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HIGH TEMPERATURE ELECTRICAL
CONDUCTIVITY OF CeO_{2-x}

JUNE 1972

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CONDUCTIVITY OF CeO_{2-x}

By

J. Lambert Bates

Fuels and Materials Department

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ABSTRACT

The electrical conductivity of CeO_{2-x} was measured from 16°C to 1998°C in argon containing a low partial pressure of oxygen. The electrical conductivity of CeO_2 increased during five heating cycles as the O/Ce ratio decreased to a final value of 1.82. The energy for conduction below 1900°C decreased during the heating cycles as the conductivity increased. Three discontinuities in the $\log \sigma$ versus $1/T$ curves were observed at approximately 1000°C, 1150°C, and 1900°C. Above 1900°C, the conductivity decreased sharply with increasing temperature. After heating to 1900°C, no discontinuities were observed in the $\log \sigma$ versus $1/T$ curve for $\text{CeO}_{1.82}$ below 1900°C.

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INTRODUCTION

Cerium dioxide is one of the most refractory oxides and has received considerable interest for use in oxidizing atmospheres at high temperatures. CeO_2 has a fluorite-type structure similar to ThO_2 , ZrO_2 (distorted), UO_2 , and PuO_2 . Because of its chemical similarity to PuO_2 , CeO_2 is often used as a stand-in in radioactive experiments.

CeO_2 , like the other fluorite-type oxides, exhibits a wide range of hypostoichiometry. A number of low-temperature stoichiometric, intermediate phases are reported between CeO_2 and the type "A" Ce_2O_3 phase.⁽¹⁻⁵⁾

A knowledge of the electrical properties, especially at high temperatures, would be valuable in estimating the properties of PuO_2 and $(\text{Pu,U})\text{O}_2$, and in understanding the defect structure and the effects of stoichiometry on the properties of similar fluorite oxides.

Since the electrical conductivity measurements were made in an inert atmosphere in the presence of refractory metals at high temperatures, the sample was expected to reduce below $\text{CeO}_{2.00}$ with changes also occurring in the electrical conductivity. Previous investigations suggest a final composition near $\text{CeO}_{1.80}$, which would be single phase at the higher temperatures.^(1,2) Below 872°C , a composition less than $\text{CeO}_{1.80}$ can be obtained only in a reducing atmosphere.⁽¹⁾ Above 685°C , there appears

to exist at all temperatures a single, nonstoichiometric solid-phase region between $\text{CeO}_{2.00}$ and $\text{CeO}_{1.72}$.⁽¹⁾

A number of investigators have measured the low-temperature conductivity of CeO_{2-x} .⁽⁶⁻¹⁵⁾ (Figure 1) At temperatures less than 300°C, the conductivity values for pure CeO_2 are less than $10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ and are associated with very small activation energies (~ 0.1 to 0.2 eV).^(6,10) Conduction in this temperature range is associated with either impurity controlled electronic conduction or ionic conduction and appears to be independent of the oxygen pressure in the measuring atmosphere.^(6,9,10)

Above temperatures between 200 and 300°C, the conductivity experiences a sharp increase which is strongly dependent upon the stoichiometry of the CeO_{2-x} and upon the oxygen pressure.^(6,7,9-11) The conductivity increases and the activation energy (1 to 2.7 eV) decreases with decreasing O/Ce.^(1,2) For pure, stoichiometric CeO_2 , the conduction is n-type and totally electronic.^(6,7) Rudolph⁽⁷⁾ found the conductivity of CeO_2 at 987°C to increase with decreasing oxygen pressure according to the relation

$$\sigma \propto P_{[\text{O}_2]}^{-1/5.7}$$

Additions of CaO to CeO_2 increases the conductivity and changes the conduction from electronic to predominantly ionic.⁽¹¹⁾

Greener et al.⁽⁹⁾ reported the conductivity of nearly-stoichiometric CeO_2 to result from two conduction mechanisms:

FIGURE 1. Summary of the Low Temperature Electrical Conductivity Data Reported by Other Investigators Compared to the Results of This Study.

