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ELECTRICAL CONDUCTIVITY OF
THORIUM DIOXIDE

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ELECTRICAL CONDUCTIVITY OF
THORIUM DIOXIDE

by

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June 1972

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TABLE OF CONTENTS

LIST OF FIGURES	ii
LIST OF TABLES	iii
ABSTRACT	iv
INTRODUCTION	1
EXPERIMENTAL PROCEDURES	2
FOUR CONTACT METHOD	2
THREE CONTACT, GUARD RING METHOD	4
RESULTS	9
HIGH TEMPERATURES	9
LOW TEMPERATURES	17
REVIEW AND DISCUSSION OF ELECTRICAL CONDUCTIVITY DATA FOR ThO_2	19
ATMOSPHERE DURING MEASUREMENTS	28
HEATING CONDITIONS	31
OXYGEN PRESSURE	31
TEMPERATURES BELOW 1400°C	31
TEMPERATURES ABOVE 1400°C	33
DOPANTS AND IMPURITIES	33
M_2O_3	33
MO	34
MO_2	35
POLARIZATION	35
GAMMA RADIATION	37
TEMPERATURE AND ACTIVATION ENERGY	39
EXPERIMENTAL PROCEDURES	41
GENERAL CONCLUSIONS	43
ACKNOWLEDGEMENTS	44
REFERENCES	45

LIST OF FIGURES

1. Sample Assembly Inserted Into Refractory Metal Furnace For Electrical Conductivity Measurements. The Voltage Probes, Sample Holder Current Probes, Thermocouple and Support Assembly Are Illustrated	3
2. Three Contact Apparatus For Measuring the Electrical Conductivity In and Out of Gamma Radiation Fields	6
3. Measured Electrical Conductivity of ThO_2 At High Temperature	10
4. Schematic of Four Probe Apparatus For Measuring Electrical Conductivity In An Atmosphere Containing Emission Currents	12
5. Measured Emission Currents Plotted Against Current Probes (Shorted) to Shield Bias Voltage at Various Temperatures	13
a. For ThO_2 Sample F-3 (B-56)	
b. For No ThO_2 Sample	
6. Measured Emission Currents Plotted Against Reciprocal Temperature	16
a. Sample to Shield Bias at + 3 Volts	
b. Sample to Shield Bias at - 3 Volts	
7. Effect of High Intensity Gamma Radiation on Electrical Conductivity of ThO_2	18
8. Review of the Electrical Conductivity of ThO_2 at Lower Temperatures	26
9. Review of the Electrical Conductivity of ThO_2 at Higher Temperatures	27
10. Review of the Electrical Conductivity Measured In Hydrogen and Oxygen	30
11. Review of the Reported Effects of Gamma Radiation On The Electrical Conductivity of ThO_2	38

LIST OF TABLES

I. Spectrographic Analysis of Thorium Oxide Samples	5
II. Summary Of The Electrical Conductivity Data And Measurements for ThO_2	20
III. Reported Activation Energies For Electrical Conductivity Of ThO_2	24
IV. Summary and Averages of Activation Energies For Electrical Conductivity of ThO_2 in Air and Hydrogen	40

ABSTRACT

The electrical conductivity of ThO_2 was measured from near room temperature to 2500°C . Measurements were also made to 800°C in a high intensity gamma radiation field. A review of the preliminary data is presented. Experimental difficulties relating to high temperature measurements and measurements in gamma field are discussed in detail. The reported electrical conductivity data for ThO_2 is reviewed considering such variables as temperature, oxygen pressure, impurities, and polarization.

The report concludes that the wide variations in reported electrical conductivity data result principally from variations in oxygen pressures, sample compositions and experimental techniques. At high temperatures, experimental measurements are complicated by the presence of large thermionic emission currents, gas conduction, and polarization. The reported increases in conductivity induced by gamma radiation are related to the ionization of the gas surrounding the sample instead of induced solid state conduction. ThO_2 is a mixed ionic-electronic conductor depending upon the oxygen pressure and dopant composition. It is a p-type conductor at low temperatures and an apparent n-type conductor above 1400°C .

ELECTRICAL CONDUCTIVITY OF THORIUM DIOXIDE

J. Lambert Bates and R. R. Schemmel

INTRODUCTION

Thorium dioxide is the most refractory of all oxides. It has a high melting point ($>3300^{\circ}\text{C}$) and a relatively low vapor pressure at high temperature. ThO_2 has been used as an additive to tungsten or as a coating on a refractory metal to increase the thermionic emission. Because of its refractory nature and low electrical conductivity, it has been used as an electrical insulator. However, its high cost and radioactivity have somewhat limited its electronic uses. As a refractory oxide, it also has potential use as a breeder fuel for nuclear reactors. Most recently, because of its high ionic conductivity, it has found expanding use as an oxide base for solid electrolytes in electrochemical oxygen cells.

The electrical conductivity of ThO_2 has been measured by many investigators⁽¹⁻⁴²⁾ under a wide variety of conditions with wide variations in reported conductivity values. The overall purpose of this study was to determine the electrical conductivity of ThO_2 from room temperature to 3000°C ; to provide a better understanding of electrical conduction in ThO_2 ; to evaluate possible reasons for the wide discrepancy in conductivity values, and to determine the useful limits for ThO_2 as an electrical insulator for nuclear applications.

This document includes preliminary conductivity data for ThO_2 from near room temperature to 2500°C , both in and out of a gamma radiation environment; some considerations of the experimental methods; an extensive review of the reported electrical conductivity data from ThO_2 ; and an analysis of the data considering such variables as temperature, oxygen pressures, polarization and sample composition.

EXPERIMENTAL PROCEDURES

The electrical conductivity was measured by two different techniques 1) a four-contact method at high temperatures in vacuum and inert or reducing atmospheres, and 2) a three-contact, guard-ring method below 1000°C in all atmospheres.

Four-Contact Method

The four-contact apparatus for making measurements at high temperatures has been described elsewhere.⁽⁴³⁻⁴⁴⁾ Briefly, a right cylinder, 0.635 cm in diameter and 1.90 cm long, was heated in a tungsten mesh resistance element 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 1.

Measurements were made with both alternating and direct current by measuring the voltage drop across an external resistor of known value in series with the sample. Measurements were restricted to conductivities greater than 10^{-6} mhos/cm. When dc measurements were made, the voltages were measured in both directions, and an average resistance was determined.

Measurements were made from 20 to 2500°C in a purified argon or an 8% H₂-92% argon atmosphere at atmospheric pressure. The inlet argon contained <1 ppm O₂, <5 ppm H₂O, ~300 ppm N₂, and ~100 ppm H₂ and CO₂. The inlet 8% H₂ - 92% argon contained <1 ppm O₂, <2 ppm H₂O, and <20 ppm N₂ and CO₂.

Temperatures were measured with a W - 5% Re versus W - 26% Re bare thermocouple inserted in an indentation on the sample midway between a voltage probe and the sample holder (Figure 1). 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 a sample holder to determine that the temperature gradient between the two thermocouples (~1.2 cm apart) was less than 2°C at 2000°C.

