole % Ta_2O_5 doped nonstoichiometric cerium dioxide (i.e. $\text{Ce}_{1-y}\text{Ta}_y\text{O}_{2-y}$; $y = 0.02$) was determined by combining thermodynamic data, $x = x(P_{\text{O}_2}, T)_{y=0.02}$ with the appropriate electrical conductivity of $\sigma = \sigma(P_{\text{O}_2}, T)_{y=0.02}$. The results of this combined analysis are shown in Fig. 3 where isotherms of σ are plotted as a function of x .

Figure 3 Isothermal plot of σ versus x for a 1 m/o Ta_2O_5 -doped CeO_2 sintered specimen.

Over a limited range of temperature and nonstoichiometry the isothermal dependence of the electrical conductivity on nonstoichiometry (i.e.

$\sigma = \sigma(x)_{T,y=0.02}$) may be described by an equation of the form

$$\sigma = A + Bx \quad (4)$$

where A and B are temperature dependent parameters.

Equation (4) may be rationalized in terms of the following simple relations.

- a) Parameter A in Eq. (4) is the electronic conductivity resulting from the electronic defects produced by doping CeO_2 with $\text{Ta}_{2.5}\text{O}_5$. The solution of $\text{TaO}_{2.5}$ in CeO_2 may be represented by the reaction

Since one electronic defect, Ce'_{Ce} , is produced for every tantalum atom, Ta_{Ce} , substituted on a cerium site,

$$A = \left(\frac{4y}{a_o} \right)^3 e\mu_e \quad (6)$$

- b) The electronic conductivity resulting from the nonstoichiometric defect reaction

is equal to the second term in Eq. (4) (i.e. Bx). Thus the product Bx is equal to the same expression used for the electronic conductivity of "pure" CeO_{2-x} ⁹

$$Bx = \left(\frac{8x}{a_o} \right)^3 e\mu_e \quad (7)$$

where a_o is the lattice parameter and μ_e is the electronic mobility.⁹

The parameter B was determined from the slope of the lines shown in Fig. 3 at 100°C intervals between 800° and 1000°C. These values of B were then used to calculate the mobility μ_e from Eq. (7). The parameter A determined from the intercept at each temperature shown in Fig. 3 was divided by the corresponding values of $e\mu_e$. The concentration of electrons obtained by this calculation ($\sim 5 \times 10^{20}/\text{cm}^3$) was found to be in close agreement with the value obtained from the relation $4\gamma/a_o^3$ ($\sim 5 \times 10^{20}/\text{cm}^3$).

On the basis of these results it can be concluded that

- i) all of the Ta_2O_5 in the 1 mole % doped specimen is in solution in the CeO_2 host lattice and
- ii) the electroneutrality expression that determines the total concentration of electrons localized on cerium atoms, $n_{\text{Ce}^{\cdot}}_{\text{Ce}}$, is given by the expression

$$n_{\text{Ce}^{\cdot}}_{\text{Ce}} = n_{\text{Ta}^{\cdot}}_{\text{Ce}} + 2n_{\text{V}^{\cdot\cdot}}_{\text{O}}$$

where $n_{\text{Ta}^{\cdot}}_{\text{Ce}}$ and $n_{\text{V}^{\cdot\cdot}}_{\text{O}}$ are the concentration ($\text{No.}/\text{cm}^3$) of $\text{Ta}^{\cdot}_{\text{Ce}}$ and $\text{V}^{\cdot\cdot}_{\text{O}}$ respectively.

Defect characterization studies employing the above combined analyses of the electrical conductivity and thermodynamic data is another example of the general usefulness of this analysis technique which eliminates problems associated with defect interaction. Since electronic conduction⁹ in "pure" CeO_{2-x} occurs by a "hopping-type mechanism", and

$$\mu_e = 5.2(10^{-2})e^{(-0.158+x)/kT} (\text{cm}^2/\text{volt-sec}) \quad (8)$$

it would be expected that a thermally activated transport process of the type

$$\mu_e = \mu_o e^{-Q/kT} \quad (9)$$

would also occur in CeO_2 doped with Ta_2O_5 . Information about the activation energy, Q , for electronic transport was obtained from the plots of $\log \sigma$ vs $1/T$ for constant composition (i.e. constant value of x) shown in Fig. 4.

