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AC CONDUCTIVITY AND EMF STUDIES.

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DEFECT MECHANISMS IN LEAD ZIRCONATE TITANATE - AC CONDUCTIVITY AND EMF STUDIES

DISSERTATION

Presented in Partial fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

John Garfield Burt, A.B., M.S.

* * * * * * *

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1970

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LIST OF SYMBOLS

atm - pressure in atmospheres
c_{i} - concentration of species, i
D_{i} - diffusion constant for species, i
E - electromotive force
E_{i} - activation energy for process, i
e - elementary unit of charge
e' - electron
F - Faraday's constant
G - Gibb's Free Energy
H - enthalpy
h' - hole
i_{i} - current density for species, i
K_{i} - equilibrium constant for reaction, i
k - Boltzmann's constant
ln - log (to base e)
log - log (to base 10)
M - metal atom or ion
m/o - mole percent
N, n, n_{i} - number, concentration, see text
P_{O2} - oxygen pressure in atmospheres
P_{\Phi}, P_{\Theta} - see text
R - universal gas constant
S - entropy
T - temperature

\( t_i \) - transference number

\( u_i \) - mobility of species \( i \)

w/o - weight percent

X - non-mental atom or ion

\( z_i \) - valence state of species \( i \)

\( \mu_i \) - chemical potential of species \( i \)

\( \sigma_i \) - conductivity

\( \phi \) - electrostatic potential
I. INTRODUCTION

Many experimental and theoretical studies have been conducted on ferroelectrics to resolve material parameters associated with domain growth, domain switching, aging, and dielectric properties. Particular interest has been generated by the Perovskite family of ceramic ferroelectrics which contains the barium-, strontium-, calcium-, and lead titanates. PZT, a solid solution composed of lead zirconate and lead titanate, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, is widely known for its excellent piezoelectric qualities and has found extensive use as a pressure transducer.

The ferroelectric and piezoelectric properties associated with polycrystalline lead zirconate titanates very possibly depend upon the material defect structure and bulk diffusion characteristics. Control of domain switching and aging properties will be greatly facilitated by a more thorough understanding of charge transport mechanisms which are present in these ceramics.

The object of this investigation is the measurement of total ac conductivity and the determination of ionic transference numbers for several compositions of PZT ceramics. This information should form a firm basis for rationalizing the defect structure and charge transport mechanisms and,
hence, permit greater control over the ferroelectric properties of these ceramics. A gaseous electrochemical concentration cell experiment and an ac conductivity experiment are used to obtain the desired results.
II. LITERATURE SURVEY

A number of theories successfully explain some of the phenomena such as polarization, hysteresis, pyroelectricity and ferroelectricity observed in perovskite ceramics. A majority of the available literature pertinent to these topics is concerned with the nucleation, growth, and aging of ferroelectric domains. Much of this work has focused on effects which result from fabrication processes and the addition of dopant materials. However, little information on the conduction mechanisms present in these materials, either as a function of temperature or the oxygen activity in the surroundings, is available. In addition, virtually no attempt has been made to relate pyroelectric or ferroelectric properties to charge motion through the bulk or to other observed characteristics dependent upon the motion of charged defects. With the large amount of information available on charge transport mechanisms in binary oxides and the development of high impedance electronic instrumentation, studies leading to a more complete understanding of these materials can now be conducted.
This investigation is concerned with the solid solution of lead zirconate-lead titanate ceramics and deals primarily with the charge conduction mechanisms at temperatures above 500°C. The complete determination of electronic and ionic conductivities requires information obtained from two related experiments. Hence, the literature survey will be divided into three sections: the discussion of ac conductivity experiments on materials similar to lead zirconate titanate (PZT), a section dealing with electromotive force experiments on oxide materials which may be pertinent to an understanding of PZT, and a review of the literature concerned with conductivity and doping in PZT.

**AC Conductivity Experiments**

In the study of a mixed conductor having both electronic and ionic charge conductivity, it is appropriate first to consider the charge transport that results from the movement of all the species. The most basic procedure used in the determination of total conductivity present in a mixed conductor is the measurement of total ac conductivity as a function of temperature and oxygen activity in the surroundings, where the total electrical conductivity is defined by the expression,

\[ \sigma_{\text{tot}} = \sigma_{\text{ion}} + \sigma_e. \]

The quantities \( \sigma_{\text{ion}} \) and \( \sigma_e \) represent respectively the ionic and electronic components of the total conductivity,
where the contribution from a single species, \( i \), is given by,
\[
\sigma_i = c_i z_i e u_i.
\]

\( c_i \) represents the concentration of the \( i \)th species, \( z_i e \) denotes the charge associated with the particular species, and \( u_i \) is the mobility of the charge carrier. The charge of any particular carrier is assumed independent of temperature and the mobility is assumed to remain essentially constant for dilute defect concentrations at a single temperature. Hence, the conductivity is directly related to the number of mobile charge carriers (ionic and electronic) per unit volume. Therefore, measurement of total ac conductivity as a function of temperature and oxygen activity gives an immediate indication of the relative number of charge carrying defects and the logarithmic plots of conductivity vs oxygen activity can be used to infer the identity of the predominant type of defect.

Zirconia

Vest, Tallan, and Tripp\(^h\) have investigated undoped zirconia in the oxygen activity range from 1 atm to \( 10^{-20} \) atm using CO - CO\(_2\) mixtures and variable leak techniques. These workers have determined that pure zirconia is a p-type semiconductor above activities of \( 10^{-8} \) atm and exhibits n-type conduction below approximately \( 10^{-20} \) atm.
In the intermediate range of activities this material is a mixed conductor with maximum ionic conductivity at $10^{-16}$ atm.

Volchenkova and Pal'guev\(^5\) have conducted ac conductivity measurements on calcia-stabilized zirconia ($\text{ZrO}_2 + \text{CaO}$) over a wide range of CaO additions (10 to 40 m/o CaO) in the temperature range of 300°C to 1000°C using an alternating current bridge, their effort being directed toward extending previous studies on this material. These workers have demonstrated that the addition of CaO on a parts per hundred basis greatly increases the conductivity over the entire range of experimental temperatures, the doped materials (above 10 m/o CaO) tending to exhibit complete ionic behavior. These authors did not specify and apparently made no effort to control the oxygen activity to determine the relationship between conductivity and oxygen concentration.

Patterson, Bogren, and Rapp\(^6\) have measured ac conductivity in calcia-stabilized zirconia and yttria doped thoria in the temperature range 800°C to 1000°C with the additional constraint of a well defined oxygen activity in equilibrium with the sample. This work is more complete than measurements\(^5\) conducted in a constant (and perhaps unknown) oxygen activity, since the gas in the environment will equilibrate with, and effectively fix, the oxygen activity in the solid. Addition of
15 m/o CaO was found to enhance the conductivity over the complete range of measurement (1 atm to $10^{-25}$ atm), the total conductivity being essentially independent of oxygen activity and, therefore, the Zr$_{0.85}$Ca$_{0.15}$O$_{1.85}$ is an ionic electrolyte. The oxygen activity was controlled over this broad range by a careful selection of metal oxide powders which were placed in equilibrium with the zirconia samples. The dissociation pressure in the gas phase at a particular temperature was calculated from well known free energies of formation available in the literature. Patterson et al. have concluded that the substitution of a calcium atom on a zirconium site leads to the creation of oxygen vacancies governed by the relation,