FIGURE 1: Four Contact-Electrical Conductivity Specimen Holder Assembly.

A circular molybdenum emitter shield was hung from each sample holder to electrically shield the sample, and a tungsten tube was inserted between the heating element and the tungsten mesh heater to provide a more uniform temperature.

The samples were prepared by cold pressing and sintering of a Sol-Gel ThO_2 powder in hydrogen (commercial grade) at 1725°C for four hours, with heating and cooling rates of 100°C/hr . The ThO_2 samples, F-2 (B-56) and F-3 were 8.6 and 9.1 g/cm^3 dense respectively. The pores were spherical, varied up to $15 \times 10^{-4} \text{ cm}$ in diameter and were concentrated near the grain boundaries. The purity of the samples is shown in Table I.

The samples were mechanically ground into 0.635 cm diameter by 1.90 cm long right cylinders. Small indentations were ground in the surface of the sample, 0.635 cm apart, for voltage probes and two holes were drilled $\sim 0.3 \text{ cm}$ from each end for the thermocouples. The samples were cleaned with acetone and with ethyl alcohol in an ultrasonic cleaner, dried, and heated for eight hours in air at 1000°C to remove volatile surface contaminants and to ensure stoichiometry at 2.00.

Three-Contact, Guard Ring Method

The electrical conductivity between room temperature and 800°C was also measured using a three-contact, guard-ring apparatus.^(4,5) (Figure 2). The sample was a disc, 1.27 cm in diameter and 0.075 cm thick.

Platinum electrodes were applied by painting and drying successive coatings of platinum paste (Englehard No. 1072). The coatings were cured at 1000°C in air for eight hours. The coating covered the entire surface on one side of the sample. The other side was coated with a central electrode approximately 0.75 cm in diameter and with an $\sim 0.15 \text{ cm}$ wide guard ring electrode on the outer edge of the disc. A 0.1 cm wide uncoated space separated the two electrodes. Current and voltage leads were platinum wire or the platinum side of Pt versus Pt - 10% Rh thermocouples.

TABLE ISpectrographic Analysis of Thorium Oxide Samples

<u>Elements</u>	<u>Impurities, ppm</u>		<u>Elements</u>	<u>Impurities, ppm</u>	
	<u>F-2 & 3</u>	<u>F-1</u>		<u>F-2 & 3</u>	<u>F-1</u>
Ag	---	<0.1	Mn	1.0	10
Al	5.0	50	Na	500	<2
B	<0.1	---	Ni	10	<10
Bi	10.0	---	Pb	0.5	--
Ca	---	500	Si	<10	<5
Cr	---	<25	Sn	0.5	<5
Cu	<50	1	V	--	<50
Mg	10	5			

APPARATUS FOR MEASURING ELECTRICAL CONDUCTIVITY IN GAMMA FIELD

FIGURE 2: Three Contact Apparatus for Measuring The Electrical Conductivity In-And-Out-of-Gamma Radiation Field.

A 0.006 cm thick platinum foil was placed between the leads and the electrode coatings. Contacts between the foil, coating, and wire were maintained by applying tension to Al_2O_3 tubes which insulated and supported the electrodes. The entire assembly and the Al_2O_3 tubes surrounding the lead wires were individually shielded with platinum foil.

The sample and contacts were supported in the desired position in the furnace using a series of high purity, high density Al_2O_3 discs and tubes (Figure 2). The tubes were positioned through holes in these discs to provide a rigid assembly. Tension was provided to the one-piece electrode insulators with coiled tungsten wire wrapped around the tubes. The springs gripped the rod and were coiled against an assembly disc. Pressure could be varied by adjusting the tension in the tungsten spring. These springs were located sufficient distance from the hot zone of the furnace to prevent loss of tension. The sample assembly was surrounded by a platinum-shielded Al_2O_3 tube. The total diameter of the assembly was 2.5 cm and the length 20 cm. All shields were grounded.

The assembly was inserted into a nichrome-wound furnace (Figure 2). The wire was wound bilaterally around the outside of an Al_2O_3 muffle tube to minimize inductive effects. The electrical leads emerged from the top of the heater. A chromel versus alumel thermocouple between the sample and the heater was used to control the temperature. The heater muffle was surrounded by another Al_2O_3 tube for thermal and electrical insulation.

The assembly was heated either with a manually controlled, dc power supply or with a SRC controlled and programmed ac power supply. A power of 300 watts was sufficient to heat the sample to 1000°C in air.

Sample temperatures were measured with a Pt versus Pt - 20% Rh thermocouple in contact with the central electrode on the sample. The Pt side of this thermocouple was also used as one of the current and voltage leads.

The total diameter of the assembly including the heater and insulator was less than 3.6 cm. This diameter was dictated by the size limit of the metal tube (4.4 cm in diameter) which was inserted into the gamma source. The unit was lowered into a closed end 5 cm diameter stainless steel tube 6.1 meters long. A smaller stainless tube, 1.3 cm in diameter, was positioned parallel to the larger tube with an outlet into the bottom of the large tube below the sample. This tube was used as an inlet for furnace atmospheres.

The 7.5 to 8 meter long electrical leads were individually shielded. In the radiation field, the insulation was high density Al_2O_3 coated with platinum. Outside the radiation field the leads were changed to doubly shielded coaxial cable. Connections were made with a high impedance connection system with shielded connectors.

Temperatures were controlled to $\pm 1^\circ\text{C}$. Because of the relatively low heat capacity, heating and cooling rates could be widely varied. The stainless steel shroud tube was cooled by the surrounding water.

The high intensity gamma radiation was provided from an array of irradiated Co^{60} elements under 5 meters of water. The maximum intensity in the element array was approximately 4×10^7 R/hr. The intensity was varied to 10^3 R/hr by moving the assembly away from the source center toward the outside of the 3.7 meter diameter containment tank.

Measurements were made in air, inert gas or 8% hydrogen - 92% argon up to atmospheric pressure.

The resistance of the sample was measured using two different procedures depending upon the sample resistance. At very high resistances ($< 10^{10}$ ohms), a megohm dc Wheatstone bridge with a high impedance, high sensitivity detector was used. The guard terminal was connected to the sample guard electrode to eliminate surface conduction on the sample. Applied voltages could be varied from 10 to 1000 volts. The accuracy was $\pm 1\%$ at 10^{12} ohms and $\pm 10\%$ at 10^{15} ohms.

At the lower resistances ($<10^{10}$ ohms), measurements were made using a constant direct current power supply with compliance potentials from 10 to 100 volts. A unity amplifier was connected to the guard ring electrode to prevent extraneous surface emission effects. The voltages across the sample were displayed on the low Z output of a 1 to 1 FET amplifier circuit with a 10^{10} ohm input impedance. Currents were determined by measuring the voltage drop across calibrated resistors in series with the sample. Polarization effects could also be determined. The resistance limit of this apparatus with $\pm 1\%$ accuracy was 10^{10} ohms. Most measurements were made using constant current. The resistance measurements obtained by the two electronic measuring systems agreed to $\pm 2\%$ in the overlap range of resistance measurements.