The activation energy was calculated from Eq. (9) and the slope of the lines shown in Fig. 4. As shown in Fig. 5 Q , which is essentially constant for small values of x (i.e. $Q \approx 0.35$ eV, $x < 0.02$), decreases with increasing x reaching a minimum ($Q_{\min} \sim 0.28$ eV at $x \sim 0.07$) and then increases with increasing x (e.g. $Q \sim 0.35$ eV at $x \approx 0.18$). Although we do not have any simple explanation for this behavior it is interesting to note that the minimum in Q occurs at approximately the same composition ($x \approx 0.07$) where $\Delta \bar{H}_{\text{O}_2}$ exhibits a maximum (see thermodynamic section). It should also be noted that the calculated electronic mobilities in Ta_2O_5 doped CeO_2 are smaller than the corresponding mobility values in "pure" CeO_{2-x} [i.e. for a given value of x and T , $\mu_e(\text{Ta}_2\text{O}_5 \text{ doped}) < \mu_e(\text{CeO}_{2-x})$]. For the Ta_2O_5 doped specimen it appears that part of the decrease in μ_e may be associated with an increased activation energy for transport. Also since $\mu_e(\text{Ta}_2\text{O}_5 \text{ doped CeO}_{2-x}) < \mu_e(\text{"pure" CeO}_{2-x})$ it may be possible that $t_i(\text{Ta}_2\text{O}_5 \text{ doped CeO}_{2-x}) > t_i(\text{"pure" CeO}_{2-x})$ at very large departures from stoichiometry.

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

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

As discussed in recent progress reports,^{6,17} a combined analysis of electrical conductivity, ionic transference and thermodynamic data on

Figure 4 Constant composition plot of log σ vs $1/T$ for several different nonstoichiometric compositions of CeO_{2-x} doped with 1 m/o Ta₂O₅.

Figure 5 The dependence of the experimental activation energy, Q , on x .

CaO-doped CeO_2 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 CeO_2 by modifying the proposed oxygen vacancy nonstoichiometric defect model for "pure" CeO_{2-x} .⁸⁻¹²

In a previous progress report¹⁷ an electrochemical cell of the type

was used to measure t_i of CaO-doped CeO_2 as a function of T and P_{O_2} . In this measuring system the oxygen partial pressure, P'_{O_2} , was controlled by flowing an analyzed tank mixture of either Ar- O_2 or CO- CO_2 over one electrode. The P_{O_2} at the other electrode was controlled by blending together two analyzed tank mixtures of similar gas compositions, either Ar- O_2 or CO- CO_2 . The oxygen content of this blended gas mixture was analyzed using an oxygen gauge. Since the oxygen gauge was located in a different furnace, the gas mixture was analyzed after the gas exited the transference measuring system. With this technique t_i was calculated from the slope of a plot of emf versus $\log \text{P}_{\text{O}_2}$ and the expression

$$\left(\frac{dE}{d \ln \text{P}_{\text{O}_2}} \right)_{\text{at } \text{P}_{\text{O}_2} = \text{P}'_{\text{O}_2}} = \frac{kT}{4e} (t_i)_{\text{at } \text{P}_{\text{O}_2} = \text{P}'_{\text{O}_2}} \quad (10)$$

The advantages of this technique are: (1) the value of t_i 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.¹⁷ Ionic transference measurements were made on sintered specimens of CeO_{2-x} doped with 10 mole % CaO as a function of temperature and oxygen partial pressure.¹⁷ These results were described in terms of a high and low

oxygen pressure region.¹⁷ At high oxygen partial pressures (i.e. $1 - 10^{-4}$ atm obtained with O_2 -Ar mixtures) the electrical conductivity is predominantly ionic. At low oxygen partial pressures t_i decreases with decreasing P_{O_2} . At the lowest P_{O_2} investigated t_i is small and the electrical conduction in this region is predominantly electronic.