$$[\text{Ca}^{II}_{\text{Zr}}] = [V^\cdot_0] \quad .$$

The introduction of mobile anion vacancies in concentrations of the same order of magnitude as that of the dopant material is sufficient to dominate the electroneutrality condition in the oxide. In this case the vacancy density outnumbers native electronic disorder by many orders of magnitude. The result is a doped electrolyte exhibiting ionic behavior over a wide range of oxygen activity, large deviations from "stoichiometry" being required to produce electronic defects in sufficient quantities to affect the total conductivity.
Studies have been conducted on thoria doped with yttria to explain the compensation produced by substitutional atoms having a different valence than that of the parent atom, with results being similar to those obtained for zirconia. The electroneutrality condition between negative and positive defects in the thoria crystal may be expressed as,

\[
\left[ Y'' \right] = 2 \left[ V^o \right],
\]

where the substitution of two yttria ions on thoria sites results in the production of a mobile oxygen vacancy. Because of unintentionally present impurities, the undoped material may exhibit predominant ionic conduction over a narrow range of oxygen activity centered about \(10^{-10}\) atm, while the material doped with 5 to 15 w/o yttria acts as a totally ionic material (ionic transference number greater than 0.99) over a broad range of oxygen activity (\(10^{-6}\) atm to \(10^{-30}\) atm). Wagner proposed in 1943 the substitutional mechanism mentioned above as an explanation for the compensation in charge upon the addition of foreign atoms having a valence state other than that of the parent atom in the lattice. Theoretical predictions for simple binary oxides at either high or low oxygen activities (far from stoichiometric compositions) indicate that the dependency of total conductivity on oxygen activity should vary according to \(P_{O_2}^{-1/n}\), where \(n\) is an integer like 4 or 6.
depending upon the charge associated with the mobile ionic defects. Kofstad\textsuperscript{14} notes that many experimental results indicate a value of $n$ which is not exactly 4 or 6 and explains this deviation in terms of foreign impurities which are inadvertently incorporated into most refractory oxides. He considers the modification of electrical conductivity in Nb$_2$O$_5$ when small traces of foreign metals having valences less than +5 are included in the oxide.

In summary, the defect state of pure and doped zirconia has generated considerable interest. In the undoped state, ZrO$_2$ has been found to exhibit p-, n-, and ionic conduction. The stoichiometric condition appears to be centered about $10^{-14}$ atm to $10^{-16}$ atm. P-type conduction begins to predominate at higher oxygen activities, while n-type conduction exists at activities below $10^{-18}$ atm. The addition of CaO and other dopants has been found to produce a material that exhibits ionic conductivity over a broad range of oxygen activities. In addition to calcia-doped zirconia, yttria-doped thoria is very useful as an electrolyte in the determination of free energies for other oxides.

Titania

Studies\textsuperscript{15} conducted on single and polycrystalline rutile (TiO$_2$) indicate that charge conduction is electronic in the range between 860°C and 1050°C at oxygen activities
below 1 atm. Below 800°C, the electrical conductivity becomes independent of oxygen activity. There is no agreement as to the predominant defect in oxygen-deficient rutile, and experimental results have been interpreted in terms of both oxygen vacancies and metal interstitials. Kofstad\textsuperscript{16} has conducted work on sub-stoichiometric (oxygen deficient) rutile at oxygen activities between $10^{-8}$ atm and $10^{-14}$ atm to determine the conductivity as a function of oxygen activity in the n-type electronic region. Results of this study indicate that the conductivity varies as $P_{O_2}^{-1/n}$, where $n$ decreases from 5.5 to 6.0 at 1000°C to about 4.5 at 1300°C. Kofstad explains this variation in terms of interstitial tri- and tetravalent titanium ions. This model is in agreement with other studies\textsuperscript{15, 17} which have determined that TiO\textsubscript{2} exhibits n-type conductivity at oxygen activities as great as 1 atm. The simultaneous presence of both Ti\textsuperscript{3+} and Ti\textsuperscript{4+} appears to be the most consistent explanation for a non-integer value for $n$ in the n-type conductivity range of rutile.

The identity of the predominant mobile ionic species in rutile is somewhat uncertain, although it has been proposed that oxygen diffusion dominates at low temperatures while titanium interstitials become increasingly important at more elevated temperatures.\textsuperscript{16}

Dopant materials\textsuperscript{16} for rutile are usually chosen with a valence less than +4 (for example Al, Fe) such
that additional oxygen vacancies are created in the material.

In conclusion, rutile is an n-type conductor at oxygen activities ranging between $10^{-16}$ atm and 1 atm. The exact identity of mobile charged species is not certain at this time, and several theories are presently under consideration.\textsuperscript{15, 17}

Lead Oxide

Because of the limited stability of the lead oxides in comparison to zirconium and titanium oxides, some confusion exists in the literature concerning the structure of the oxides of lead.\textsuperscript{19} In addition to PbO, and PbO\textsubscript{2}, there are several complex oxides of stoichiometry near the intermediate Pb\textsubscript{3}O\textsubscript{4} compound.\textsuperscript{20} Intermediates Pb\textsubscript{12}O\textsubscript{19} and Pb\textsubscript{12}O\textsubscript{17} have been obtained by White and Roy\textsuperscript{21} in a study of the phase relations in the system lead-oxide.

Pamfilov, Ivancheva, and Drogomiretskii\textsuperscript{22} have investigated the electrical properties of lead oxides in the temperature range 200\degree C to 350\degree C using thermoelectric probes. Results indicate that above oxygen pressures of 100 torr ($10^{-1}$ atm), PbO, Pb\textsubscript{2}O\textsubscript{4}, and PbO\textsubscript{2} are predominantly p-type semiconductors.

Thompson and Strong\textsuperscript{23} concluded in a study of oxygen self diffusion in lead oxide that lead vacancies are a predominant defect at temperatures between 500\degree C and 600\degree C. However, the oxygen activity in the surrounding media was not reported.
As in the case of rutile, some disagreement exists as to the exact mechanisms for charged particle motion in lead oxide. Much of the difficulty stems from the instability of lead oxide and the existence of intermediate oxides which occur simultaneously.

Electromotive Force and Polarization Experiments

The measurement of total charge conduction as a function of temperature and oxygen activity can be used to infer the predominant defects in simple oxide systems. However, additional experiments must be used to separate the partial conductivities of the electronic and ionic species which contribute to the total charge transport through the crystal.²⁴, ²⁵

The partial conductivity of either the ionic species or the electronic species (electrons and/or holes) can be measured by means of polarization techniques which isolate one species by electrically blocking the contribution from the other. In the latter experiment the electrodes on both sides of the sample are chosen to be either completely ionic or electronic in transport characteristics, thereby effectively blocking any net charge transport by the species other than that to be measured.

In addition to polarization experiments, electromotive force studies²⁶, ²⁷ using gas phase electrodes and/or metal/oxide electrodes represent another method of resolving whether the dominant conduction mode present in a solid is
ionic or electronic (although the exact identity of the charged species cannot be resolved). In the EMF experiment a chemical concentration gradient is developed across the sample using gas phase electrodes and/or metal oxide electrodes, which have well defined oxygen activities.

The comparison of measured voltage developed by the galvanic cell with thermodynamic calculations leads to the ionic transference number \( t_{\text{ion}} = \sigma_{\text{ion}} / \sigma_{\text{tot}} \).

Schmalzried has discussed in detail the theoretical considerations pertinent to the analysis of partial conductivities using emf cell techniques. Particular emphasis has been given by this author to simple binary oxides of the form \( A_{0_{1-x}} \) (or \( A_{1+x} \)) and the more complex ternary compounds having the form \( A_{1-x} B_y O_{1-z} \). Starting from first principles, general statements regarding the emf of a galvanic cell as a function of ionic and electronic partial conductivities are developed, and certain limiting cases are considered. A brief summary which deals with a number of high temperature electrolytes is included in addition to the discussion of an apparatus for conducting EMF investigations.