The sample for the three contact technique (F-1) was prepared by conventional cold pressing and sintering at 1700°C in $8\% \text{H}_2 - 92\% \text{argon}$. The density of the sample was 9.5 g/cm^3 , and the purity of the sample is given in Table I. The discs, 1.27 cm diameter and 0.075 to 0.100 cm thick, were ground to the desired dimensions, ultrasonically cleaned sequentially in acetone and ethyl alcohol, and heated for eight hours in air at 1000°C to remove volatile contaminants and to control stoichiometry to 2.00.

RESULTS

High Temperature

The high temperature conductivities of ThO_2 samples F-2 and F-3 (B-56) are shown in Figure 3. A wide variation in conductivity values, especially at the lower and higher temperatures were observed even with the same sample. Fair agreement was obtained between 1200 and 1800°C . At the lower temperatures, wide variations in conductivity occurred after the sample had been heated to higher temperatures in the reducing $8\% \text{H}_2$ atmosphere. These changes did not follow any particular pattern as observed during heating cycles 2, 3, and 4 for sample F-3.

FIGURE 3: Measured Electrical Conductivity of ThO_2 At High Temperatures.

The $\log \sigma$ versus $1/T$ curve can be separated into two different temperature regions each with different activation energies which possibly represent changes in conduction mechanisms.

Sample F-2 exhibited an anomolous decrease in conductivity above 2500°C. The existence of such a decrease, if not due to experimental error, is difficult to explain. A similar decrease has been reported for CeO_{2-x} .⁽⁴⁶⁾

Some difficulties which had not been observed in previous measurements were encountered during the electrical conductivity measurements of ThO_2 . Large currents and emf's were measured at the high temperatures. The currents and voltages were often larger than those from the applied power supply. Originally, this phenomena was attributed to thermoelectric voltages arising from large thermal gradients across the sample. However, a second thermocouple was installed in the sample indicating the temperature gradient to be <2°C at 2000°C. Subsequent evaluation⁽⁴⁷⁾ suggested that these extraneous currents and emf's resulted from thermionic emission from the sample, emission from the tungsten heater and holder and/or gas conduction.

An extensive investigation was made of the currents present in the measurement system at high temperatures. A report on this study has been published.⁽⁴⁷⁾ Emission currents present in the measurement system were monitored at high temperatures by shorting the current probes (as connected to the ends of the sample), biasing them relative to the molybdenum shield, and monitoring the current at various temperatures (Figure 4). Measurements were taken both in vacuum and in a 92% Ar - 8% H_2 atmosphere, with current probe-to-shield biasing voltages between -10 volts and +20 volts. Results were recorded for a ThO_2 sample in both environments and in similar experiments with the sample absent but maintaining the same system geometry (Figure 5). Both graphs show the current collected by the shield versus probe-to-shield basis at various temperatures.

FIGURE 4: Schematic For Four Probe Measurement Technique
In An Atmosphere Containing Emission Currents.

FIGURE 5: Measured Emission Currents Plotted Against Current Probes (Shorted) To Shield Bias Voltage at Various Temperatures.

- (a) For ThO_2 , Sample F-2
 (b) For No Sample In The System

The current-voltage (I-V) curves show the current saturation common to thermionic emission. In vacuum, a slight increase in collected current results with increasing voltage. The slope of these curves appears to be temperature dependent. In the Ar-H₂ atmosphere, current saturation with voltage proved more dramatic. However, at high temperatures ($T > 1800^{\circ}\text{C}$), current increased significantly with voltages. There seems to be little difference between the curves with and without a sample in the same environments. The main significance of the curves lies in the magnitudes of the currents.

Under positive bias, electrons flow from the shield to the sample region. With the electrodes only 0.125 inch from the shield, most of the emitted current will be collected there. The currents collected below 1400°C are larger with the ThO₂ sample present, while introduction of atmospheric pressure 92% Ar - 8% H₂ decreases the current. At temperatures greater than 1400°C , the current magnitude depends less on these conditions. For ThO₂, a good emitter, more current can be expected with the sample present. The presence of Ar-H₂ at atmospheric pressure can either increase or decrease the current.

In a system used for performing electrical measurements at elevated temperatures in a controlled atmosphere, a space charge due to thermionic emission from heated surfaces will always be present. Any voltage gradient maintained in the system will result in net currents in the gas phase. For the four-probe arrangement, maintenance of a voltage gradient between the current probes will cause a net emission of electrons by one probe and a net collection by the other with the current path entirely in the gas phase. The result will be a net current in the external circuit indistinguishable from any sample current. The magnitude of such emission-induced current can possibly exceed that of sample current for a given voltage applied to the sample.

For the case of ionic conduction in the sample, current will flow until the sample becomes sufficiently polarized to balance the potential difference imposed by the external voltage source. Actual sample current can be transient, decreasing to zero as a potential equilibrium is reached. If net emission currents occur, significant current need not flow through the sample. For an emission-induced current large enough to build sufficient space charge at the ends of the sample to maintain the voltage gradient, the observed current will be determined by the applied voltage and the impedance of the external circuit. In any event, with these conditions, the current observed in the external circuit will not equal the actual current passing through the sample.

Estimation of the sample resistivity, therefore, requires knowledge of the effect that emission currents have on the sample and on the measurements. It is advantageous to maintain a net emission current in one direction (i.e., from sample to shield) by biasing the sample relative to the shield. An ammeter or standard resistor in series with the biasing battery monitors the net emission current between the shield and the measurement system. Maintenance of a voltage gradient across the sample initiates additional current paths in the system.

To illustrate the problem that these emission currents can cause, the ThO_2 sample was removed from the system and the effective resistivity of the electrode gap was measured in vacuum. The resistance was determined from the slope of the gas current versus probe voltage curve for both the biased and unbiased case. The emission current from probes-to-shield was held constant at each temperature.

The results in Figure 6 indicated that shunting currents in the environment around the sample (or between the current probes) may exceed any sample current. This indicated that the sample conductivity was equal to or less than the calculated value, thus complicating measurement

FIGURE 6: Measured Emission Currents Plotted Against Reciprocal Temperatures
 (a) Sample to Shield Bias at +3 Volts
 (b) Sample to Shield Bias at -3 Volts.

of the resistivity. The slope change near 1400°C also occurred in the thermionic emission experiments as it did in the conductivity measurements. The experimental error associated with these preliminary investigations limits any definite conclusions regarding the relative magnitudes of the currents for different conditions. The significance lies in the fact that the measured conductivities seem to be independent of the presence of a ThO₂ sample in the system.

Low Temperatures

The electrical conductivity of ThO₂ was measured from room temperature to 800°C in and out-of-a-gamma radiation field. The results are illustrated in Figure 7. In the absence of a gamma radiation environment, the electrical conductivity in air fit a log σ versus 1/T linear relationship with an activation energy of approximately 1.8 eV.