The ionic transference data, $t_i = t_i(P_{O_2}, T)_{y=0.1}$, was combined with the total electrical conductivity, $\sigma = \sigma(P_{O_2}, T)_{y=0.01}$, to obtain both the ionic, σ_i , and electronic, σ_e , conductivities as a function of P_{O_2} and T for $y = 0.1$.

At higher oxygen pressures ($1 - 10^{-4}$ atm) both σ_i and σ_e decrease slightly with decreasing P_{O_2} . At lower oxygen pressures, obtained with CO-CO₂ mixtures, both σ_i and σ_e increase with decreasing oxygen pressure. The minimum in the electronic conductivity which occurred in the oxygen pressure region 1 to 10^{-4} atm was attributed to a p to n transition. No attempt was made to explain the apparent minimum in σ_i that occurs between the high and low oxygen region. The oxygen pressure could not be accurately controlled in this region because of the low "buffering" capacity of tank mixtures with gas ratios (i.e. O_2/Ar , CO_2/CO) less than 10^{-3} .²¹

In the current study we attempted to circumvent this problem of "buffering" by using an electrochemical cell of the type

A schematic diagram of this cell is shown in Fig. 6. Since an oxygen gauge is located at each electrode it should be possible in principle to accurately measure the oxygen partial pressure $P_{O_2}^I$ and $P_{O_2}^{II}$ over a continuous range of values.

Schematic diagram of the cell:

Figure 6 A schematic diagram of the cell

The results of the ionic transference measurements using the above electrochemical cell are shown in Fig. 7 as isothermal plots of t_i vs $\log P_{O_2}$ at 100°C intervals between 800° and 1000°C for CeO_2 specimens doped with 10 mole % CaO . With this measuring system $t_i = 1$ within experimental error between approximately 1 and 10^{-4} atm of oxygen. The ionic transference data $t_i = t_i(P_{O_2}, T)_{y=0.1}$, was combined with the total electrical conductivity, $\sigma = \sigma(P_{O_2}, T)_{y=0.1}$ to obtain both the ionic, σ_i , and electronic, σ_e , conductivities as a function of P_{O_2} and T for a nominal composition of $y = 0.1$. As shown in Figs. 8 and 9 for $\log \sigma_i$ vs $\log P_{O_2}$ and $\log \sigma_e$ vs $\log P_{O_2}$ it is apparent that for this composition of CaO doped CeO_2 neither σ_i nor σ_e exhibit a minimum with decreasing P_{O_2} .

The inconsistency between this observation and the previously reported minimum in σ_i and σ_e may be readily explained based on the following observation. The same procedure used previously for determining t_i was utilized with the new measuring system (see Fig. 6). An analyzed gas tank mixture (i.e. $Ar-O_2$ or $CO-CO_2$) was passed over one electrode (e.g. P'_{O_2}) and the P_{O_2} at the other electrode (P''_{O_2}) was varied by blending gases together. It was observed that as P''_{O_2} was increased P'_{O_2} also increased. It was also observed that varying P'''_{O_2} (see Fig. 6) did not appear to effect either P'_{O_2} or P''_{O_2} . Thus it is apparent that the permeability of oxygen through the CaO doped CeO_2 sample is sufficiently high that the oxygen content at the electrode with the lower oxygen pressure may be altered by varying the oxygen pressure at the other electrode. With this measuring system, however, the problem is eliminated because the oxygen partial pressure is measured at each electrode. However, in the previously employed measuring system the oxygen partial pressure at only one electrode was measured and this was measured in an external oxygen gauge. Since an

Figure 7 Ionic transference number vs oxygen partial pressure.

