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"The Temperature Dependence of the Electrical Conductivity of Nonstoichiometric $\text{Ce}_{1+y}\text{O}_2$ "*

R. N. Blumenthal and R. L. Hofmaier**

Metallurgy and Materials Science, College of Engineering
Marquette University, Milwaukee, Wisconsin 53233

ABSTRACT

The electrical conductivity of sintered specimens of nonstoichiometric $\text{Ce}_{1+y}\text{O}_2$ was measured as a function of temperature from 1000° - 300°C as well as a function of composition over the range $0.00214 \leq y \leq 0.0977$. These results were described in terms of a high temperature and low temperature region. In both temperature regions the conductivity exhibits an exponential dependence on temperature.

$$\sigma = \sigma_0 e^{-Q/kT}$$

In the high temperature region the activation energy increased with increasing values of y (i.e. 0.22 eV at $y = .00214$ to 0.37 eV at $y = .098$). The activation energy, $0.61 \pm .03$ eV, in the low temperature was independent of y .

The temperature of the intersection between the high and low temperature regions for each composition was compared with the composition-temperature dependence of the miscibility gap reported by Brauer and Gingerich. The temperature dependence of the conductivity in the high

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temperature region was attributed to a change in both the carrier concentration and carrier mobility. An approximate value of the standard enthalpy of formation for the defect reaction

was determined from the temperature dependence of the conductivity in this study and from the temperature dependence of the electron mobility reported in the literature.

INTRODUCTION

Nonstoichiometric cerium dioxide, $\text{Ce}_{1+y}\text{O}_2$, has been the subject of several x-ray,¹⁻³ thermodynamic,⁴⁻⁶ and electrical conductivity investigations.⁷⁻¹³ Based on these experimental observations, $\text{Ce}_{1+y}\text{O}_2$ may be classified as a metal-excess, n-type semiconductor.

Brauer and Gingerich^{3,4} studied the influence of temperature on the phase relations in the cerium-oxygen system by measuring the oxygen dissociation pressure in the region CeO_2 - $\text{Ce}_{1.33}\text{O}_2$, from 600° to 1000°C, and by x-ray powder-diffraction analysis in the region CeO_2 - $\text{Ce}_{1.11}\text{O}_2$ over the temperature range 20° - 1050°C. They reported a miscibility gap which has the boundaries CeO_2 and $\text{Ce}_{1.105}\text{O}_2$ at room temperature contracts with rising temperatures and closes with a composition of approximately $\text{Ce}_{1.042}\text{O}_2$ at 685°C. At higher temperatures a homogeneous cubic solid solution extends from CeO_2 to about $\text{Ce}_{1.20}\text{O}_2$ and from $\text{Ce}_{1.20}\text{O}_2$ - $\text{Ce}_{1.33}\text{O}_2$ a two-phase region exists.

Bevan and Kordis⁶ also studied the oxygen dissociation pressures of the cerium-oxygen system from 636° to 1169°C. Based on their results they constructed a cerium-oxygen phase diagram at these temperatures between the composition $\text{Ce}_{1.539}\text{O}_2$ and CeO_2 . They also report a miscibility gap which appears to have a similar compositional dependence on temperature as reported by Brauer and Gingerich.^{3,4}

The defect structure responsible for the metal excess behavior of $\text{Ce}_{1+y}\text{O}_2$ has been inferred from the analysis of thermodynamic and electrical conductivity studies.⁷⁻¹³ Although defect models involving oxygen vacancies and cerium interstitials have been proposed the most recent investigation¹³ of the electrical conductivity over a wide range of

temperature and oxygen pressures appears to be consistent with the defect model involving triply and quadruply ionized cerium interstitials and electrons localized on normal cerium atoms. Based on an analysis of this conductivity data using the law of mass action the standard enthalpies of formation for the following defect reactions in $\text{Ce}_{1+y}\text{O}_2$ were determined:

No tolerances were placed on the values of ΔH_b° and ΔH_c° since these were regarded as approximate values only. Kofstad and Hed¹⁴ have also proposed a defect model involving cerium interstitials, singly and doubly ionized, and localized electrons based on analysis of the thermodynamic data of Bevan and Kordis.⁶ It should be noted, however, that most of the thermodynamic data was obtained at lower oxygen pressures than those employed in the above conductivity study. Thus it appears that if the cerium interstitial model is correct, then the degree of ionization of the cerium interstitials is probably a function of both temperature and departure from stoichiometry (i.e. as y increases, cerium interstitials with lower states of ionization become more important).