The initial measurements indicated that electrical conduction could be induced in ThO₂ with a high intensity, gamma radiation. The induced conductivity (σ_i) was conveniently fitted to an exponential relationship

$$\sigma_i = A \cdot \dot{\gamma}^n \quad (1)$$

where $\dot{\gamma}$ is the radiation field and n is a constant. For ThO₂ in air, $A = 2.2 \times 10^{-13}$ mhos (cm-R/hr)⁻¹ and $n = 0.43$.

Although the results initially seemed consistent and logical, some unexpected experimental results raised serious questions regarding the reliability of the data measured in the gamma field. The apparent resistance of the sample at any one temperature in the gamma field increased with an increase in applied voltage when a constant current was used. As the temperature increased, the resistance decreased slightly, resulting in a series of isotherms with the resistance increasing with increasing voltage. The induced resistivity for the same sample at a constant

EFFECT OF RADIATION ON ELECTRICAL CONDUCTIVITY ThO_2

TEMPERATURE, $^{\circ}\text{K}$

FIGURE 7

temperature was a function of the atmosphere used to make the measurements. The conductivity was higher in argon, or in 8% H₂ - argon, than in air.

With the electrodes in position but with the sample removed, the resistance of the system in air was the same magnitude as the resistance with a sample in position where $\sigma_i = 2.8 \times 10^{-15} \dot{\gamma}^{0.954}$.

If the radiation ionizes the gases, the number of carriers (ions) will be constant at any one radiation intensity level and at any one temperature. An increase in temperature or in radiation intensity would increase the number of carriers. Thus, at constant temperature and radiation intensity, the number of carriers will be constant and an increase in voltage at constant current will result in an increase in sample resistance.

Thus the apparent conduction possibly results, not from an induced current flow in the solid, but from a current flowing through the gas surrounding the sample which is ionized by the gamma radiation. Such conduction should be relatively temperature independent and directly related to the intensity of the radiation. It appears, therefore, that all studies which indicate a radiation induced conductivity in ThO₂ and other oxide insulators are suspect.

REVIEW AND DISCUSSION OF ELECTRICAL CONDUCTIVITY DATA FOR ThO₂

The electrical conductivity data ⁽¹⁻⁴²⁾ for ThO₂ measured under a wide variety of conditions has been summarized in tabular form in Tables II and III and graphically as a function of the reciprocal temperature in Figures 8 and 9. Included is a review of the sample description, measuring conditions and techniques where available.

Although there appears to be a wide scatter in the data, especially below 1400°C, attempts were made to relate the scatter to specific factors.

TABLE II.

Summary of Electrical Conductivity Data-Measurements for ThO₂

Investigator		Sample Description				Measuring Technique					Miscellaneous	
Name	Reference	Density (g/cm ³)	Size (cm)	Fabrication Method	Purity	Atmosphere	Pressure	Temperature Range, (°C)	Electrode Material	Furnace Type	Electronics	
Podszus	1	NR	1x1.4x0.13	Sintered at 2000°C in N ₂	NR	Vacuum N ₂ H ₂	~10 ⁻⁵ torr 1 atm 1 atm	1823-2233 1883-2273 1798-1943	W	W heater in glass jar	Self heating, ac 2 contact	
Rogener	2	NR	NR	NR		Air	1 atm	400-1100	Pt	Pt wound ceramic tube	2 contact-dc	Slight polarization noted
Wright	3,4	NR	Tube 0.35 OD with 0.05 wall	Extrusion and sintered	NR	Vacuum	NR	1623	Ta	W wire down center of tube	NR	30 ohm cm ΔH = 1.1 eV, sample color changed
Foex	5,6	7.8 (24% open porosity)	2-3 long x 1 dia.	Sintered 2100°C in vacuum	Some oxides of Ce and elements of La group	Air N ₂ H ₂ O ₂ Vacuum CO CO ₂	1 atm 1 atm 1 atm 1 atm NR 1 atm 1 atm	600-1200 800-2100 800-1800 600-1200 600-1200 600-1200 600-1200	Pt Mo Mo Pt Pt Pt	Chromel wound ceramic tube to 1200°C; carbon resistance furnace for N ₂ and H ₂	Samples coated with Pt or Mo: Four contact - dc	
Hansley	7	NR	Coating 0.003 thick	Evaporated coating on W	NR	Vacuum	NR	1150-1550	--		Calculated from emission measurements	

TABLE II. (Continued)

Summary of Electrical Conductivity Data-Measurements for ThO₂

Investigator		Sample Description				Measuring Technique						Miscellaneous
Name	Reference	Density (g/cm ³)	Size (cm)	Fabrication Method	Purity	Atmosphere	Pressure	Temperature Range, (°C)	Electrode Material	Furnace	Electronics	
Mesnard and Uzan	8-10		Tube 0.01 dia. x 0.025 - coated on W			Vacuum	NR	1060-1852	W		2 contact ac in parallel with W tube	Polarization observed
Danforth and Morgan	11-13	~7	2 long x 0.3 OD	Sintered	CP grade mantle grade	Vacuum	5 x 10 ⁻⁶ to 1 x 10 ⁻⁷ torr	800-1800	Mo	W heating coil with dc Mo shield, glass container	4 contact	Polarization observed. σ function of current density.
Danforth and Bodine	14-16	10	0.5 x 0.5 0.2	Fused crystal	0.01 Al, La,T-Cr, Cu,Si,Be, Ti,Ce,Y and Zr.	Vacuum	10 ⁻⁶ torr	850-1300	Pt		2 contact dc Pt surfaces 4 contact	Polarization
Danforth	17	10.0	0.57 x 0.55 x 0.13 0.45 x 0.54 x 0.24 0.30 x 0.30 x 0.15	Single crystal	See Danforth and Bodine ⁽¹⁴⁾	Vacuum	1 x 10 ⁻⁶	450-1350	Pt	W furnace in Ta tube	2 contact - dc polarization	Polarization
Danforth	18		~.5 x 0.5 x .1-.2		See Danforth and Bodine ⁽¹⁴⁾	Vacuum	10 ⁻⁶ torr	920-1285	Pt	W heater in Ta tube	2 contact dc	Polarization

TABLE II. (Continued)

Summary of Electrical Conductivity Data-Measurements for ThO₂

Investigator		Sample Description				Measuring Technique					Miscellaneous	
Name	Reference	Density (g/cm ³)	Size (cm)	Fabrication Method	Purity	Atmosphere	Pressure	Temperature Range, (°C)	Electrode Material	Furnace Type	Electronics	
Hund and Mezger	19-20	9.7	1 dia disc	Sintered 1500°C Vacuum	50 ppm Si 10 ppm U 1 ppm P <0.1 B,Cu, Mg,Mn, Sm,Eu, Gd,Oy	Air NR	1 atm	893-1351	Pt			
Susman	21	NR	5 x 0.64 x 0.4 or 2.5 x 0.6 x 0.4	Sintered 1500°C	99.9% 50 ppm SO ₃ 10 ppm Fe + Cr + Ni 5 ppm Ca,Mg 25 ppm Na + K + Li	Argon	1 atm	700-1000	Pt	Ta resistance	4 contact	In contact with Al ₂ O ₃
Rudolph	22	NR	0.5 x 0.6 dia	Sintered 1500-1600°C	NR	O ₂ O ₂ Vacuum H ₂	375 torr 1 torr 10 ⁻⁴ torr 380 torr	500-1050 860-1500	Pt	NR	4 contact ac	
Palighev	23-26	NR	NR	Sintered in air at 1550°C	<0.01 total metal	Air Variable Po ₂	1 atm	500-1000	NR	NR		
Subbaro	27	9.7	Discs	Sintered in air at 1800°C (20 μ grain size)	Starting material <30 ppm detected but <500 ppm 15 ppm Si 3 ppm Co, Mg,Zn,Na	Air	1 atm	800-1400	Pt	Ceramic tube Pt windings	O ₂ half cell type - 2 con- tact ac (1000 cycles)	