Figure 8. Ionic conductivity vs oxygen partial pressure

Figure 9 Electronic conductivity vs oxygen partial pressure.

analyzed tank mixture was used at the other electrode, the oxygen partial pressure at this electrode was assumed to remain constant when the oxygen partial pressure at the other electrode was varied. Based on the above observations this assumption is incorrect and hence the previously reported minimum in σ_i and σ_e are incorrect.

The results obtained to date using the improved ionic transference measuring system may be summarized as follows:

a) Under isothermal conditions

$$\sigma_i \propto x \quad (11)$$

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

$$\sigma_i = B[y+x]e_{V_O} \exp(-E_i/kT) \quad (12)$$

The deviation of Eq. (12) is based on a defect model involving doubly ionized oxygen vacancies.^{7,17}

b) Under isothermal conditions

$$\sigma_e \propto P_{O_2}^{-1/4} \quad (13)$$

and

$$\sigma_e \propto x \quad (14)$$

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

To complete the aforementioned analysis of the dependence of σ_i and σ_e on composition (i.e. x and y) and temperature will require additional conductivity data (i.e. $\sigma_i = \sigma_i(x, T)_y$ and $\sigma_e = \sigma_e(x, T)_y$) for different

values of y . Ionic transference measurements using the improved technique will be made as a function of P_{O_2} and T on samples of CeO_2 doped with 1 and 7 mole % CaO . These dopant concentrations were selected because electrical conductivity and thermodynamic data was available for these compositions.

2. Thermogravimetric measurements on doped nonstoichiometric CeO_{2-x} .

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} .

a. CeO_2 doped with lower valent cations.

In our earlier thermodynamic studies we have been concerned primarily with the effect of low valent cations (i.e. CaO , SrO , Y_2O_3 and La_2O_3) with different ionic radii (i.e. $r_{Y^{+3}} < r_{Ca^{+2}} < r_{La^{+3}} < r_{Sr^{+2}}$) on the variation of $\Delta\bar{S}_{O_2}$ with x which is consistent with a defect model involving randomly distributed doubly ionized oxygen vacancies and electrons localized on normal cerium sites.¹⁷ The range of nonstoichiometry with which this defect model fits the experimental results increases with increasing dopant concentration.¹⁷ In this same nonstoichiometric region $\Delta\bar{H}_{O_2}$ 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 $\Delta\bar{H}_{O_2}$ is essentially independent of x .

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).¹⁷ It has been shown that doping CeO_2 with these lower valent cations produces oxygen vacancies.¹⁷ Thus the solution of

MO or $\text{M}'_2\text{O}_3$ in nonstoichiometric cerium dioxide may be represented by the formulae $\text{Ce}_{1-y}\text{M}_y\text{O}_{2-y-x}$ and $\text{Ce}_{1-z}\text{M}'_z\text{O}_{2-z/2-x}$ respectively where $\text{M} = \text{Ca}, \text{Sr}$ and $\text{M}' = \text{Y}, \text{La}$. In the composition region near stoichiometry (i.e. for x between approximately 10^{-3} and 10^{-2}).

In the last progress report¹⁷ an attempt was made to relate the dependence of $\Delta\bar{H}_{\text{O}_2}$ on the dopant concentration for the lower valent foreign cation (e.g. $y/2$ for $\text{Ce}_{1-y}\text{Ca}_y\text{O}_{2-y-x}$ and $z/4$ for $\text{Ce}_{1-z}\text{La}_z\text{O}_{2-z/2-x}$). From plots of $\Delta\bar{H}_{\text{O}_2}$ versus $y/2$ and $z/4$ it was observed that $\Delta\bar{H}_{\text{O}_2}$ increases monotonically with $y/2$ or $z/4$.