The electron mobility in $\text{Ce}_{1+y}\text{O}_2$ was also calculated as a function of temperature by combining electrical conductivity and thermogravimetric data for the temperature and oxygen pressure region where the atomic defect predominates in one state of ionization.¹⁵ The mobility was characterized by an exponential dependence on temperature with an activation energy of 0.14 eV. These results are consistent with a hopping type

conduction mechanism where the electrons localized at normal cerium sites move to adjacent cerium sites.

The purpose of the present study was to measure the electrical conductivity of $\text{Ce}_{1+y}\text{O}_2$ as a function of temperature and nonstoichiometry and to relate this data to the defect structure in the temperature region above the miscibility gap and to investigate the behavior of the conductivity below the miscibility gap.

THEORY

Information about the defect structure of $\text{Ce}_{1+y}\text{O}_2$ can be obtained from measurements of the electrical conductivity as a function of temperature at constant oxygen composition (i.e. fixed values of y in $\text{Ce}_{1+y}\text{O}_2$). For example, since $y = f(T, P_{\text{O}_2})$, the composition of a specimen may be controlled by fixing the temperature and oxygen partial pressure. If the specimen is then placed in an atmosphere which allows the oxygen composition to be maintained, the observed temperature dependence of the electrical conductivity may then be attributed to changes in the number of charge carriers and/or a change in the carrier mobility with temperature.

If the predominant nonstoichiometric defects are triply and quadruply ionized cerium interstitials, the departure from stoichiometry y is given by the expression

$$y = \text{Constant} = [\text{Ce}_i^{\bullet\bullet\bullet}] + [\text{Ce}_i^{\bullet\bullet\bullet\bullet}] \quad (4)$$

where $[\text{Ce}_i^{\bullet\bullet\bullet}]$ and $[\text{Ce}_i^{\bullet\bullet\bullet\bullet}]$ are the concentrations of triply and quadruply ionized cerium interstitials, respectively. The electroneutrality equation relating the concentration of localized charge carriers $[\text{Ce}_{\text{Ce}}']$ to the concentration of defects in each state of ionization is

$$[\text{Ce}_{\text{Ce}}'] = 3[\text{Ce}_i^{\bullet\bullet\bullet}] + 4[\text{Ce}_i^{\bullet\bullet\bullet\bullet}]. \quad (5)$$

Applying the law of mass action to the reaction

for the ionization of triply ionized cerium interstitials to quadruply ionized cerium interstitials, yields the relation

$$K = [\text{Ce}'_{\text{Ce}}][\text{Ce}_i^{\bullet\bullet\bullet\bullet}]/[\text{Ce}_i^{\bullet\bullet}]. \quad (7)$$

where K is the mass action constant which is temperature dependent only.

Combining Eqs. (4, 5 and 7) yields the expression

$$K = ([\text{Ce}'_{\text{Ce}}] - 3y)[\text{Ce}'_{\text{Ce}}] / (4y - [\text{Ce}'_{\text{Ce}}]) \quad (8)$$

which relates the departure from stoichiometry, concentration of electronic charge carrier, and the mass action constant. Values for K can be calculated from Eq. (8) by employing conductivity, mobility, and thermodynamic data.