Mitoff has investigated the mixed conductor MgO using gas phase electrodes having oxygen activities established via the equilibrium reactions between CO-CO\(_2\), H\(_2\)O-H\(_2\), and oxygen-argon mixtures. Results indicate that electronic conduction is favored at high temperature
(temperature above $1300^\circ$C) and extremes of high and low oxygen activity. Ionic conduction predominates at lower temperatures and intermediate oxygen concentrations in the range $10^{-2}$ atm to $10^{-4}$ atm (temperature below $1200^\circ$C). The author also notes that the effect of temperature upon the defect structure dominates that which results from the variation in oxygen activity over the range of study.

Kiukkola and Wagner$^{29}$ have conducted studies using galvanic cells to determine the free energy of formation for several binary oxides at elevated temperatures. The cell was comprised of stabilized zirconia or thoria electrolytes situated between electrodes composed of the metal oxide compacts under investigation. One electrode was iron-iron oxide having a well defined oxygen activity, while the other electrode consisted of either Co-CoO, Ni-NiO, or Cu-Cu$_2$O which was under investigation. The doped-zirconia and thoria electrolytes are essentially ionic conductors over an extremely wide range of oxygen activity ($10^0$ atm to $10^{-25}$ atm), and these workers used the emf developed across the cell to determine the dissociation pressure of oxygen (therefore the free energy of formation) in the Co-O, Ni-O, and Cu$_2$O using the iron oxide as a standard electrode. Results obtained in this study indicate that in the temperature range $750^\circ$C to $1150^\circ$C an emf cell utilizing an ionic electrolyte can be used to experimentally measure with great accuracy free
energies of formation. Data obtained in this study proved to be in good agreement with previous measurements.

A similar investigation has been conducted by Alcock and Steele\textsuperscript{30} using calcia and yttria doped zirconia as well as calcia and yttria doped thoria electrolytes. This effort was primarily directed toward obtaining comparative data using the four electrolytes to define the optimum material and dopant to be used in free energy studies. Results of this work demonstrate that at very low oxygen activities associated with materials having an energy of formation in the range \(-150\) \text{ kcal/mole} at \(1000^\circ\text{C}\), doped thoria is the superior electrolyte. Emf data obtained using calcia zirconia indicate that at very low oxygen activity the electron contribution to the total conduction is sufficient to reduce the measured voltage to a value less than that calculated using the standard electrodes present in the experiment. Additional work by these authors indicates that the properties of electrolytes can be altered by maintaining them at high temperatures and low oxygen activities for extended periods of time. Color changes and increased electronic conductivity take place after 100 hours at \(1000^\circ\text{C}\) and \(1400^\circ\text{C}\) with \(10^{-16}\) atm oxygen pressure.

Tretyakov and Rapp\textsuperscript{31} have investigated the ternary compound \(\text{LiFe}_5\text{O}_8\) using an ionic electrolyte as an oxygen pump and meter to control the oxygen activity in a closed
crucible system containing the lithium ferrite. The data indicate that the calcia-stabilized zirconia electrolyte can be driven with an externally applied voltage source in the millivolt range to control oxygen concentration over a wide range, the activity being determined by the applied voltage and consideration of gas leaks present in the system. These workers have determined that the predominant defect in lithium ferrite are interstitial lithium (or iron) ions, and substitutional iron (or lithium) ions.

Stephenson and Flanagan\textsuperscript{32} have investigated ceramic Pb(Zr\textsubscript{0.53}Ti\textsubscript{0.47})O\textsubscript{3} + 1 w/o Nb\textsubscript{2}O\textsubscript{5} using as electrodes the metal oxide compacts of Pb and Cu. At 250°C, the emf developed by this cell was found to be 0.205 volts, which is close to the thermodynamically calculated value, indicating predominant ionic conduction in the PZT electrolyte. In an additional study these authors used the same PZT composition as the electrolyte in an oxygen-hydrogen fuel cell. Results, although not consistent, indicate a significant ionic transference number which may result from oxygen vacancies in the ceramic.

Heckman et al.,\textsuperscript{33} have utilized ceramic PZT compositions (having 1 w/o Nb\textsubscript{2}O\textsubscript{5}) with zirconium molar content ranges from 1.0 to 0.52 in an electrochemical concentration cell driven by argon-oxygen gas mixtures. Results of this work indicate that between 250°C and 500°C significant
ionic conduction is present in compositions having more than .90 (molar content) zirconium. Using the reversible gas phase electrodes, these authors obtained consistent values for the emf developed by the cell.

**Lead Zirconate Titanates and Other Perovskite Materials**

Documented studies on lead zirconate titanates, barium titanates, and other perovskite ferroelectrics are not as extensive as those dealing with the more elementary oxides which have been discussed in the previous sections. The conductivity in PZT has been of secondary nature in most investigations, the principal effort being directed toward improving the aging and dielectric properties by donor additions and sintering procedures.

Gerson and Jaffe\(^3\) have investigated the electrical properties of PZT between \(300^\circ\)C and \(600^\circ\)C in an attempt to determine the predominant charged defect. Using a dc megohmmeter, pure and doped materials were studied to determine the role played by aliovalent additions. Unfortunately, few details concerning the sample preparation for this work are given, and dc rather than ac conductivity was measured. The applied field of 100 volt/mm would appear to introduce considerable polarization across the samples. Seebeck coefficients obtained for the pure PZT materials indicate that \(p\)-type conduction is predominant. These authors propose that hole conduction results from an over-oxidized condition in the crystal brought about during sintering stages of fabrication.
Gerson and Jaffe also conducted measurements on PZT compositions doped with Group III and Group V oxides. Additions of 1 w/o Nb$_2$O$_5$ (Nb$^{5+}$) were found to increase the resistivity by several orders of magnitude, while the introduction of scandium (Sc$^{3+}$) resulted in a significant reduction in dc resistivity (although less than one order of magnitude). Based on ionic radius, the site of substitutional niobium was surmised to be at the titanium position. Similar substitution is expected for scandium. Since the normal valence state for niobium is +5, it is proposed that the substitutional niobium acts as an electronic donor to the crystal, resulting in the creation of lead vacancies. The lead vacancies, acting to maintain electroneutrality, induce a large reduction in hole density, thereby reducing the conductivity. The addition of scandium (which has a normal valence state of +3) results in an elevation in conductivity associated with an increased electronic hole density. The effects of donor compensation on the conductivity gives additional evidence that pure PZT is a p-type ceramic. If PZT were predominantly n-type, the changes in resistivity resulting from donor additions would be reversed.

A study conducted by Thoman has concluded that the addition of Group III donor atoms to PZT will lead to the creation of vacancies at lead sites in the crystal, with a corresponding reduction in p-type conductivity. This
result is not in agreement with the work by Gerson and Jaffe, \(^3\) but can be explained by considering the position at which the dopant atom locates. The addition of Group V elements on Zr or Ti sites can be compensated by the removal of lead from its lattice position. Similarly, lead vacancies will be produced by the addition of a Group III element, if substitution occurs at the lead lattice sites. The lattice position where the dopant atoms locate will determine the new electroneutrality condition, and hence, the compensation which results from this substitution. The addition of Group I materials was found by Thoman to produce the expected increase in conductivity which results from a decrease in lead vacancies and an increase in holes.