In the current study the thermodynamic behavior of CeO_2 doped with 7 mole % Y_2O_3 and 7 mole % CaO was investigated. The 7 mole % CaO doped CeO_2 specimen was studied because analysis showed that the previously reported nominal 7 mole % CaO doped sample contained only 4.5 mole % CaO .¹³ The 7 mole % Y_2O_3 sample was studied because only one Y_2O_3 composition (14 mole % Y_2O_3) was investigated previously. The thermodynamic behavior of the 7 mole % CaO and Y_2O_3 samples are consistent with the previously reported results on CeO_2 doped with oxides with lower valent cations.

In the current study we again attempted to determine the effects of ionic radius, valence and concentration of the dopant on $\Delta\bar{H}_{\text{O}_2}$. We used the results of both the previously reported thermodynamic studies^{13,17} (i.e. CeO_2 doped with CaO , SrO , Y_2O_3 and La_2O_3) and the above thermodynamic data for CeO_2 doped with lower valent cations. These combined results are shown in Fig. 10 where $\Delta\bar{H}_{\text{O}_2}$ is plotted versus the site fraction of charge compensating oxygen vacancies formed by the lower valent cation dopant (e.g. $y/2$ for $\text{Ce}_{1-y}\text{M}_y\text{O}_{2-y-x}$ and $z/4$ for $\text{Ce}_{1-z}\text{M}'_z\text{O}_{2-z/2-x}$ where $\text{M} = \text{Ca}, \text{Sr}$ and $\text{M}' = \text{Y}, \text{La}$). The values of $\Delta\bar{H}_{\text{O}_2}$ used in Fig. 10 were determined in the near stoichiometric region (i.e. where $\Delta\bar{H}_{\text{O}_2}$ exhibits either a small

dependence or is independent of x). As discussed in previous publications^{12,13} and reports,^{6,17} this is the same region of nonstoichiometry where the variation of $\Delta\bar{S}_{O_2}$ 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 .

An interesting observation to be made from Fig. 10 is that the dependence of $\Delta\bar{H}_{O_2}$ on the oxygen vacancy concentration appears to be linear within a band of approximately ± 0.2 eV. It also appears that the dependence of $\Delta\bar{H}_{O_2}$ 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 $\Delta\bar{H}_{O_2}$ 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).

Utilizing the above linear dependence of $\Delta\bar{H}_{O_2}$ on $y/2$ or $z/4$ and the previous reported relation for the dependence of x and y or z on $\Delta\bar{S}_{O_2}$, we will try to obtain a generalized quantitative expression which will fit $x = x(P_{O_2}, T)$, y or z data for CeO_2 doped with lower valent cations.^{13,17}

b. ThO_2 doped CeO_2 .

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.¹⁷ 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 study²⁰ has shown that ThO_2

Figure 10 $\Delta \bar{H}_{O_2}$ vs site fraction of charge compensating oxygen vacancies formed by dopant.

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

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

$$\mu = \mu_{\text{O}} e^{-A/kT} \quad (2)$$

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 $x = x(T, P_{\text{O}_2})$ was determined for value of $y = 0.10$. These results are shown in Fig. 11 where $\log x$ is plotted vs $\log P_{\text{O}_2}$.

As shown in Fig. 11, at small deviations from stoichiometry (i.e. for x less than approximately 0.01) the nonstoichiometric behavior is best characterized by the relation

$$x \propto P_{\text{O}_2}^{-1/4} \quad (3)$$

As discussed in the electrical properties section the electrical conductivity of ThO_2 doped CeO_2 samples was effected by the presence of impurities. The nonstoichiometric dependence, x , on P_{O_2} given by Eq. (3) is consistent with the behavior observed for CeO_2 doped with lower valent cations (e.g. Ca, Sr, Y, La).¹⁷ 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.

Figure 11 A plot of $\log x$ vs $\log P_{\text{O}_2}$ for 10 m/o ThO_2 -doped specimen.