In a similar manner, expressions may be derived for other defect ionization reactions. If doubly and triply ionized cerium interstitials are the predominant nonstoichiometric defects then

$$K' = (2y[\text{Ce}'_{\text{Ce}}] - [\text{Ce}'_{\text{Ce}}]^2) / ([\text{Ce}'_{\text{Ce}}] - 3y). \quad (9)$$

For the case where the predominant nonstoichiometric defects are singly and doubly ionized cerium interstitials the expression is

$$K'' = (y[\text{Ce}'_{\text{Ce}}] - [\text{Ce}'_{\text{Ce}}]^2) / ([\text{Ce}'_{\text{Ce}}] - 2y). \quad (10)$$

EXPERIMENTAL

Constant composition electrical conductivity measurements were made on sintered CeO_2 specimens. The CeO_2 powder, approximately 6 gm, was mixed with 4-5 drops of distilled water and pressed under a pressure of 6000 psi into bars 2 inches long, 1/4 inch wide and approximately 1/4 inch thick. The pressed bar was then placed in a high purity recrystallized alumina boat and completely covered with CeO_2 powder. These specimens were then sintered in a molybdenum wound resistance furnace at 1600°C for two hours in air. The impurity analysis of these specimens is shown in Table I.

Four probe conductivity specimens were prepared from the sintered bars of CeO_2 by wrapping with 0.01 inch dia. platinum wire. Two current leads were wrapped near the ends of the specimen and two potential leads were wrapped closer to the center with a spacing of approximately 1 cm. Notches approximately 0.01 inch deep were cut with a diamond saw in the edge of the specimens to aid in holding the leads in place. These notches were painted with a coat of Hanovia No. 6082, fluxed platinum paste, to minimize contact resistance.

A schematic drawing of the conductivity jig is shown in Fig. 1. A brass head containing Kovar seals for electrical leads and a thermocouple plus gas inlet and outlet ports was sealed to the open end of a 30 mm quartz envelope with an O-ring. Four platinum lead wires and a Pt:Pt-13%Rh thermocouple extend from the brass head to the specimen through three, two-hole 1/4 inch alumina insulators which were cemented into the brass head. The specimen was attached to the lead wires and the thermocouple positioned as close to the specimen as possible.

A vertically mounted nichrome wound resistance furnace was used for the isothermal reduction of the specimen and the cooling and heating cycles. A crank and gear assembly allowed the furnace to be lowered or raised so that the conductivity jig, mounted on a rack above the furnace, could be cooled or heated rapidly. This assembly allowed various cooling and heating rates to be obtained by lowering or raising the furnace at different rates relative to the stationary specimen. The furnace temperature was controlled with a Barber Colman Model 477P Capacitrol and Model 621 Power Controller.

The various oxygen partial pressures used to reduce the specimen were achieved with premixed and analyzed tank mixtures of CO-CO₂. For these mixtures the oxygen partial pressure was calculated as a function of temperature from the well known reaction

In order to maintain the oxygen composition of the specimen after equilibration with a CO-CO₂ mixture the system was purged with purified He. The He was purified by passing it over a mixture of TiO₂-Ti₂O₃ powder at approximately 950°C.¹⁶ This procedure reduced the oxygen partial pressure in the helium to approximately 10⁻¹⁶ atm as measured by an oxygen gauge.

A standard four-probe DC technique was employed for the electrical conductivity measurements. An Altair Model C2 constant current source with a continuously variable range from 1 μA to 50 mA was used to supply the current. The voltage across the potential probes was recorded on a Sargent Model DSR two-channel recorder. The second channel was used to record the thermocouple emf. Measurements of the electrical conductivity were made using the following procedure. A specimen of ceria was reduced

in a known CO-CO₂ mixture at approximately 1000°C. When equilibrium was obtained the specimen had a fixed oxygen composition which was determined from the thermodynamic data obtained in this laboratory. The system was then purged with purified helium to preserve this oxygen composition. After a time sufficient to purge the system of CO-CO₂, usually about ten minutes, the voltages across the potential leads and thermocouple were recorded during both the cooling and heating cycle. A plot of temperature and inner probe voltage versus time for a typical cooling cycle is shown in Fig. 2. The cooling rate was a maximum at approximately 900°C, 150°C/min, and decreased with decreasing temperature until at the lowest temperatures it was approximately 50°C/min.