Glower and Heckman\(^{36}\) have studied barium titanate (perovskite) using gas phase electrodes in the temperature range 100°C to 500°C to ascertain the principal defect moving through the crystal. Through the use of two gas phase electrodes, \((P_{O_2} \text{ from } 10^{-1} \text{ atm to } 10^{-2} \text{ atm})\), the authors were able to determine built-in bias conditions simply by reversal of the gases to the surface of the sample. Results of this work indicate that single crystal barium titanate is essentially an electronic conductor over the experimental range (100°C to 500°C), while polycrystalline ceramic samples exhibit appreciable ionic transference numbers below 500°C. Neutron activation analysis (using BaTiO\(_3 +\) Fe\(_2\)O\(_3\)) has demonstrated that
the titanium ions are not mobile in this range. Ionic conductivity was concluded to be the result of oxygen migration or transport of barium ions through the material.

Additional studies on PZT have been conducted by Kulcsar in an attempt to improve the electromechanical properties of the ceramic by dopant additions. Starting with a basic PZT composition of Pb(Zr\textsubscript{0.54}Ti\textsubscript{0.46})\textsubscript{3}O\textsubscript{3}, a large variety of Group III and Group V doped materials were produced using hot-press techniques. Ac conductivity measurements conducted with a ratio-arm-transformer bridge circuit in the temperature range between 100°C and 500°C indicated that Group V additions produce the same increase in resistivity as reported by Gerson and Jaffe. The oxygen activity during resistivity measurements was not specified.

Northrup has reported the results of a study of PbO loss from PZT and finds that the oxide weight loss proceeds in two steps. Using a Pb(Zr\textsubscript{0.65}Ti\textsubscript{0.35})\textsubscript{3}O\textsubscript{3} composition produced from several cold pressing techniques, the author has measured the weight loss as a function of time in the temperature range between 690°C and 1130°C in an evacuated (10\textsuperscript{−4} torr) chamber. The first rapid weight loss was proposed to result from the vaporization of unreacted lead oxide which remains after fabrication. The second stage proceeds at a much slower rate and is
assumed to be controlled by the diffusion of lead and oxygen (at roughly the same rate) through a thickening lead depleted surface layer. Northrup has extended the vaporization measurements on Pb(Zr_{0.65}Ti_{0.35})O_2 to hot-press samples. Results of this study on sample densities greater than 99% theoretical indicate that the hot-press ceramics exhibit a low weight loss during the preliminary step (due to unreacted lead oxide). The latter diffusion controlled stage was noted for all cases, indicating the diffusion of lead and oxygen ions to the surface. The vapor pressure above the PZT samples was determined by mass spectrometry to be the same as that produced by pure lead oxide. It was concluded that the charged lead and oxygen ions move from the bulk to the surface where they recombine and vaporize.

Walters and Grace have extensively investigated the formation of point defects in single crystal strontium titanate at temperatures between 900°C and 1300°C. At oxygen activities corresponding to H_2-H_2O equilibrium, these authors conclude, on the basis of electrical conductivity and thermoelectric probe measurements, that oxygen vacancies are the predominant ionic defect. The conductivity as a function of oxygen pressure is characterized by a negative slope which indicates n-type conduction in the substoichiometric region.
Using the oxides of lead and copper as electrodes, Stephenson and Flanagan\textsuperscript{32} have measured the EMF developed by Pb(Zr\textsubscript{0.53}Ti\textsubscript{0.47})\textsubscript{0.3} + 1 w/o Nb\textsubscript{2}O\textsubscript{5} compositions. At 250\textdegree C results indicate essentially ionic conductivity is taking place in the ceramic. This is in contrast to the results of the gas phase emf study conducted by Heckman \textit{et al.}\textsuperscript{33}. These workers\textsuperscript{33} report significant ionic conduction only in PZT compositions having greater than 90 m/o zirconium. This study was conducted at oxygen activities obtained by the mixing of argon and oxygen and is considerably higher than the activity produced by copper and lead oxides. It is reasonable to conclude that the work by Heckman \textit{et al.}\textsuperscript{33} was at an activity where the PZT was overoxidized, while the measurements by Stephenson and Flanagan\textsuperscript{32} were in a region where the compositions were approximately stoichiometric.

A recent work by Ezis\textsuperscript{41} was conducted on a variety of PZT compositions with zirconia content ranging from 95 m/o to 65 m/o and 1 w/o Nb\textsubscript{2}O\textsubscript{5}. This investigation was conducted using a double ended gas phase EMF cell with oxygen activities fixed at 10\textsuperscript{-2} atm and 5 x 10\textsuperscript{-2} atm. In the temperature range between 500\textdegree C and 700\textdegree C significant ionic conductivity in compositions having greater than 90 m/o zirconia were reported, with maximum ionic transference numbers at approximately 550\textdegree C. At temperatures greater than 650\textdegree C, and in compositions having less than
90 m/o zirconia, the ionic conductivity was greatly reduced. The ionic transference number became essentially zero below 60 m/o zirconia content, in agreement with Heckman et al.\textsuperscript{33} It was proposed that titanium ions change ionization state from $+4$ to $+3$, thereby producing reduced ionic transference in the higher titanium content compositions.

The data reviewed here represent a foundation for future efforts to resolve the details of charge transport mechanisms in perovskite ceramics such as barium, strontium, and lead zirconate titanates. Although not as complete as classic studies on binary oxides, most reported works on perovskite ceramics indicate that defect mechanisms are governed by fundamental relations proposed by Wagner\textsuperscript{26} and Krüger.\textsuperscript{12}
III. THEORY

Both theoretical and experimental evidence have established that diffusion in solids results from the motion of defects or imperfections which are always present in materials at temperatures above absolute zero. A knowledge of these defect mechanisms is required for an understanding of bulk diffusion which is responsible for oxidation, conductivity, and other macroscopic phenomena. The design and execution of an experimental investigation into charge conduction mechanisms which result from imperfections must be based on a firm theoretical foundation, a great quantity of work having been reported by previous investigators. This section on theory is divided under three headings: the first topic deals with the occurrence and interrelations between point defects as they exist in bulk materials, a section containing the development of ac conductivity resulting from the motion of charged imperfections, and a final section covering the electromotive force resulting from the gradient of charged defects.

General Considerations of Point Defects in Solids

Although six major kinds of point imperfections are known to exist in bulk materials, only five defects will be
considered in detail: electrons and holes, misplaced atoms, foreign atoms, interstitials, and vacant lattice sites. The concentrations of these defects are not independent, and the relationships between defects will be considered for both stoichiometric and non-stoichiometric materials, since a knowledge of interrelations between defects may lead to the regulation of a particular type of defect. The notation used will be that due to Kroger.\(^{12}\)

At temperatures above absolute zero, point imperfections are created in any ideal crystal with an accompanying increase in energy associated with each imperfection. The free energy of the system attains a minimum value because of a compensation between the increase in configuration entropy of the system and the increase in internal energy. For any temperature an equilibrium concentration of point defects will exist for a material. In principal all previously mentioned point defects can be formed, but the differences in energy of formation required for the various defects will dictate which of the imperfections will predominate in a particular solid at a given temperature. The compositional range of stability for some compounds straddles the stoichiometric composition and these materials are called "stoichiometric," although they are exactly stoichiometric at only one activity of non-metal (or metal). The composition of the compound varies according to the activity of the non-metal (or metal) in equilibrium with the bulk material, with an accompanying
change in the point defects present in the crystal. In a binary compound with the exact stoichiometric composition, three types of defects may occur:

i. Frenkel disorder: equal numbers of interstitial cations and anion vacancies, which are present according to:

\[ MX \rightarrow M(1-\delta) (V_M)^\delta (M_i)^\delta X \cdot \]

ii. Anti-Frenkel disorder: equal numbers of anion interstitials and cation vacancies, according to:

\[ MX \rightarrow MX(1-\delta) (V_x)^\delta (X_i)^\delta . \]

iii. Schottky defects: an equivalent number of cation and anion vacancies, which are given by the relation:

\[ MX \rightarrow M(1-\delta) x(1-\delta) (V_M)^\delta (V_x)^\delta . \]

In almost all instances, only one of the three previously mentioned defects will be present, since the energies of formation are generally sufficiently different to favor only one defect.