TABLE II. (Continued)

Summary of Electrical Conductivity Data-Measurements for ThO₂

Investigator		Sample Description				Measuring Technique					Miscellaneous	
Name	Reference	Density (g/cm ³)	Size (cm)	Fabrication Method	Purity	Atmosphere	Pressure	Temperature Range,(°C)	Electrode Material	Furnace Type	Electronics	
Kuhlman	28-32	NR	4 x 1 dia	Isostatically NR pressed, sintered 2200°C in H ₂ and air at 1400°C		H ₂ He (Po ₂ varied)	1 atm 1 atm	1400-2200	W	W heater furnace	4 contact dc	
Steele - Alcock	33-34	9.9	.2-.3 x 1 dia	Isostatically NR pressed, sintered vacuum 2000°C		O ₂ O ₂ O ₂	1 atm 10 ⁻⁶ atm 10 ⁻¹⁵ atm	700-1100°C	Pt		2 contact ac (>1000 hertz) galvanic cell	
Bregar and Davis	35-37	~8 (connected 2 OD porosity) 1.7 ID	5 long	Flame sprayed		Vacuum	NR	38-1197	Ni coated with W or Mo electrodes in quartz tube	Mo wire on mullite tube	2 contact dc (no guard ring)	~30-140°C gradient across wall. Measured also in-reactor core
Bauerele	38	~9.7	0.1 x 0.1 x 1	Sintered 2200°C in O ₂	Starting ThO ₂ <30 ppm detected but <500 ppm total 15 ppm-Si 3 ppm-Cu, Mg,Zn,Na	O ₂ + inert gas O ₂ + H ₂ + H ₂ O (varying Po ₂) from 1 to 10 ^{-14.6} atm)	1 atm total pressure	1000	Pt	Al tube furnace	4 contact	
Rapp and Lasker	39-41	9.3		Sintered 2100°C in vacuum; 1400°C in air	99.9% ThO ₂ with 100 ppm Mg 500 ppm Na + .K. + Li	Varying O ₂ with O ₂ - inert gas mixtures (1 to 10 ^{-27.5} Po ₂)	1 atm	800-1100	Pt	Mullite tube furnace- wire wound	2 contact ac in galvanic cell	

TABLE III.

Reported Activation Energies for the Electrical Conductivity
of ThO₂

	<u>Ref.</u>	<u>Temp - Range</u>	<u>ΔH (eV)</u>	<u>Atmosphere</u>	<u>Comments</u>
Podszus	1	1600-2000 1600-2000 1500-1700	2.63 2.94 3.45	Air N ₂ H ₂	
Rögener	2	400-1100	1.45	Air	
Wright	3,4	to 1600	~1.1	Vac	Data questionable
Foex	5	600-1200 800-2100 800-1800 600-1200 900-1200 600-1200 600-1200	1.40 1.48 2.00 1.48 1.60 1.87 1.48	Air N ₂ H ₂ O ₂ Vac CO CO ₂	Break in curve at 900°C
Mesnard and Uzan	9	1060-1852	1.78	Vac	Data variable and questionable
Danforth and Morgan	11				
<u>CP</u>					
low I/cm ² pulsed		800-1800 1550-1800	1.0) 3.2)	Vac	Low current density
<u>Mantle Grade</u>					
low I/cm ² pulsed		850-1800 1550-1800 800-1550	1.66) 2.8) 0.8	Vac Vac	Low current density

TABLE III. (Continued)

Reported Activation Energies for the Electrical Conductivity
of ThO₂

	<u>Ref.</u>	<u>Temp - Range</u>	<u>ΔH (eV)</u>	<u>Atmosphere</u>	<u>Comments</u>
Danforth and Bodine	14	850-1300	1.1	Vac	
Danforth	15	450-1350	1.2	Vac	
Danforth	16	920-1285	1.1	Vac	
Hund and Mezger	20	893-1351	1.26	Air	
Susman	21	700-1000	1.30	Argon	
Rudolph	22	500-775	1.58)	O ₂ (3.75 torr)	
		775-1050	1.18)		
		550-775	1.74)	O ₂ (1 torr)	
		775-1050	1.25)		
		575-1050	1.48	Vac	
		700-1050	2.26	H ₂ (380 torr)	
Paliguev et al	26	600-1000	1.58	Air	
Kuhlman	32	1200-1600	1.41)	He	
		1600-2200	3.39)		
		1200-1500	1.14)	H ₂	
		1500-2200	3.08)		
		1400-2000	3.57	O ₂ (10 ⁻¹³ atm)	
Subbarao	27	800-1400	1.2	Air	
Bregar - Davis	36,37,50	500-1200	1.20	Vac	Variable and decreasing below 500°C
Bates and Schemmel	This Study	60-800	1.77	Air	
		750-1200	2.61)	8% H ₂ -Argon	<1 ppm O ₂ <5 ppm H ₂ O
		1400-2400	3.08		
		830-1175	2.60	8% H ₂ -Argon	Energy above 1400 increasing with temperature

FIGURE 8: Review of the Electrical Conductivity of ThO₂ at Lower Temperatures.

FIGURE 9: Review of the Electrical Conductivity of ThO₂ at Higher Temperatures.

The effects discussed in this review include:

- Atmosphere during measurements
- Heating conditions
- Oxygen pressure
- Dopants and impurities
- Polarization and non-ohmic behavior
- Gamma Radiation
- Temperature and activation energy
- Experimental procedures.

It was apparent that some reported data were not valid because of the experimental techniques used to measure the conductivity. The data of Wright^(3,4) were made indirectly during emittance measurements of a ThO₂ and tungsten powder mixture coated on tantalum. The author states that the conductivity values were approximate. Hanley⁽⁷⁾ reported the conductivity for ThO₂ coated on tungsten. These conductivities were determined indirectly by emittance measurements. The author⁽⁷⁾ suggested that these data were subject to considerable error and should be considered approximate since the data involved the measurement of small differences between two large quantities. These two data sources are, therefore, not considered further in this report.

Atmosphere During Measurements

Some of the first investigators of the electrical conductivity of ThO₂ observed significant differences in the conductivity values when different gases were used during measurements.

Podszus⁽¹⁾ observed at temperatures above 1800°C that the $\log \sigma$ was linear with T^{-1} and that the conductivity was higher in H₂ than in N₂ or in vacuum (Figure 8). Kuhlman⁽²⁸⁻³²⁾ observed a similar shift in conductivity above 1500°C with the conductivity in H₂ greater than in He. A break in the $\log \sigma$ versus T^{-1} curve was observed at 1500°C (Figure 8).