- An oxygen pressure (0.006 to 1.0 atm.) dependent conduction which predominates above 1100°C and which is entirely defect controlled.
- An oxygen pressure independent conduction which occurs over the entire temperature range.

Thus, below 1100°C, the conduction is mixed resulting from two mechanisms, a n-type defect controlled, electronic conduction and an oxygen independent contribution which is most probably ionic.

The purpose of this study was to determine the electrical conductivity of CeO_{2-x} from room temperature to temperatures as near the melting point of CeO_{2-x} as possible and to observe the effects of stoichiometry changes which were expected during the measurements at high temperatures. The measurements were designed only as cursory investigations at the high temperatures where other measurements are lacking.

EXPERIMENTAL TECHNIQUES

The electrical conductivity of the sintered CeO_2 was measured using a four-contact method.^(16,17) Briefly, a right cylinder sample was heated in a tungsten mesh resistance furnace surrounded by tungsten heat shields. The current leads, sample holder, and voltage probes were tungsten. The test assembly which was inserted into the refractory metal furnace is illustrated in Figure 2.

The measurements were made using a direct current applied potential. The voltage drop across a known resistor in the circuit was

FIGURE 2. Sample Assembly Inserted into Refractory Metal Furnace for Electrical Conductivity Measurements Showing Voltage Probes, Sample Holder, and Current Probes, Thermocouples and Supporting Assembly.

measured with current flowing in both directions, and an average resistivity was calculated.

Measurements were made from 20 to 2000°C in a purified argon atmosphere at atmospheric pressure. The inlet gas contained < 1 ppm O₂ and < 5 ppm H₂O. The major gas impurities were ~ 300 ppm N₂ and ~ 100 ppm H₂ and CO₂.

Temperatures were measured with a W - 5% Re/W - 26% Re bare thermocouple inserted in a hole drilled in the sample midway between a voltage probe and the sample holder (Figure 2). An optical brightness pyrometer was focused on the surface of the sample as a secondary check of the sample temperature. A second thermocouple was later inserted between the other voltage probe and sample holder to determine the temperature gradient across the sample (not shown in Figure 2). The temperature gradient between the two thermocouples (~ 1.2 cm apart) was less than 2°C at 1500°C.

Measurements were made during five heating cycles, the first three to temperatures less than 1000°C and the fourth and fifth to near 2000°C. A summary of the heating conditions is compiled in Table I.

The CeO₂ sample was prepared by cold pressing and sintering in air at 1600°C to 6.78 g/cm³, 95% of the theoretical density. The CeO₂ was initially stoichiometric and contained ~ 1290 ppm impurities, the largest impurity being Cd (1000 ppm), Table II. The sample was 1.905 cm long and 0.635 cm in diameter.

TABLE I. *Electrical Conductivity Measurements for CeO₂.*

<u>Heating Cycle</u>	<u>Temperature Range, °C</u>	<u>Comments*</u>
1	416 → 980	Measurements made only on heating.
2	286 → 976 → 532	Measurements made both on heating and cooling.
3	462 → 740	Measurements made only on heating.
4	195 → 1995 → 17	Measurements made both on heating and cooling.
5	17 → 1998 → 18	Measurements made both on heating and cooling.

* Measurement of electrical conductivity values less than $10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ are difficult in this apparatus.

TABLE II. *Spectrographic Analysis of CeO_{1.82} Composition of CeO₂.**

<u>Element</u>	<u>ppm**</u>	<u>Element</u>	<u>ppm**</u>
Al	50	Ni	10
Ca	100	Pb	5
Cd	1000	Si	30
Fe	10	Sn	20
Ga	2	W	50
Mg	2		

* Measured after electrical measurements.