RESULTS AND DISCUSSION

The electrical conductivity of sintered specimens of nonstoichiometric $\text{Ce}_{1+y}\text{O}_2$ was measured as a function of temperature from 300° to 1000°C, as well as a function of composition over the range $0.00214 \leq y \leq 0.0977$. The upper limit of y was fixed by the largest CO/CO_2 ratio, 97.3%, used in this investigation. The lower limit of y was determined by the experimental technique since for compositions close to stoichiometry a fixed oxygen composition could not be maintained in the specimen.

Typical results of the electrical conductivity measured as a function of temperature for two different oxygen compositions, $y = 0.00214$ and $y = 0.0204$, are shown in Fig. 3 as a plot of $\log \sigma$ vs $1/T$. As illustrated in Fig. 3 the conductivity for the cooling and heating curves are in good agreement for the case where $y = 0.0204$. However, for the case $y = 0.00214$ the conductivity for the heating cycle is slightly lower than the cooling cycle. The explanation for this observation is as follows. Since $\mu_{\text{O}_2}(\text{sample}) < \mu_{\text{O}_2}(\text{gas})$ the specimen will "getter" oxygen from the surrounding atmosphere and thus both y and the conductivity decrease with time. The oxygen in the inert atmosphere is obtained from the impurities in the inert gas (e.g. O_2 , CO_2 , H_2O). Since the rate controlling step is probably the removal of oxygen from the inert gas, the specimen with the smallest value of y will experience the largest % change in the conductivity. Thus the conductivity data obtained on cooling was considered to be more representative of the actual data because the amount of time the specimen was in contact with the inert atmosphere at elevated temperatures (e.g. 1000° - 600°C) was much less than corresponding time required for heating.

The conductivity data obtained on cooling from 1000°C is shown in Fig. 4 as a composite plot of the log of the electrical conductivity as a function of the reciprocal temperature for several different values of y . The straight lines shown in Fig. 4 are obtained from a least square curve fit of the conductivity data for sintered specimens which were normalized for porosity using the expression¹⁷

$$\sigma_{\text{norm}} = \sigma_{\text{meas}} \frac{\rho_{\text{theor}}}{\rho_{\text{meas}}} \quad (12)$$

where ρ_{meas} is the density of the sintered specimen. These results may be described conveniently in terms of a high temperature and a low temperature region. Since in both of these temperature regions the conductivity exhibits an exponential dependence on temperature, the conductivity in each region may be characterized by an Arrhenius type expression

$$\sigma = \sigma_0 e^{-Q/kT} \quad (13)$$

The parameters σ_0 and Q which characterize the lines shown in Fig. 4 and the corresponding compositions are tabulated in Table 2. In the high temperature region the activation energy, Q , increases with increasing departure from stoichiometry. The magnitude of the electrical conductivity is also very dependent on the value of y between $y = 0.00214$ and $y = 0.0447$. For values of $y > 0.0741$ the conductivity is less dependent on y . In the low temperature region, however, with the exception of the largest value of y , the activation energy does not appear to be a function of y and the magnitude of σ increases only slightly with increasing y . Another interesting observation is that the temperature at which the lines in the high and low temperature region intersect, increases with increasing values

of y up to about $y = 0.0447$. For larger values of y , however, the temperature at which the intersection occurs decreases with increasing y .

The temperature of the intersection for each composition and the composition-temperature dependence of the miscibility gap reported by Brauer and Gingerich are shown in Fig. 5 for purposes of comparison. The error bars shown for the x-ray study were estimated on the basis of the precision of their lattice parameter measurements and the dependence of the lattice parameter on composition which they report. The error bars shown for the data determined in this study were calculated from a least square analysis assuming a 95% confidence limit and from the reproducibility of the data. With the exception of two points all of the data from this study are within experimental error of the results obtained by Brauer and Gingerich.⁴ It should be noted, however, that most of the data points obtained in this study lie below the reported miscibility gap. The question arises as to whether the data points from the conductivity study are truly representative of equilibrium conditions for the miscibility gap or do they represent a metastable case. In the x-ray study nonstoichiometric specimens were annealed for at least three hours at temperature before measurements were made. Thus these measurements are probably representative of equilibrium conditions. In the conductivity study, however, measurements were made on nonstoichiometric specimens that were cooled very rapidly (e.g. $50^\circ - 150^\circ\text{C}/\text{min}$). Since the transformation occurs very rapidly in this study it may correspond to a metastable transformation. More accurate x-ray data is needed in order to answer this question.