Consider now the formation of a Frenkel disorder according to:

\[ M_m \rightarrow M_i'' + V_M'' , \]

where \( M_m \) is a cation on a cation site, \( M_i'' \) is a (positive) divalent interstitial cation, and \( V_M'' \) represents a
(negative) vacant cation site (charge being specified relative to the perfect lattice). The free energy change, $\Delta G$, associated with the formation of $n_f$ Frenkel defects within the crystal is given by the relation:

$$\Delta G = n_f(H_i - T \Delta S_{vib} - T \Delta S_{con}),$$

where $H_i$ is the enthalpy change for removal of the cation from its lattice site, $\Delta S_{vib}$ is vibrational entropy, and $\Delta S_{con}$ is configurational entropy of the system. From statistical thermodynamics for the placement of lattice sites, interstitial sites, and interstitials on the proper locations within the material, the configurational entropy is determined to be:

$$\Delta S_{con} = k \ln \frac{N!}{n_f!(N-n_f)!} + k \ln \frac{N!}{n_f!(N-n_f)!},$$

where $N$ is the total number of atoms in the lattice, $N'$ represents the total possible interstitial positions, and $n_f$ is total interstitial cations. The assumption is made that the creation of the Frenkel defect results in no change in vibrational modes for the displaced atom and the vacancy nearest neighbors.

The equation for free energy now assumes the form:

$$\Delta G = n_f(H_i - T \Delta S_{vib}) - n_f kT \Delta S_{con},$$

where the last term represents a negative contribution to the total free energy of the system. To calculate the
equilibrium number of cation interstitials, $n_{fe}$, it is only necessary to find the stationary value of free energy with respect to the Frenkel defect concentration,

$$\left( \frac{\partial \Delta G}{\partial n_f} \right)_{T,N,N'} = 0 = \Delta H_1 - T \Delta S_{\text{vib}} + kT \ln \frac{n_{fe} n_{fe}}{(N'-n_{fe})(N-n_{fe})}$$

Using the Sterling approximation ($n_{fe}$ much less than $N$, or $N'$), the result for equilibrium Frenkel defect concentration is given by the expression,

$$n_{fe} = N N' \exp \left( \frac{\Delta S_{\text{vib}}}{2K} \right) \exp \left( -\frac{\Delta H_1}{2KT} \right)$$

Therefore, the contribution of configurational entropy to the free energy of the system demands that defects be present at temperatures above absolute zero, and the defect concentration is given in terms of energy of formation. Similar expressions may be obtained for the other point imperfections which occur in a stoichiometric crystal by the substitution of appropriate enthalpy changes required for defect formation, and proper selection of atom site, and interstitial site densities for the material.

The intrinsic electronic disorder present in a crystal as a function of temperature may be treated in an analogous fashion, where the result is found to be,

$$[e'] [h'] = K_i = C_i \exp \left( -\frac{E_i}{KT} \right)$$
C_i represents the entropy associated with formation of a conduction electron and a hole, and E_i is an energy of activation which is frequently denoted as the band gap energy.

In a crystal having both atomic and electronic disorder, a complete description of the defect concentration will depend upon a knowledge of mass action equations relating the various types of defects as a function of the metal (or non-metal) activity in the bulk material, in addition to equilibrium imperfection concentrations. In this more general case, the electronic disorder in the crystal is associated with the creation of an atomic imperfection, in that electrons connected with the atomic defect may lie in an intermediate energy level somewhere between the valence and conduction bands. Frequently this intermediate trapping level may be slightly below the conduction band, resulting in a high probability for excitation into the conduction band. Atomic imperfections which introduce additional levels for electronic occupation in the forbidden band fall into two categories:

i. donor imperfections; where the electrons associated with the defect lie in energy levels immediately adjacent to the conduction band, and readily contribute to n-type electronic conduction.

ii. acceptor imperfections; valence electrons associated with the atomic defects at energy
levels somewhat above the valence band,
leading to p-type electronic conduction.
Figure 1 depicts the energy levels associated with donor and acceptor defects which are described in the following equations and discussion.

An atom previously removed from its lattice site becomes a donor according to the reaction,

\[ M_i^X \rightarrow M_i^* + e^- E_1 \]

where \( E_1 \) is the energy required for transfer of the electron from \( M_i^X \) to the conduction band. The expression for the secondary ionization for the same interstitial atomic defect will then be given by,

\[ M_i^* \rightarrow M_i^{**} + e^- E_2 \]

where \( E_2 \) is the energy which must be supplied for the second ionization. The analogous expressions for the primary and secondary ionization of a non-metal acceptor interstitial atom will be given by,

\[ X_i^{**} \rightarrow X_i^{*} + h^* - E_1 \]

and

\[ X_i^{*} \rightarrow X_i^{**} + h^* - E_2 \]

where \( h^* \) represents an electronic hole in the valence band. Vacancies in the metal lattice act as hole donors to the valence band, while vacancies in the non-metal lattice tend
FIGURE 1. Energy levels for metal and non-metal interstitials. (Above) Metal interstitials which act as donors to the conduction band, where the ionization energy is considerably less than the intrinsic band gap. (Below) Non-metal interstitials which act as acceptors from the valence band, with appropriate ionization energies.
to accept holes from the crystal. The equations describing these reactions are similar to the results obtained for the ionization of interstitials.

Consider now the complete equilibrium situation for a stoichiometric crystal having Frenkel defects as the dominant imperfection, where the reactions are noted below on the left and the appropriate equilibrium constants are listed in the right column. Assuming a completely stoichiometric crystal, the intrinsic defects for atomic and electronic imperfections can be listed according to the following two relations:

$$M_m^x \leftrightarrow M_1^x + V_m^x$$

$$\text{Null} \leftrightarrow e^\prime + h^\prime$$

\[ \begin{bmatrix} V_m \end{bmatrix} \begin{bmatrix} M_i \end{bmatrix} = K_f \quad 19 \]

\[ \begin{bmatrix} e' \end{bmatrix} \begin{bmatrix} h' \end{bmatrix} = K_i \quad 20 \]

In both reactions, the defects annihilate to form a "zero" or null "species" which corresponds to: 1) an atom located at its proper lattice site, and 2) an electron removed from the conduction band. The following two equations (21 & 22) demonstrate the ionization reactions for both the metal interstitials and vacancies remaining in the crystal after creation of the atomic imperfections.

$$M_1^x \leftrightarrow M_1^\prime + e'$$

$$V_m^x \leftrightarrow V_m^\prime + h^\prime$$

\[ \begin{bmatrix} e' \end{bmatrix} \begin{bmatrix} M_1^\prime \end{bmatrix} = K_1 \quad 21 \]

\[ \begin{bmatrix} h' \end{bmatrix} \begin{bmatrix} V_m^\prime \end{bmatrix} = K_2 \quad 22 \]
The remaining equations (23 & 24) express the conservation of mass in the assumed stoichiometric crystal, and the electroneutrality condition which must hold in all materials.