** Determined by emission spectroscopy.

RESULTS AND DISCUSSION

Below 1000°C

The electrical conductivity (σ) near room temperature of the starting stoichiometric CeO_2 was below the measurable limits ($10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$) of the four-contact apparatus. Therefore, initial measurements for the CeO_2 were began at $\sim 400^\circ\text{C}$. The conductivity increased rapidly with temperature and showed two discontinuities in the $\log \sigma$ versus $\frac{1}{T}$ curve (Curve 1, Figure 3). These breaks occurred at $\sim 550^\circ\text{C}$ and $\sim 950^\circ\text{C}$ with the slope of the curve between these two temperatures less than the slope at both the higher and the lower temperatures. Similarly shaped curves were observed during Cycles 2 through 4 below 1000°C . Each cycle resulted in significant increases in conductivity and in a reduction of activation energy. In each instance, the slope above and below the break between 200 to 300°C decreased during subsequent heating cycles. The conductivity values on cooling (Cycle 4) were higher than the values on heating and agreed much more closely to the values obtained during the final heating cycle (Cycle 5).

Above 1000°C

Above approximately 1000°C , the electrical conduction increased significantly with increasing temperature. All of the conductivity curves for those heating cycles where the maximum temperature had not exceeded 1000°C , converge into the relative straight line observed in Cycle 4, (Figure 3). At approximately 1130°C , another sudden change occurred in the temperature dependence of the $\log \sigma$ versus $1/T$ curve. In the small temperature range from 1000 to 1130°C , the conductivity increased approximately 250 times compared to an increase of 2 to 3 times in the

FIGURE 3. Electrical Conductivity of CeO_{2-x} .

larger temperature interval from 1130 to 1900°C. The electrical conductivity decreased from 12 to 3 ohms⁻¹ cm⁻¹ during an increase in temperature from 1900 to 1995°C.

Measurements during the fifth cycle were conducted to determine if the changes in the electrical conductivity observed during the cooling portion of Cycle 4 and the unusual decrease in conductivity above 1900°C could be reproduced.

The electrical conductivity during both heating and cooling agree within the experimental error with the electrical conductivity values measured during cooling of Cycle 4 (Figures 3 and 4). The values during heating were slightly less than those during the previous high temperature cycle. Both exhibited a decrease in conductivity above 1900°C with the change occurring at a slightly higher temperature during the final heating cycle.

Slight changes in linearity in the log σ versus 1/T curve between 1000 and 1300°C were observed in both high temperature cycles. A slight hysteresis was observed on heating and cooling in this temperature range during Cycle 5 (Figure 4). However, the electrical conductivity values in the cooling portion of Cycle 4 and in Cycle 5 appear to be representative of the CeO_{2-x} at the end of the electrical conductivity measurements.

The appearance of the sample changed considerably during the electrical conductivity measurements. The original stoichiometric sample was white with a yellowish-brown cast. At the termination of

FIGURE 4. High Temperature Electrical Conductivity of CeO_{2-x} for Cycles 4 and 5. (Values not corrected for dimensional changes which occurred near the apparent melting point.)

the experiments, the sample was a dark blue-black. The sample, although still intact, showed a glassy-like appearance and evidence of material flow (Figure 5). This was interpreted to have resulted from partial melting of the CeO_{2-x} sample near 2000°C . The CeO_{2-x} was extremely friable and broke into small pieces when removed from the tungsten holders.

An analysis of the changes in the sample cross-sectional area (a) and the voltage probe spacing (x) resulting during the electrical conductivity measurements showed a decrease of 15% in the area-to-length ratio. Although these changes are small compared to the gross changes in conductivity, the conductivity was corrected for these dimensional changes, and the results are illustrated in Figure 6.

Thermogravimetric analysis in air of the CeO_{2-x} showed a strong oxidation reaction between 200 to 250°C and a smaller reaction near 450°C . Very little weight change was observed from 450 to 950°C . The O/Ce ratio for two samples was determined to be 1.82.

The microstructures of the $\text{CeO}_{1.82}$ after the conductivity measurements are illustrated in Figures 7 through 9. The oxide near the outer shiny surface was made up of large grains relatively free of porosity. This area, which was near the tungsten holders, contained metallic inclusions of tungsten, a darker second phase, and was grossly cracked.