As shown in Fig. 11a, it is interesting to note that $\Delta\bar{H}_{O_2}$ is independent of x in the region near stoichiometry. In this same composition region the magnitude of $\Delta\bar{H}_{O_2}$ 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 $\Delta\bar{H}_{O_2}$ 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 $\Delta\bar{H}_{O_2}$ appears to be more of a second order effect because the above change in $\Delta\bar{H}_{O_2}$ 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 .

To minimize problems associated with impurities we will use specimens of ThO_2 doped CeO_2 prepared by dry mixing high purity CeO_2 and ThO_2 powder and sintering. After the problems with impurities are resolved we will continue the thermodynamic study on $Ce_{1-y}Th_yO_{2-x}$ to determine (a) $x = x(P_{O_2}, T)_y$ for several values of y , (b) the dependence of $\Delta\bar{H}_{O_2}$ on y and (c) compare the variation of $\Delta\bar{S}_{O_2}$ with x and y with theoretical models.¹²

c. Ta_2O_5 doped CeO_2 .

As discussed in the electrical properties study all of the previous studies on doped CeO_2 have been limited to foreign cations 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 electronic defects on $\Delta\bar{H}_{O_2}$, we initiated a thermodynamic study on Ta_2O_5 doped cerium dioxide. 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.

Figure 11a A comparison plot of $\Delta \bar{H}_{02}$ vs $\log x$ for "pure" and 10 m/o ThO_2 -doped CeO_2 specimen.

Thermogravimetric measurements were made on nonstoichiometric cerium dioxide doped with 1 mole % Ta_2O_5 as a function of temperature and oxygen partial pressure. From this data the deviation from stoichiometry $x = x(T, P_{\text{O}_2})^y$ was determined for values of $y = 0.02$. These results are shown in Fig. 12 as isothermal plots of $\log x$ vs $\log P_{\text{O}_2}$.

Although there does not appear to be any simple relationship between $\log x$ and $\log P_{\text{O}_2}$, it is interesting to note that for the same value of P_{O_2} and temperature the value of x is much larger for $\text{Ce}_{.98}\text{Ta}_{.02}\text{O}_{2-x}$ than the corresponding value for CeO_2 doped with lower valent oxides.

The thermodynamic quantities $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$ were calculated from $x = x(T, P_{\text{O}_2})^y$ data. The dependence of $\Delta\bar{H}_{\text{O}_2}$ is plotted versus $\log x$ for the 1 mole % Ta_2O_5 doped CeO_2 specimen. For comparative purposes the results of a recent study on "pure" CeO_{2-x} are also represented in Fig. 13. Discussion of the dependence on $\Delta\bar{H}_{\text{O}_2}$ on x is directed toward two different regions of x .

In the composition region $10^{-3} < x < 0.07$, $\Delta\bar{H}_{\text{O}_2}$ decreases with increasing x . This is in contrast to the behavior exhibited by both "pure" CeO_{2-x} and CeO_2 doped with lower valent cations. Another surprising observation for $\text{Ce}_{.98}\text{Ta}_{.02}\text{O}_{2-x}$ is the significant increase in $\Delta\bar{H}_{\text{O}_2}$ compared with "pure" CeO_{2-x} (i.e. ~ 4 eV at $x \sim 10^{-2}$). It is apparent from the large variation of $\Delta\bar{H}_{\text{O}_2}$ with x that the law of mass action cannot be applied to this system. Although there is no simple explanation for the above thermodynamic behavior it would seem reasonable that coulombic attractive forces would be reduced by screening effects resulting from the high concentration of electronic defects.

The thermodynamic study on $\text{Ce}_{1-y}\text{Ta}_y\text{O}_{2-x}$ will be continued to determine (a) $x = x(T, P_{\text{O}_2})^y$ for several values of y , (b) the dependence

Figure 12 A comparison plot of $\log x$ vs $\log P_{\text{O}_2}$ for "pure" and 1 m/o Ta_2O_5 -doped CeO_2 specimen.