\[
\begin{align*}
\left[ V_m^x \right] + \left[ V_m' \right] & = \left[ M_1^x \right] + \left[ M_1' \right] & 23 \\
\left[ e' \right] + \left[ V_m' \right] & = \left[ h' \right] + \left[ M_1' \right] & 24
\end{align*}
\]

There are now six equations in six unknowns describing the ionic and electronic defect concentrations represented by the four reaction equations, plus the stoichiometry and neutrality conditions. Given the values for the equilibrium constants \( K_i, K_e, K_1, \) and \( K_2 \) it is possible to determine the concentrations for the various defects. However, all equilibrium constants are rarely known, and an exact solution is generally not possible.\(^4\)\(^6\)

Equilibrium between the crystal and the gas environment, in which the material is situated is expressed by a suitable reaction equilibrium according to,

\[
\frac{1}{2}(x_2)_g \rightarrow x_x^x + V_m^x; \quad \left[ V_m^x \right] = K_{\text{ox}} P_x^2.
\]

Since the metal (or non-metal) activity is now dependent upon the environment surrounding the crystal, the previously listed intrinsic stoichiometry condition is no longer applicable, and should be replaced by the above equilibrium equation. The stoichiometry of the crystal can now be varied by an adjustment of the independently controlled environment.
In the process of solving the system of six equations, two reasonable procedures may be followed. It is possible to adapt computer methods to the problem of six equations and six unknowns, but the uncertainty associated with the equilibrium constants again pose a great problem. The second method involves the use of experimental data in the formulation of predictions concerning the behavior of the various defects. An iteration procedure is used until the observed results agree with predictions. Brouwer has proposed a method for approximating solutions with reasonable simplicity by considering certain limiting cases in the system. In this approach, one takes the logarithms of the mass action equations and makes a suitable approximation for the electroneutrality condition. The application of Brouwer's method to the equations (19, 20, 21, 22, 24 & 25) describing the Frenkel defects gives the following results:

\[
\begin{align*}
\text{Log } [V_m^X] + \text{Log } [M_1^X] &= \text{Log } K_f &\text{19A} \\
\text{Log } [e'] + \text{Log } [h^*] &= \text{Log } K_i &\text{20A} \\
\text{Log } [e'] + \text{Log } [M_{1'}] - \text{Log } [M_1] &= \text{Log } K_1 &\text{21A} \\
\text{Log } [h^*] + \text{Log } [V_m'] - \text{Log } [V_m^X] &= \text{Log } K_2 &\text{22A} \\
\text{Log } \{ [e'] + [V_m'] \} &= \text{Log } \{ [h^*] + [M_{1'}] \} &\text{24A} \\
\text{Log } [V_m^X] &= \text{Log } K_{ox} P_{X_2}^{\frac{1}{2}} &\text{25A}
\end{align*}
\]
All equations are linear relations between logarithms except for 24A (the electroneutrality condition). The approximation is made that on both sides of Eq. 24A one of the two terms will dominate, and consequently, the electroneutrality condition can be replaced by an equation of the form,

$$\log [A] = \log [B],$$

which is also linear. Since the independent variable is the concentration of non-metal in the gas phase, the limiting cases for the term $K_{ox}P_{x_2}^{\frac{1}{2}}$ will first be considered. At extremely small values of $K_{ox}P_{x_2}^{\frac{1}{2}}$ corresponding to very reducing conditions, the electroneutrality condition will become,

$$[e'] = [M_1'],$$

while for the other extreme, a very oxidizing environment, the electroneutrality condition becomes,

$$[h'] = [V_m'].$$

Placing this first simplified electroneutrality condition into the logarithmic equations (19A, 20A, 21A, 22A 24A & 25A), it is possible to solve for the concentration of defects in terms of $K_{ox}P_{x_2}^{\frac{1}{2}}, K_1, K_1, K_2,$ and $K_f$, the results being as follows:

$$\log [V_m^x] = \log K_{ox}P_{x_2}^{\frac{1}{2}}$$
It can be seen that $h^*$, $V_m^x$, and $V_m^y$ increase with increasing non-metal activity, while $e^'$, $M_{i, x}$, and $M_{i, y}$ decrease. For decreasing non-metal activity, however, the opposite is true, and a point is reached where $e^'$ begins to dominate $V_m^y$, or $M_{i, y}$ will overtake $h^*$. At this activity, a new electroneutrality condition will govern the system, taking the form,

$$ \begin{bmatrix} e' \\ h' \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} $$

In this case, the material will be an intrinsic semiconductor. At the other extreme,

$$ \begin{bmatrix} V_m' \\ M_{i, y} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} $$

which is the necessary but not sufficient electroneutrality condition for an ionic conductor. Substitution of either of these electroneutrality conditions into the mass action equations will lead to a set of relations between the defects in this new range of non-metal activity, and experiment will determine which condition is indeed the case. The
extension of Brouwer's method results in predictions concerning the defect concentration over the entire range of non-metal activity, and the results plotted in log-log form as shown in Figure 2 are known as the Krcemir-Vink plot for the material. This plot has become the standard method for the display of defect concentrations over the entire range of non-metal (or metal) activity.

The theory presented in the preceding pages predicts a variation in defect concentration with the composition of the atmosphere in the surrounding environment. The theory can be verified by comparison with experimental properties such as electronic and ionic conduction, photoconductivity, optical absorbance, and other related macroscopic phenomena.

Foreign atoms which are added to crystals are found to influence the properties of the material, the changes being particularly pronounced when the valence state of the foreign atom differs from that of the parent lattice atom. Since materials must maintain a strict charge balance over all ranges of environment, the substitution of foreign atoms having a different valence state must lead to a shift in point defects concentrations. Although the foreign atom can substitute at either a lattice position or an interstitial position, it will generally replace a parent atom having the closest electronegativity present in the crystal. The analysis of a crystal "doped" with a foreign atom remains essentially the same as for the undoped material, and is based on
FIGURE 2. Kroger-Vink diagrams for a semiconductor and an electrolyte.  (Above) An electrolyte having predominant ionic conduction in the 'stoichiometric' region, defect concentrations obtained using methods described in the text.  (Below) An intrinsic semiconductor which exhibits predominant electronic conduction over the entire range of oxygen activity.
ionization reactions, an equilibration reaction with the gas phase, and an electroneutrality condition. The system equations for a Frenkel defect material having an additional foreign atom which can become singularly ionized are as follows:

\[
\begin{align*}
    [v^x_m] &= K_{ox} P x_2^2 \\
    [e'] [h'] &= K_1 \\
    [M_1^+] [V_m'] &= K_f \\
    [e'] [M_1^+] &= K_I \\
    [h'] [V_m'] &= K_2 \\
    [V_m^x] &= K_3
\end{align*}
\]

Additional equations, resulting from the addition of dopant atoms, state that:

\[
\begin{align*}
    \frac{[e'] [F_m^+]}{[F_m^x]} &= K_3 \\
    [F_m^x] + [F_m^-] &= [F_m] \text{ total} \\
    [e'] + [V_m'] &= [h'] + [M_1^+] + [F_m^-].
\end{align*}
\]

Equation (38) represents the new electroneutrality condition, which must take into account the additional charged foreign
atoms, $F_m$. Applying Brouwer's technique to the system with appropriate approximations to the neutrality conditions and the equation for the total number of foreign atoms, a Kroger-Vink diagram for the compound can be plotted.

The addition of foreign material to a crystal can be used to enhance or suppress electrical characteristics of the starting material and thereby allow a tailoring of material properties to the ultimate use of the material.