The conductivity in the low temperature region cannot be accounted for on the basis of a simple phase mixture rule. Only one conduction mechanism appears to predominate below the miscibility gap since the activation energy was independent of composition in this region. An interesting question that cannot be explained from the conductivity data in this study is the following. Why is the activation energy for the low temperature conductivity larger than for the high temperature conductivity? Is it because the mobility exhibits a larger temperature dependence or because the concentration of charge carrier varies more rapidly or both? Hall mobility measurements in this temperature region would help provide an explanation to this question.

In the high temperature region in this study the compositions of the $\text{Ce}_{1+y}\text{O}_2$ specimens were in a single phase region. If the proposed defect model for the departure from stoichiometry (i.e. cerium interstitials with multiple states of ionization and localized electrons) is valid and the predominate states of ionization of the cerium interstitials are plus three and four, then as described in the theory section the expression which relates y , $[\text{Ce}_{\text{Ce}}^{\text{I}}]$ and K is

$$K = \frac{([\text{Ce}_{\text{Ce}}^{\text{I}}] - 3y)[\text{Ce}_{\text{Ce}}^{\text{I}}]}{4y - [\text{Ce}_{\text{Ce}}^{\text{I}}]} \quad (8)$$

In order to calculate K from the conductivity data it is first necessary to determine $[\text{Ce}_{\text{Ce}}^{\text{I}}]$. The most direct method of calculating $[\text{Ce}_{\text{Ce}}^{\text{I}}]$ would be to combine the conductivity and mobility data with the expression

$$\sigma = [\text{Ce}_{\text{Ce}}^{\text{I}}]e\mu \quad (14)$$

The calculation of $[Ce'_{Ce}]$ requires the use of the absolute value of the conductivity, σ , and the mobility, μ . Since sintered specimens were used in this study the measured conductivity value would have to be corrected for porosity by the use of Eq. (12).

Unfortunately the functional relation for K is very sensitive to small errors in $[Ce'_{Ce}]$ and y . To illustrate this a plot of the calculated values of $\log K$ vs $[Ce'_{Ce}]$ for the case where $y = 0.00214$ is shown in Fig. 6. Since only triply and quadruply ionized cerium interstitials are assumed to predominate the calculation of K from $[Ce'_{Ce}]$ and Eq. (8) for a fixed composition was subject to the following constraint

$$4y < [Ce'_{Ce}] < 3y . \quad (15)$$

To circumvent the problem of calculating K from the absolute value of $[Ce'_{Ce}]$ an indirect method of determining $[Ce'_{Ce}]$ as a function of temperature was employed. Since the conductivity was characterized by an equation of the form

$$\sigma = \sigma_0 e^{-Q/kT} \quad (13)$$

where σ_0 and Q are functions of y and the electronic mobility was reported to be of the form¹⁵

$$\mu = \mu_0 e^{-\Delta E/kT} \quad (16)$$

the concentration of the localized electrons may be represented by an equation of the form

$$[Ce'_{Ce}] = Ce^{-Q'/kT} . \quad (17)$$

The procedure used to solve for the temperature dependence of K was to select the conductivity data for a specimen with a value of $y = 0.00214$ which was in a composition region where according to the thermodynamic data triply and quadruply ionized cerium interstitials predominate. This region of composition was determined from the oxygen pressure dependence of y (i.e. where $5 > m > 4$ for the case where $y \propto P_{O_2}^{-1/m}$). The value of Q' , 0.08 eV, in Eq. (17) was then calculated for this composition by subtracting the reported values of $\Delta E = 0.14 \pm .01$ eV from the corresponding value of Q given in Table 2.