Kuhlman⁽²⁸⁻³²⁾ observed a similar shift in conductivity above 1500°C with the conductivity in H_2 greater than in He. A break in the $\log \sigma$ versus T^{-1} curve was observed at 1500°C (Figure 8).

Foex^(5,6) observed at temperatures below 1400°C an effect opposite to that at higher temperatures; the conductivity in O_2 > in air > in vacuum, in N_2 and in CO_2 > in CO > in H_2 . All $\log \sigma$ versus T^{-1} curves were linear with approximately the same activation energy (Figure 8).

Rudolph⁽²²⁾ found the conductivity in hydrogen to be less than that in oxygen (Figure 9). Weinreich and Danforth⁽⁴²⁾ reported the conductivity in O_2 > in vacuum > in H_2 . The data from this study also indicated a significantly higher conductivity in air than in 8% H_2 - 92% A (Figure 3).

Because of these consistent variations in conductivity in different atmospheres, the data in one atmosphere of air and in oxygen pressures of 10^{-19} atmospheres were compared separately. These results are illustrated in Figure 10. It is very apparent that at all temperatures the scatter between data obtained in the same atmosphere are greatly reduced, well within a factor of ten. The average conductivity in air is higher than the average conductivity in H_2 . The scatter in the data for H_2 is larger, however, the reducing atmospheres are also the most difficult to control.

One would infer from these analyses, that at temperatures below 1400°C, an increase in the oxygen pressure increases the conductivity, while the reverse is true at higher temperatures. However, in a conducting atmosphere ($T > 1400^\circ C$) an increase in $P_{[O_2]}$ should decrease the gas conductance because of the electronegativity of the oxygen ions. The electron mean free path for emitted electrons decreases and n-type conduction would be indicated if gas phase conduction currents are measured.

FIGURE 10: Review of the Electrical Conductivity Measured In Hydrogen and Oxygen.

Heating Conditions

An effect which appears related to atmosphere effects is the change in conductivity resulting from heat treatment in vacuum at 1225 to 1925°C in the presence of tungsten.⁽⁸⁻¹⁰⁾ Similar changes were observed in this study below 1200°C for Sample F-3 (Figure 3). Although no consistent change in conductivity was apparent, the changes may be related to changes in oxygen activity in the sample or in the atmosphere during measurements.

Oxygen Pressure

Temperatures Below 1400°C

Rudolph⁽²²⁾ observed a linear rise of $\log \sigma$ with $\log P_{[O_2]}$ in the oxygen pressure range from 10^{-4} to 375 torr with a power dependence of 1/5.6 to 1/5.95 from temperatures up to 1310°C and of 1/5.5 from 1200 to 1500°C. A decrease in power dependence in the conductivity at low $P_{[O_2]}$ was observed at elevated temperatures.

Lasker and Rapp⁽³⁹⁾ found the conductivity in the $P_{[O_2]}$ range from 10^{-6} to 1 atmosphere to follow a good approximation of a 1/4 power ($P_{[O_2]}$) dependence and suggested that Rudolph's⁽²²⁾ data fit a 1/4 power dependence better than the reported 1/5.5 dependence. A 1/6 dependence is predicted theoretically assuming positive hole conduction in a nonstoichiometric lattice of interstitial oxygen ions in the lattice and an infinite dilute solution of defects.

Perhaps the most comprehensive and most reliable data are the results of Lasker and Rapp⁽⁴¹⁾ measured at 1000°C. At intermediate oxygen pressures ($<10^{-10}$ atm), the conductivity is essentially independent of the $P_{[O_2]}$.^(33,34,38-41) At the very low oxygen pressures ($<10^{-20}$ atm), the data suggest that the conductivity again becomes dependent upon the $P_{[O_2]}$ but with a n-type conduction instead of p-type conduction.⁽³⁹⁻⁴⁰⁾

With the exception of the results reported by Rudolph,⁽²²⁾ there is a general agreement that at temperatures below 1400°C and at high oxygen pressures $<10^{-10}$ atm, the conduction for "pure" ThO_2 is mixed p-type and ionic.^(33,34,38-41) In the region of the $P_{[\text{O}_2]}$ independent plateau, the conduction is $>99\%$ ionic.^(33,34,38-41) The conduction again becomes mixed at the very low oxygen pressures with the electronic conduction being n-type. For example, at 1000°C for "pure" ThO_2 oxygen in 1 atm, σ is $<10\%$ ionic and $>90\%$ p-type electronic while at an $P_{[\text{O}_2]}$ of 10^{-6} atm, σ is approximately 75% ionic and at $\leq 10^{-12}$ atm oxygen σ is essentially 99% ionic

For "pure" ThO_2 , the oxygen pressure independent ionic conductivity could be due either to a very high concentration of intrinsic defects, i.e., oxygen interstitials ions and vacant oxygen sites, or to unintentionally added impurity ions and ionic defects which compensate for these impurity ions and which give rise to predominantly ionic conductivity. The latter appears to be the most reasonable.⁽³⁸⁻⁴¹⁾

The electronic contribution in the so-called "pure" ThO_2 is reported to result from a small number of oxygen vacancies, due either to a doping effect of certain cation impurities or to intrinsic Frenkle or Schottky defects. Whatever the origin, excess O_2 may go into vacancies and contribute holes as

where V_{O}^{2-} is oxygen vacancy, O^{2-} is oxygen ion, and h is a hole. Application of mass action law⁽¹¹⁾ gives

$$N_h = K N_v^{1/4} P_{[\text{O}_2]}^{1/4}$$

where N_h is hole concentration and N_v is the concentration of vacancies. Thus, total conductivity is given

$$\sigma_T = \sigma_{\text{ion}} + \sigma_e P_{[\text{O}_2]}^{1/4}$$

The thermoelectric results support the p-type conduction for the electronic conduction to 1000°C. At approximately 775°C, the thermoelectric power exhibits a change attributed to a transition from p-type to n-type at high $P_{[O_2]}$.⁽²²⁾ A break is observed in the $\log \sigma$ versus T^{-1} curve with a higher energy at lower temperatures.

Temperatures Above 1400°C

At the higher temperatures above 1400°C, the conductivity exhibits an oxygen pressure effect opposite to that observed at lower temperatures. Kuhlman⁽²⁸⁻³²⁾ observed the conductivity to decrease by an order of magnitude for every seven orders of magnitude that the $P_{[O_2]}$ increases. Kuhlman suggests that as the $P_{[O_2]}$ increases, the oxygen vacancies in the lattice apparently decrease. Since an oxygen vacancy puts an electron into the conduction band, a decrease in the number of vacancies results in fewer electrons in the conduction band, resulting in decreased conduction. However, this is not consistent with the thermoelectric results at high temperatures which suggests that conduction is n-type. However, considerations should be given to thermionic emission effects and to gas conduction which can result in increase in apparent conduction.