### Ac Conductivity in Solids

The transport of mobile charged defects which are present in all bulk materials at elevated temperatures may be considered in terms of two contributing phenomena:

i. migration resulting from the interaction of charged particles with an external electric field, the driving force being electrostatic.

ii. migration (more properly called diffusion) resulting from the presence of concentration gradients within the material, the driving force resulting from the chemical potential gradient.

In the event that the two forces are present simultaneously, the current of charged particles can be broken down into drift and diffusion terms,

$$ i = i_{drift} + i_{diffusion} $$

The drift component from the $i^{th}$ species may be written (in one dimension) explicitly as,

$$ i_{drift} = -c_i z_i e u_i \nabla \phi $$
c_i is the concentration of particles, u_i denotes the mobility in the solid, and z_i e represents the charge associated with the particle. The diffusion component of current for the same species can be written in the form of Fick's law,^1^2

\[ i_{\text{diff}} = - z_i e D_i \nabla c_i, \]

where D_i is the diffusion coefficient for the i^{th} species.

The chemical potential for the species i is defined according to,^5^0

\[ \mu_i = \mu_i^0 + kT \ln c_i. \]

\( \mu_i^0 \) represents the chemical potential when the substance is in its standard state and the activity coefficient is assumed to be unity. Differentiating Equation 42, inserting the result into Equation 41, and combining the result with Equation 40, the total current from the species i will be,

\[ i_i = - c_i z_i e u_i \nabla \phi - c_i z_i e D_i \nabla \mu_i \]

Equation 43 represents the total contribution from the species i when the mobile charged particles are under the influence of both electrostatic and chemical potentials. Making use of the Einstein-Townsend relationship,^4^1

\[ u_i = \frac{z_i D_i e}{kT}. \]
and collecting terms in Equation 43, the partial current from the $i^{th}$ species may be put into the form,

$$i_i = \frac{-z_i e c_i D_i (\nabla \mu + z_i e \nabla \phi)}{kT}.$$  

Equation 45 may be further simplified by recalling the basic definition of electrical conductivity,

$$\sigma_i = c_i z_i e u_i.$$  

Making a second use of the Einstein-Townsend relation, one obtains,

$$i_i = \frac{-\sigma_i}{z_i e} (\nabla \mu + z_i e \nabla \phi).$$  

When a total conductivity measurement is conducted on oxides, the external field applied to the samples is generally ac rather than dc to minimize polarization effects that may result from a sustained dc field. In addition, the sample materials are allowed to come to complete chemical equilibrium with the controlled gas phase.\textsuperscript{12,25} The chemical potential, therefore, must be conserved at the boundaries between the sample and the gas, and consequently, remain constant throughout the material bulk. The partial current due to the species of interest under these conditions reduces to a single drift term,

$$i_{i_{ac}} = -\sigma_i \nabla \phi_{ac}.$$  

where it has been assumed that the ac current component is essentially the same as that measured using a dc applied potential (neglecting polarization effects). The approximation is reasonable since most ac conductivity bridges used for these measurements operate in the low kHz range, and the typical relaxation times in a solid after application or removal of dc fields is of the order of nanosec.

Equation 47 states that the current contribution from the $i^{th}$ species is directly related to the defect concentration in the bulk, $c_i$, and proportional to the applied field and defect mobility. In many simple oxides the concentration of native defects can be considered to be dilute, therefore, the defect mobility can be assumed independent of concentration for a particular temperature. In addition, in the oxygen activity range where a particular electroneutrality condition is valid, the charge associated with a vacancy or interstitial is assumed to remain fixed. The expression for the partial current associated with a particular species can be simplified further to the form,

$$\left(i_i\right)_{ac} OC c_i$$

As noted in the previous section dealing with defect formation vs oxygen activity, the concentration of all defects in the crystal will depend upon the equilibrium constants, and possibly, upon the oxygen activity. The partial current can finally be simplified to
This result represents the basis for the measurement of ac conductivity as a function of oxygen activity, since by experiment, the correct dependence may be determined, and the results compared with the predictions which result from theoretical analysis.

**Development of EMF**

The case where an oxide material and associated reversible electrodes are situated between two gas phases having different oxygen activities is now considered. This situation is shown in Figure 3, and the conditions are as follows:

1. Thermodynamic equilibrium exists at the two solid-gas interfaces such that the chemical potential is conserved at the boundary.
2. Dilute defect concentrations are assumed so that defect-defect interactions are minimized and the mobilities $u_i$ can be assumed concentration independent.
3. No electric field exists across the material other than that generated by the diffusion of charged defects induced by the differing chemical potentials at the two faces.
4. Metalized porous electrodes are attached to each face, and to the external circuitry via
FIGURE 3. Diagram depicting a metal oxide compact with a chemical potential gradient applied to the two opposing faces of the sample. Porous platinum electrodes applied to the faces act as electrical connections to the external circuit, and must not block the flow of oxygen to the surface of the compact where the reaction is taking place. Equilibrium conditions between the gas phase and the solid phase are such that the chemical potential in the gas is equal to that in the solid at the respective faces of the sample.
electronic conducting wires. These electrodes are assumed non-blocking to $X_2$.

Upon the application of the different oxygen activities at the two faces of the sample, a reaction will begin to take place at both surfaces. Since the activity of $X_2$ in the two gas-phases differ, the equilibrium defect concentration at each surface will vary according to the law of mass action. By the time when the defects at each of the two surfaces come to dynamic equilibrium with the respective gas phases, concentration gradients will be present from one side to the second. The assumption is made that Schottky-Wagner defects prevail in this idealized crystal. Therefore, metal and oxygen vacancies will be the predominant mobile defect and can constitute an ionic current flow. The tendency will be for $X_2$ molecules in the region of higher activity to be adsorbed at the surface of the sample, and, after attachment of electrons from the lattice, the anions diffuse toward the side having lower oxygen activity. This migration of anions from one gas phase to the second will result in a gradient of anion vacancies $V_{x}^{X^+}$, and cation vacancies, $V_{m}^{n^+}$.

The development of pertinent equations describing the EMF generated by a chemical potential applied to an oxide containing point defects begins with Equation 46, which designates the total contribution for the $i^{th}$ species in the presence of chemical and electrostatic potentials.
Consideration of an oxide having predominant Schottky-Wagner defects leads to four independent mobile defects which can contribute to the total charge conduction: electrons, holes, anion and cation vacancies. Since no external sources or sinks exist which can supply either charge or defects to the material (other than molecular oxygen from the gas phases), the net change in mass of the sample must tend to zero at equilibrium. Hence, the condition of electroneutrality dictates that,

\[ i(e^\prime) + i(h^\prime) + i(V^{x^\prime}_x) + i(V^{m\prime}_m) = 0. \]

Substitution of the partial currents given by Equation 50 into Equation 46 and noting the proper charge for each species, the following equation for \( \nabla \phi \) results,

\[ \frac{d \phi}{dx} = \frac{1}{e} \left( \dot{\mu}(e) \left[ t_e + t_h \right] + \dot{\mu}(V^{x^\prime}_x) \left\{ \frac{t_{V^{x^\prime}_x}}{x} + \frac{b_{V^{m\prime}_m}}{am} \right\} \right). \]

Use has been made of the transference numbers \( t_i \) of the individual defects, which are defined by the expression,

\[ t_i = \frac{\sigma_i}{\sigma_{tot}} \frac{c_i z_i e u_i}{\sum \text{ion} + \text{el}}. \]