A sharp demarkation was observed between the high density area near the surface and the interior of the sample. The interior was free of the metallic phase and darker oxide second phases. The sample interior was interlaced with fine cracks, which made the sample very friable and

$\text{CeO}_{1.82}$

Tungsten
Holder

FIGURE 5. Bottom View of $\text{CeO}_{1.82}$ Sample in Tungsten Holder after 5th Heating Cycle Showing Glassy Appearance of Oxide Surface and Areas of Sample Flow.

FIGURE 6. High Temperature Electrical Conductivity of CeO_{2-x} Corrected for Dimensional Changes Estimated After Electrical Measurements.

FIGURE 7. Microstructures of $\text{CeO}_{1.82}$ after Electrical Conductivity Measurements showing Large Grains Near Sample Surface in Areas of Sample Flow. (As-Polished, 100X).

FIGURE 8. Microstructure of $\text{CeO}_{1.82}$ Sample after Electrical Conductivity Measurements (500X).

0.01 cm

Sample
Surface

FIGURE 9. Microstructure of $\text{CeO}_{1.82}$ after Electrical Conductivity Measurements (500X).

difficult to polish. This structure was very similar to the structure observed in CeO_2 which had formed during melting point measurements.

No melting of the sample had been anticipated during the measurements to 2000°C , since the reported melting point for stoichiometric CeO_2 varied between 2600 and 2800°C .⁽¹⁸⁻²⁰⁾ However, a decrease in melting point with decreasing O/Ce is consistent with similar decreases reported for UO_{2-x} .⁽²¹⁾

The electrical conductivity results are consistent with the results reported by other investigators (Figure 1). The magnitude of the conductivity values falls amid the reported values. The conductivity increases and the activation energy decreases with decreases in O/Ce values.

The sharp change in conductivity which occurred between 1000 and 1300°C as the O/Ce decreases is consistent with the changes in conduction which were reported by Greener et al.⁽⁹⁾ and would suggest that the conduction is electronic and results from the anticipated defect structure which occurs with hypostoichiometry.

The electrical conductivity results are also consistent with the reported phases of $\text{CeO}_2 - \text{Ce}_2\text{O}_3$ which form above 800°C in oxygen pressures between 10^{-7} to 10^{-14} atm. and with reduction to a single phase, fluorite-type hypostoichiometric oxide.^(1,2) The actual composition of the CeO_{2-x} at the higher temperatures is not known and can only be surmised from the reported phase diagrams, since on slow cooling the composition should revert to $\text{CeO}_{1.82}$.⁽²⁾ However, a single

phase CeO_{2-x} with a stoichiometry less than 1.82 could possibly exist at the higher temperatures. However, the relatively linear $\log \sigma$ versus $1/T$ during the fifth measuring cycle below 1900°C suggests that if a lower stoichiometry did exist it had little effect on conduction values.

The slight hysteresis between 1130 to 1900°C during Cycle 5, although the variations are within experimental error, could be related to phase changes or stoichiometry changes as the sample is heated and cooled in this temperature range.

The sudden decrease in conductivity between 1900 and 2000°C suggests either a dramatic change in conduction mechanism, e.g., to metallic-like conductivity, and/or to a change in oxide structure. However, the effects are reproducible but cannot be related to any cause.