Figure 13 A comparison plot of $\Delta\bar{H}_{02}$ vs log x for "pure" and 1 m/o Ta_2O_5 -doped CeO_2 specimen.

of $\Delta\bar{H}_{O_2}$ on x and y and (c) compare the variation of $\Delta\bar{S}_{O_2}$ with x and y with theoretical models.

d. Construction of a tensi-metric thermodynamic measuring system.

As described in the last progress report¹⁷ all of the thermodynamic data that has been obtained in this laboratory to date has been determined using a thermogravimetric technique.^{12,13} With this technique the limit of sensitivity in measuring x is about $2-3 \cdot (10)^{-5}$. The determination of the thermodynamic quantities is thus limited to a range of $x > 10^{-3}$ to avoid large errors in $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$. If the sensitivity for detecting x could be improved so that $x < 10^{-6}$ could be measured, then it should be possible to obtain additional thermodynamic data which would permit the determination of $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ in the region nearer stoichiometry (e.g. $10^{-4} < x < 10^{-3}$).

As discussed above $\Delta\bar{H}_{O_2}$ exhibits a small dependence on x in the composition region, $10^{-3} < x < 10^{-2}$ for "pure" CeO_{2-x} ¹² and CeO_2 -doped with lower dopant concentrations.^{13,17} If the predominant defects are those represented by the nonstoichiometric defect reaction in Eq. (1) (in the composition region $10^{-4} < x < 10^{-3}$) then it would be expected that the dependence of $\Delta\bar{H}_{O_2}$ on x would decrease with decreasing x and for values of $x \approx 10^{-4}$ $\Delta\bar{H}_{O_2}$ would be independent of x . Thus, the determination of $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ in the composition region $10^{-4} < x < 10^{-3}$ would provide a more rigorous test of the proposed defect model in "pure" CeO_2 and CeO_2 with lower dopant concentrations.^{12,13,17} It would also be easier to determine the effect of the dopant concentration on $\Delta\bar{H}_{O_2}$ at lower dopant concentrations since the effect of x could be eliminated in this region of nonstoichiometry.^{13,17}

Recently a tensi-volumetric method has been employed to measure oxygen nonstoichiometry as a function of P_{O_2} and T .²² This technique uses

a sensitive capacitance manometer to measure the change in oxygen content of the oxide sample. The ultimate sensitivity of this technique is approximately 10^{-12} moles of oxygen. This system was originally designed for use with radioactive oxides where the sample weight is the order of a milligram and the reported sensitivity in x for these measurements was about $\pm 10^{-3}$, we will modify this system so that larger oxide samples may be used (i.e. ~ 1 gram). Preliminary calculations indicate that with the larger samples we should obtain an ultimate sensitivity in x of about 10^{-8} to 10^{-9} .

We have attempted to extend our measuring capabilities of oxygen nonstoichiometry in the region nearer stoichiometry (i.e. $x < 10^{-5}$) by constructing a tensi-metric system similar to that used by Turcotte, Chikalla and Eyring.²² This system is about completed; when it is finished we will test it by comparing the thermodynamic data obtained from this system with the data previously reported on "pure" CeO_{2-x} obtained using a thermogravimetric measuring system.¹²

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 $\Delta \bar{H}_{\text{O}_2}$ and $\Delta \bar{S}_{\text{O}_2}$, and (3) the nonstoichiometric defect structure. This understanding can then provide a framework in which the basic assumptions of the simple defect model^{12,13,17} for $\Delta \bar{S}_{\text{O}_2}$ in "pure" and doped- CeO_{2-x} may be relaxed so that an extended defect model incorporating the variation of $\Delta \bar{H}_{\text{O}_2}$ with dopant addition and nonstoichiometry may be developed. As described above the results of these studies will also be utilized in the combined analysis of the electrical conductivity and transference studies to obtain information about the mobility of electrons and oxygen vacancies in doped CeO_{2-x} .

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