The range of values for the parameter, C , in Eq. (7) which are consistent with the inequality

$$4y < [Ce'_{Ce}] < 3y \quad (15)$$

were determined using the above value of Q' . K was then calculated as a function of temperature by combining Eq. (8) and the above expression for $[Ce'_{Ce}]$ where the value of y was fixed. Since C may take on a range of values, this calculation was repeated for several different values of C . These results for the case where $y = 0.00214$ are shown in Fig. 7 where $\log K$ vs $1/T$ is plotted for several different values of C . As illustrated in Fig. 7 the temperature dependence of K may be characterized by the expression

$$K = K_o e^{-\Delta H/kT} \quad (18)$$

for all permissible values of C , except for those values of C which correspond to the limiting cases where $[Ce'_{Ce}] = 4y$ and $[Ce'_{Ce}] = 3y$. In Eq. (18) ΔH is the standard enthalpy of formation for the defect reaction given by Eq. (6). With the exception of these cases which are not

consistent with the thermodynamic data it is interesting to note that the calculated values of $\Delta H = 1.6$ eV agree within ± 0.2 eV for the different values of C.

The effect of changing the value of Q' on ΔH was also investigated. The precision of the value of Q' was assumed to be ± 0.01 eV since the reproducibility of the value of Q was reported to be ± 0.01 eV. The above calculation of ΔH was repeated for the case where $Q' = 0.07$ and 0.09 eV. The results of these calculations are shown in Table III. It is apparent from these results that a small change in the value of Q' produces a large change in the calculated value of ΔH . Thus the calculated values of ΔH should be regarded as approximate values only. It is interesting to note however the agreement between the results obtained in this study with the approximate value $\Delta H_c = 1.9$ eV (see Eq. (3)) obtained from an analysis of the oxygen pressure dependence of the electrical conductivity.¹³ Another point of interest is that based on the defect analysis presented here for donors involving multiple states of ionization, the activation energy which characterizes the temperature dependence of the electrical conductivity for a fixed composition is much smaller than the calculated value of the ionization energy of the defect. This observation should also apply to other systems where the donor exhibits multiple states of ionization.

Based on a defect analysis of the thermodynamic data of Bevan and Kordis⁶ by Kofstad and Hed¹⁴ singly and doubly ionized cerium interstitials should predominate at larger departures from stoichiometry. An analysis of the aforementioned type of the conductivity data in a composition region where Eq. (10) is valid should permit the calculation of the energy

required to ionize a singly ionized cerium interstitial. Similar analysis should also allow one to calculate the energy required to ionize a doubly ionized cerium interstitial. If only two states of ionization of the cerium interstitial predominate in a given composition region (e.g. Ce_i^{**} and Ce_i^{***} or Ce_i^* and Ce_i^{**}) then the ratio $\text{Ce}_i^{****}/\text{Ce}_i^{***}$ should be very small. The ratio $\text{Ce}_i^{****}/\text{Ce}_i^{***}$ was calculated as a function of y from Eq. (7) using the calculated value of K shown in Fig. 7 and actual values of $[\text{Ce}'_{\text{Ce}}]$ for different values of y and temperature. The results of these calculations are shown in Table IV for three different temperatures, 700°, 800° and 1000°C. At the higher temperature the ratio $\text{Ce}_i^{****}/\text{Ce}_i^{***}$ is always greater than one even when y is large. The results of these calculations indicate that the concentration of Ce_i^{****} is important at high temperatures even at large departures from stoichiometry. Thus the assumption that only two states of ionization predominate singly and doubly or doubly and triply are probably incorrect.

Thus, in order to calculate the ionization energy to remove an electron from a singly or doubly ionized cerium interstitial, an equation similar to (8) would have to be derived which employed an electroneutrality expression which contains the cerium interstitial in at least three states of ionization. Unfortunately this introduces an additional adjustable parameter in the analysis which results in an increased uncertainty in the calculated results. Hofmaier¹⁸ has attempted this type of analysis and found that the calculated values of ΔH for the defect ionization reaction $\text{Ce}_{\text{Ce}} + \text{Ce}_i^{**} = \text{Ce}_i^{***} + \text{Ce}'_{\text{Ce}}$ was a negative quantity.