Dopants and Impurities

Additives or impurities can influence both the electronic and ionic conduction. The effects of adding metal oxides of type M_2O_3 have been studied most extensively since these solid solutions are widely used as solid electrolytes.

Additions of La_2O_3 and Y_2O_3 increase the total conductivity at low temperatures.^(21,22,27) No high temperature data have been reported. Associated with these increases are increases in the ionic transference number to near unity with a corresponding extension of exclusively ionic conductivity to higher and lower oxygen pressures. A decrease in activation energy also occurs with an increase in dopant composition. Although

there is also a simultaneous increase in the electronic conduction, it is overshadowed by the large increase in ionic conduction.

The conductivity of ThO_2 containing La_2O_3 is reported to be 10% higher than for ThO_2 containing Y_2O_3 . However, both exhibit a maximum ionic conductivity and minimum p-type electronic conductivity near $0.85 \text{ ThO}_2 - 0.15 \text{ MO}_{1.5}$.^(33,34,39-41) A minimum in the activation energy is also observed at this same composition. Rudolph⁽²²⁾ reports the break in the $\log \sigma$ versus T^{-1} curve reported for ThO_2 to be removed with additions of La_2O_3 .

The increase in ionic conduction with the introduction of M_2O_3 into the lattice results from the formation of positive holes and the trapping of the holes by Y^{3+} . For every two moles of $\text{YO}_{1.5}$, an equivalent of one mole of vacancies is produced.

Additions of Ta_2O_3 have a different effect on the conduction of ThO_2 .⁽²²⁾ The conductivity is relatively high in H_2 and vacuum. However, in O_2 an irreversible reduction in σ occurs with the conduction and the activation energy increasing with a decrease in $P_{[\text{O}_2]}$. The Seebeck coefficient indicates n-type conduction.

MO

At 1000°C , small additions of MgO , CaO , SrO , and BaO cause an initial sharp increase in conductivity. Larger additions of these oxides result in a slow decrease in conductivity.^(25,26) BeO exhibits a steady increase in conductivity to 60% BeO .⁽²⁵⁾

Steel and Alcock⁽³³⁾ reported that $\text{ThO}_2\text{-CaO}$ does not become a totally ionic conductor except at oxygen pressures lower than that for $\text{ThO}_2\text{-Y}_2\text{O}_3$. The $\text{ThO}_2\text{-CaO}$ also has a relatively higher electronic conductivity.

Additions of CeO_2 to ThO_2 decrease the conductivity with no change in the activation energy.⁽²¹⁾ This decrease (a factor of 2.2) is attributed to increased lattice scattering.

Thus, additives have a marked influence on the electrical properties of ThO_2 and any impurities in the ThO_2 could also significantly change the electrical properties. Perhaps the unknown differences in impurities (Figures 1 and 2 and Tables I and II) are a significant cause of the scatter in the data. Unfortunately, only a few of the investigators reported the impurities present in the samples.

Polarization and non-Ohmic Behavior

Complicating both the measurement of the electrical conductivity and the interpretation of the data are the polarization* and potential non-ohmic effects resulting during the electrical conductivity measurements. Danforth et al.^(11,12,14,17,18,42) have extensively studied these effects. Working primarily but not exclusively with single crystals of ThO_2 in vacuum to 1800°C, the conductivity and activation energy were observed to vary with current density during dc measurements. The conductivity increased and the activation energy decreased as the direct current passing through the sample increased.^(11,12) The application of a dc potential to a platinum electrode coated on the ThO_2 caused the voltage to drop abruptly, then decay slowly.⁽¹⁷⁾ The rate of decay depended upon the series resistance and the shunting capacitance of the measuring system. Current decay persisted for hours. Using a four-contact technique, the polarizing charge would concentrate near the electrodes, then slowly distribute itself throughout the crystal specimen. For times less than one minute, Danforth^(14,17,18) found the emf to be

*Polarization as used in this report refers to the phenomena where in the presence of an externally applied voltage to a specimen, a counter emf is produced which persists for a measurable time after the applied voltage is removed. This counter emf is caused by the motion of ions over distances large in respect to lattice dimensions of the solid.

confined to a region near the electrodes. For longer times, the polarization was non-uniformly distributed along the sample length but was symmetrical with respect to the center of the specimen. It was assumed that the electrodes were blocking.

The rate of polarization was dependent upon the current density.^(14,18) At high currents, the probe potential in a four-contact method changed in minutes. At much lower current, there was no divergence.

Danforth and Bodine⁽¹⁴⁾ at three temperatures between 1305 and 1235°C found the polarization in volts to be proportional to t^n where t is the time in seconds and n is a constant which varies between 0.37 and 0.39.

Bauerele⁽³⁸⁾ using one volt and a current of 0.01 to 100 μ A found no evidence of non-ohmic behavior using a four-contact method.

Thus, polarization effects can occur and must be considered during conductivity measurements, particularly in regard to the choice of technique, electrodes, and evaluation of the results.

Under conditions in which a significant portion of the current is ionic, measurements of the properties of insulators require careful attention to details. It cannot be assumed that ionic conductors obey Ohm's law in the strictest linear sense. Blocking contacts require that charges collect at interfaces, introducing a depolarizing field within the sample. In a two- or three-contact measurement, such effects cause a current decay with time after application of voltage to a sample which has been in electrical equilibrium. The sample acts similar to a capacitor in parallel with a resistor and sample current measurements are influenced by the magnitude, polarity and time of electrification.

When employing the four-probe technique the measured potential drop (dV) at the voltage probes will vary with time as the polarizing charge distributes itself throughout the specimen, with a non-linear potential

distribution accompanying this interfaced polarization. Consequently, this measured voltage can be represented by $[I_0 R_s + V_p]$ where $I_0 R_s$ is the "ohmic potential drop" between the probes, and $-V_p$ is the depolarizing voltage generated by the charge buildup. As a result of this polarization, the probe voltage is dependent upon both the current flow and the total applied voltage history of the measurement. Unless considerable care is taken, only order-of-magnitudes estimates can be made regarding the sample resistance. Resistivities calculated from the ratio of probe voltage to external current are subject to error due to non-linearity in dV with applied voltage and time, and changes in I_0 with time.

From this discussion it is apparent that dc measurements should be made using only small currents to minimize charge buildup at electrodes. Calculated resistivities should be taken from the slope of a voltage-versus-current plot to eliminate extraneous potentials. Current measurements should be made at specific time intervals after application of applied voltage. Voltages should be applied with successively alternating polarity, with the sample "shorted" in between applications to allow the discharge of polarization.

Gamma Radiation

The effects of gamma radiation have also been studied by Bregar et al.,⁽³⁵⁾ Bregar,⁽³⁶⁾ and George et al.⁽⁴²⁾ These data are summarized in Figure 11. Bregar⁽³⁵⁻³⁶⁾ found during in-core measurement in vacuum for polycrystalline ThO_2 that the induced conductivity (σ_i) could be expressed as

$$\sigma_i = 1.47 \times 10^{15} R \cdot e^{-0.081/kT} \cdot t^{3/2}$$

where R is the specific reactor power. It was concluded that the results could fit a theoretical model⁽³⁷⁾ based on a single electron-trapping level with an excitation level of 0.081 eV. In addition, σ_i was observed only at temperatures below 400°C.