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REFERENCES

1. D. J. M. Bevan and J. Kordes, "Mixed Oxides of the Type MO_2 (Fluorite) - M_2O_3 - I: Oxygen Dissociation Pressures and Phase Relationships in the System CeO_2 - Ce_2O_3 at High Temperatures," J. Inorg. Nucl. Chem., Vol. 26, pp 1509-1523, Pergamon Press Ltd. (1964).
2. D. J. M. Bevan, "Ordered Intermediate Phases in the System CeO_2 - Ce_2O_3 ," J. Inorg. Nucl. Chem., Vol. I, Pergamon Press Ltd., London, 1955, pp 49-59.
3. C. J. Kevane, "Über die Oxydes des Cers-V," J. Inorg. Nucl. Chem. 16, 87-99, 1960, AD-274510 (1962).
4. G. Brauer, K. A. Gingerich, and U. Holtschmidt, "Oxides of Cerium: IV," J. Inorg. Nucl. Chem. 16, 77-86, 1960.
5. P. Kofstad and A. Z. Hed, "Defect Structure Model for Nonstoichiometric CeO_2 ," J. Am. Cer. Soc. 50, No. 12, 681-682 (1967).
6. A. W. Czanderma and J. M. Honig, "The Stoichiometry, Resistivity, and Thermoelectric Power of Cerium Dioxide Below 500°C ," AFOSR-57-602 (1957), Phys. & Chem. Solids 6, 96 (1958).
7. J. Rudolph, "Über den Leitungsmechanismus Oxydescher Halbleiter bei hohen Temperaturen," Z. Naturforsch 14a, 727-737 (1959).
8. C. J. Kevane, E. L. Holverson, and R. D. Watson, Bull. Am. Phys. Soc. 7, 497 (1962).
9. E. H. Greener, J. M. Wimmer, and W. M. Hirthe, "Electrical Conductivity of Near-Stoichiometric $\alpha\text{-CeO}_2$," pp 539-54 in Rare Earth Research II New York, Gordon and Breach, 1964.
10. D. N. Polyboyarinov, E. Ya Shipiro, V. S. Bakunov, and F. A. Akopov, "The Change in the Electrical Conductivity and Creep Rate During Reduction for Sintered Ceramic Prepared from CeO_2 ," Izvestiya Akademii Nauk SSSR Neorganicheskie Materialy, Vol. 2, No. 2, 336-342 (1966) (in Russian).

11. R. N. Blumenthal and B. A. Pinz, "Nature of Electrical Conduction Transients Observed in CeO_2 and Ca-Doped CeO_2 ," J. Appl. Phys. 38, No. 5, 2376-2383 (1967).
12. W. Noddack and H. Walsh, Z. Physik. Chem. 211, 194 (1959).
13. I. V. Vinokurov, Z. N. Zonn, and V. A. Ioffe, "Electrical Properties of Cerium Dioxide Single Crystals," Sov. Phys. Solid State (Engl. Trans.) 9, 2659-63 (1968); N.S.A. 22, No. 17, 37030, Sept. 15, 1968.
14. N. P. Bogoroditskii, et al., "Electrical Properties of Oxides of Rare Earth Elements," Dokl. Akad. Nauk. SSSR, 160: 578-71 (Jan. 21, 1965) (Russ.).
15. S. F. Pal'gnev, et al., J. Inst. Elektrokhim, Akad Nauk, SSSR, Uval'sk, No. 2, 193-197 (1961). (Investigation of oxide sintering by the electrical conductivity method.)
16. J. L. Bates, C. A. Hinman, and T. Kawada, "Electrical Conductivity of Uranium Dioxide," J. Am. Cer. Soc. 50, No. 12, 652-656 (1967).
17. J. Lambert Bates, The Electrical Conductivity of Uranium Dioxide, Part II, Final Report, BNWL-296, Pt II, October 1967.
18. S. J. Schneider, "Compilation of the Melting Points of the Metal Oxides," National Bureau of Standards, Monograph 68, pp 10-11 (1963).
19. W. G. Bradshaw and C. O. Matthews, Properties of Refractory Materials: Collected Data and References, LMSD-2466, pp 18 (1960).
20. H. H. Hausner, Data Book on Physical and Engineering Properties of Materials for Nuclear Fuel Elements, Sylvania-Corning Nuclear Corporation Bayside, New York, pp 51 (no date).
21. J. Lambert Bates, "Melting Points of Hypostoichiometric Uranium Dioxide," J. Am. Cer. Soc. 49, No. 7, 395-396 (1966).

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