Although this result is speculative it could be rationalized on the basis of a large strain energy contribution which would be associated with the large ionic radius for the Ce_i^{**} state. The observed increase in the

activation energy for the electrical conductivity with nonstoichiometry might also be rationalized on the basis of donor defects such as cerium interstitials exhibiting multiple states of ionization.

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TABLE I

MASS SPECTROGRAPHIC ANALYSIS OF
A TYPICAL SINTERED SPECIMEN OF CeO_2 (ppmw)

Element		Element	
Li	0.3	Ag	≤ 0.2
Be	< 0.01	Cd	< 0.2
B	$\leq 7.$	In	< 0.1
F	20.	Sn	0.2
Na	15.	Sb	< 0.2
Mg	2.	Te	< 0.3
Al	15.	I	< 0.1
Si	20.	Cs	< 0.06
P	2.	Ba	$< 1.$
S	7.	La	< 0.5
Cl	10.	Ce	-
K	15.	Pr	10.
Ca	300.	Nd	10.
Sc	< 0.1	Sm	$< 1.$
Ti	2.	Eu	10.
V	≤ 0.03	Gd	$< 5.$
Cr	0.2	Tb	2.
Mn	0.2	Dy	1.
Fe	6.	Ho	≤ 0.3
Co	0.4	Er	≤ 0.5
Ni	20.	Tm	< 0.1
Cu	0.2	Yb	$\leq 1.$
Zn	1.	Lu	≤ 0.3
Ga		Hf	2.
Ge	< 0.2	Ta	$\leq 3.$
As	< 0.02	W	< 0.2
Se	< 0.4	Re	< 0.3
Br	< 0.3	Os	$< 1.$
Rb	$< 1.$	Ir	< 0.2
Sr	0.2	Pt	< 0.4
Y	0.5	Au	< 0.4
Zr	10.	Hg	< 0.4
Nb	< 0.02	Tl	< 0.2
Mo	< 0.07	Pb	1.
Ru	< 0.1	Bi	< 0.1
Rh	< 0.02	Th	50.
Pd	< 0.2	U	< 0.06

TABLE II

The parameters σ_0 and Q from $\sigma = \sigma_0 e^{-Q/kT}$ which characterize the high temperature and low temperature behavior of the electrical conductivity of $\text{Ce}_{1+y}\text{O}_2$ for fixed values of y .

y	HIGH TEMPERATURE		LOW TEMPERATURE	
	$\sigma_0 (\Omega\text{-cm})^{-1}$	$Q(\text{eV})$	$\sigma_0 (\Omega\text{-cm})^{-1}$	$Q(\text{eV})$
0.00214	2.42	$0.22 \pm .009$	1398.9	$0.592 \pm .05$
0.00603	6.44	$0.227 \pm .006$	3501.2	$0.637 \pm .02$
0.0204	32.1	$0.284 \pm .02$	2809.4	$0.616 \pm .04$
0.0447	52.70	$0.309 \pm .02$	3604.1	$0.635 \pm .02$
0.0741	81.65	$0.351 \pm .007$	4280.9	$0.617 \pm .07$
0.0977	96.57	$0.371 \pm .003$	461.7	$0.471 \pm .04$

TABLE III

The dependence of ΔH for the ionization of triply ionized cerium interstitials, Eq. (6), on Q' from Eq. (17).

Q' (eV)	ΔH (eV)
0.07	$1.3 \pm .2$
0.08	$1.6 \pm .2$
0.09	$1.8 \pm .2$

TABLE IV

Calculated values of the ratio $C_{e_i}^{\text{****}}/C_{e_i}^{\text{***}}$ from Eq. (7) using the calculated values of K and actual values of $[C_{e_i}']$ for different values of γ and temperature.

γ	$(C_{e_i}^{\text{****}}/C_{e_i}^{\text{***}})$	$(C_{e_i}^{\text{****}}/C_{e_i}^{\text{***}})$	$(C_{e_i}^{\text{****}}/C_{e_i}^{\text{***}})$
	1000°C	800°C	700°C
0.00214	5.13	0.538	0.0654
0.00603	2.05	0.219	0.0276
0.0204	0.69	0.081	0.0111