These authors failed to recognize, however, the possibility of gamma induced currents in the system which may in no way be related to conduction in the sample. The results reported in this study conclude that the increase in conductance due to radiation is not related to a radiation-induced conduction of the sample but to the ionization by the high intensity radiation of the atmosphere surrounding the sample. Thus data for ThO_2 as well as other oxides which suggest that gamma radiation results in an induced solid conduction should be suspect.

Temperature and Activation Energy

The conductivity in some reported data experiences a change in the slope of the $\log \sigma$ versus T^{-1} curve near 500°C with a decrease in slope at temperatures between 500 and 1400°C . However in some data, including the low temperature data in this study using the three contact method, no inflections are observed (Figure 7). Such changes in slope were observed using the four contact method, both with and without a sample (Figure 3). One might conclude that such inflections may not be real, but result from emission currents and experimental techniques.

Above 1400°C , the slope increases significantly as the conduction appears to become n-type. The reported activation energies are summarized in Table IV. Since the energy changes with oxygen pressure and furnace atmosphere, the energies reported by the various investigators can only be compared if a common $P_{[\text{O}_2]}$ was used, e.g., air or very low oxygen pressures ($<10^{-11}$ atm).

Below 1200°C in air, the average activation energy is $1.43^{+0.15}_{-0.25}$ eV. The value in this study was 1.8 eV. Above 1400°C Podszus⁽¹⁾ reported a value of 2.63 eV in air. In all atmospheres except air above 1400°C , the average activation energy is 3.2 ± 0.4 eV. The value determined in this study was 3.1 eV. Considering the various difficulties associated with high temperature measurements and the variations in sample composition, the values are in surprising agreement.

TABLE IV.

Summary Activation Energies for the Electrical Conductivity
of ThO₂ in Air

Above 1400°C

Podszus	2.63
---------	------

Below 1400°C

Rögener	1.45
---------	------

Foex	1.40
------	------

Hund	1.26
------	------

Rudolph	1.58
	1.18

Paliguev	1.58
----------	------

Subbarao	1.2
----------	-----

This Study	<u>1.77</u>
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Average	1.43 + 0.15 - 0.25
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Above 1400°C in All Atmospheres Except Air

Podszus	2.94
	3.5

Danforth and Morgan	3.2
	2.8

Kuhlman	3.4
	3.1
	3.6

This Study	<u>3.1</u>
Average	3.2 + 0.4 - 0.4

Experimental Procedures

The effects of experimental techniques on the electrical conductivity data are difficult to assess principally because many authors failed to describe completely the details used to make measurements. The techniques used were probably accurate enough for many technical purposes. However, for accuracies necessary to understand the basic conduction mechanism, the techniques were in most instance inadequate. There are a number of problems relating to the measurements of ThO_2 conductivity due to the high resistances at low temperatures and emission and gas conduction at the high temperatures. These problems have been discussed in previous sections of this report and related where possible to the data for ThO_2 .

In many oxides, large thermal gradients can result in relatively large thermoelectric voltages requiring direct current measurements to be made in both directions and the results averaged. Although alternating current can be used, care must be exercised in the choice of frequency, especially in ionic compounds.

At very high temperatures, little consideration has been given previously to complications resulting from thermionic emission. Emission can create currents which greatly exceed the externally applied current especially for ThO_2 which has an unusually high emittance.

Although the presence of extraneous currents from surface conductance is generally recognized and considered in electrical conduction measurements, similar concern must be given to potential leakage through the gas. Loup and Anthony⁽⁴⁸⁾ and Peters et al.⁽⁴⁹⁾ called attention to the problem when measuring MgO and Al_2O_3 . It was observed that unless consideration was given to these effects, the surface conduction in Al_2O_3 was significantly greater by orders of magnitude at low temperatures than the sample conductance. The air-gap conductance was even greater than the surface conduction.

Thermally emitted electrons contribute to the generation of a plasma which surrounds the sample and all electrodes in the measurement volume as shown in Figure 1. Any voltage gradient maintained within this region will result in net currents in the gas phase. The measurement system as a whole will assume an equilibrium potential relative to the shield so that no net exchange of current exists. During experiments on any high resistance material, the actual sample current may be transient, decreasing towards zero as a potential equilibrium is reached due to communication of electrodes via the highly conducting gas phase. As a result, the atmosphere surrounding the sample offers parallel paths of lower resistance to current flow. If this "gas phase resistance" between electrodes becomes very small compared to the bulk sample resistance, the significant portion of the measurable external current will not flow through the sample.

The problem of determining I_0 at high temperatures has been discussed by other authors,⁽⁵⁰⁻⁶⁴⁾ but thus far only hypotheses that gas and surface currents may shunt sample currents have been given.

Measurements during this study showed that the magnitude of possible emission currents between the heated system and measurement probes can be of the same order as assumed sample currents.⁽⁴⁷⁾

Current versus voltage plots showed current saturation common to thermionic emission. Work functions derived from the slopes of I/T^2 versus $1/T$ curves were consistent with the materials present.

Just as important as these atmospheric currents is the effect that this gas phase space charge, or partially conducting plasma, has on the measurements of potentials within the system. If the sample is surrounded by a sufficiently conducting atmosphere, the electrodes employed for the crucial measurement of potential difference between the probes will exhibit electrical communication with other heated metallic surfaces in the system. These results indicated that atmospheric currents between the current probes can exceed any sample current and prevent any effective measurement of the sample conductivity.

GENERAL CONCLUSIONS

The following general conclusions can be made from this study and review:

- At temperatures below 1200°C, the electrical conductivity increases with an increase in atmospheric oxygen pressure. At temperatures above 1400°C, the electrical conductivity decreases with an increase in the oxygen pressure.
- When the variation in atmosphere is minimized, the scatter in the reported electrical conductivity data is substantially reduced. The changes in conductivity reported during heating and cooling are probably related to changes in the oxygen activity and to the stoichiometry of the sample.
- Conduction in ThO_2 is characterized by changes in the activation energy near 1200-1400°C and is related to an electronic p- and n-type transition. Activation energies vary widely in air below 1200°C, 1.4 to 1.8 eV. Above 1400°C in air, the activation energy is 2.6 eV which increases to approximately 3.2 eV in an inert or reducing atmosphere.
- The electrical conductivity of ThO_2 below 1400°C is readily influenced by impurities and oxide additions with the ionic conduction being influenced most strongly. M_2O_3 additions (with exception of Ta_2O_3) increase both the ionic and electronic conductivity. This results from an increase in the number of oxygen ion vacancies. The activation energy also decreases. MO additions result in an initial increase in conductivity followed by a slow decrease as the oxide concentration increases. MO_2 additions tend to decrease the electrical conductivity of ThO_2 .

- The reported increases in conductivity resulting during high intensity gamma radiation are probably related to conduction through the ionized gas surrounding the sample, instead of an induced conduction through the dielectric ThO_2 .

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