The summation extends over all mobile charge defects in the material. Using the Duhem-Margules relation, and
the phase equilibrium condition at the surface, the chemical potential of anion vacancies can be replaced by an appropriate expression involving the chemical potential of the gaseous oxygen,

$$\frac{d\phi}{dx} = \frac{1}{e} \left[ \frac{d\mu(e)}{dx} \left\{ 1 - t_{V_{m}^{m}} + \frac{bx}{am} t_{V_{m}^{m'}} \right\} + \frac{d\mu(x)}{dx} \left\{ \frac{t_{V_{x}^{m}}}{x} + \frac{bt_{V_{m}^{m'}}}{am} \right\} \right]$$

Spatial integration of Equation 53 results in an equation that describes the electrostatic potential difference developed between the two reversible electrodes as a consequence of the applied chemical potential between these electrodes. For the case where all charged ionic species are in their normal valence state, the following equation is obtained,\(^{41}\)

$$\phi_{II} - \phi_{I} = \frac{1}{e} \int_{(x)}^{(x)} \left\{ t_{V_{m}^{m}} + t_{V_{x}^{m'}} \right\} \frac{d\mu(x)}{dx} + \frac{1}{e} \left\{ \mu_{II}(e) - \mu_{I}(e) \right\}$$

This expression describes the electrostatic potential difference that appears across the two electrodes which is equal and opposite to the diffusion potential resulting from the differing non-metal activities in the gaseous phases. The existence of a finite voltage is dependent upon ionic transference numbers greater than zero. Since the mobility of electronic defects is roughly three orders of magnitude greater than the mobility of ionic defects, there must be significantly more ionic defects than
electronic imperfections before a measurable potential exists. As noted earlier, the external measuring circuit consists of electronic conductors, and only the potential from the first term can be measured. Finally, the electromotive force developed across the cell can be noted as,

$$\phi_{II} - \phi_I = \frac{1}{nF} \int \frac{\mu_{II}(x)g}{\mu_I(x)g} t_{ion} \, d\mu(x)g,$$

where $t_{ion}$ represents the transference number for the mobile ionic species, and we have considered molar equivalents.

Recalling the general form for defect dependence obtained in Equation 49, and the definition of ionic transference number contained in Equation 52, the form of $t_{ion}$ can be recast into,

$$t_{ion} = \left[ 1 + \frac{P_0}{P_0} \right]^{-1/n} \left[ 1 + \frac{P_0}{P_0} \right]^{-1/n}$$

$P_0$ and $P_0$ represent the oxygen activity such that the ionic conductivity $\sigma_{ion}$ is equal to hole and electron conductivities, respectively.

In the derivation of Equation 56, the assumption has been made that: the ionic conductivity is independent of oxygen activity, the hole conductivity follows a positive-
power oxygen dependence, and the electron conductivity obeys a negative-power oxygen dependence.

Insertion of this form of $t_{\text{ion}}$ into Equation 55 and integration from one boundary to the other leads to the result,

$$\phi_{\text{II}} - \phi_{\text{I}} = \frac{nRT}{4F} \left[ \ln \left( \frac{1}{P_{\text{II}} + P_{\text{O}_2}} \right) + \ln \left( \frac{1}{P_{\text{I}} + P_{\text{O}_2}} \right) \right].$$

With this general description of EMF in terms of oxygen pressure, it is possible to consider a number of interesting cases. Under the extremes of either very high or low non-metal activities, electronic defects created by the non-stoichiometry of oxides become the predominant mobile defects. As a result of n-type conduction in reducing activities and p-type conduction in the over-oxidized regions, non-zero ionic transference numbers are possible only in an oxygen activity at or near the stoichiometric region of the material. Keeping these limits in mind, it is useful to consider the following experimental regions;

1. $P_{\text{O}_2} << P_{\text{O}_2} << P_{\text{e}}$ or $P_{\text{e}} << P_{\text{e}} << P_{\text{O}_2} << P_{\text{O}_2}$

Substitution of these conditions into Equation 57 shows that the measured EMF will be zero. Both of these cases correspond to the situation where the activities at both electrodes are either too high or too low to have appreciable ionic conductance in the electrolyte. The emf cannot
develop across the sample because the electronic conductors are electrically "shorting" the diffusion potential. In the instance where,

\[ P_e \ll P_o \ll P_o^2 \ll P_o^2 \]

the activity at the electrode having the low oxygen concentration lies in the region of significant ionic transport, while the high concentration electrode is at an activity where p-type conductivity dominates. The emf of the cell will be given by,

\[ E = \frac{RT}{4F} \ln \left( \frac{P_e}{P_o^2} \right) \]

A similar result occurs when the gas phase having greater activity lies in the stoichiometric range while the low side of the sample is at an activity where significantly large n-type conduction is taking place. For this case the result is,

\[ E = \frac{RT}{4F} \ln \left( \frac{P_o^2}{P_e} \right) \]

If the oxide has a narrow range of activity where appreciable ionic transport exists, and the activities of both electrodes lie outside this region, combining the results from the two previous examples, \((60, 61)\) the emf will be given by the expression,
A final and most important case exists, where the gas phase activities are such that ionic conduction prevails at all activities, the relationship between partial pressures being,

\[ P_e \ll P_{O_2} \ll P_{O_2}^{''} \ll P_0 \]

Substitution of these limits\(^{63}\) into Equation 57 gives the following result,

\[ E_{\text{max}} = -\frac{RT}{4F} \ln \left( \frac{P_{O_2}^{''}}{P_{O_2}} \right) \]

The EMF measured across the two electrodes for this case corresponds to the thermodynamic maximum which can also be calculated from first principles using the laws of thermodynamics for reversible processes.\(^{44}\) In the study of electrolytes this maximum value will only be obtained when the ionic transference number, \(t_{\text{ion}}\), is unity in Equation 55. It is possible, therefore, to make use of emf measurements by comparison with the maximum free energy obtained from thermodynamical calculation to obtain the average transference number in solid electrolytes according to,

\[ t_{\text{ion}} = \frac{E_{\text{exp}} - E_{\text{exp}}^{''}}{E_{\text{max}} - \frac{RT}{4F} \ln \left( \frac{P_{O_2}^{''}}{P_{O_2}} \right)} \]
Figure 4 represents a plot for a typical electrolyte having an ionic conduction region about stoichiometry, and p- and n-type conduction in non-stoichiometric regions. The oxygen activity at the horizontal center of the figure is assumed to represent the gas-phase/solid-phase coexistence pressure such that atomic native defects predominate and ionic conduction prevails. The activity of one electrode will be fixed at this stoichiometric activity while the other is first increased over many orders of magnitude. At the point to the right of $P_{\text{stoich}}$ where $P_{\text{O}_2}''$ is equal to $P_\Phi$, the measured emf will attain a constant value, independent of any further increase in oxygen partial pressure. Conversely, this same electrode can be subjected to consistently decreasing oxygen activities until a point is reached to the left of $P_{\text{stoich}}$ where $P_{\text{O}_2}'$ is equal to $P_\Theta$, and again the emf will assume a constant value. These two limits of $P_\Theta$ and $P_\Phi$ represent the activities over which the sample metal oxide can be considered an ionic conductor, the maximum cell emf being given in Equation 62.

In many experimental investigations, the oxygen activity of greatest interest lies in the vicinity of $P_\Theta$ and/or $P_\Phi$. According to Equation 55, the emf developed across the electrolyte depends upon the average ionic transference number $\langle t_{\text{ion}} \rangle$. To obtain a well-defined functional relationship between emf and oxygen activity, graphical methods represent the optimum technique, since rarely is the exact form of ionic transference vs oxygen activity known.
FIGURE 4. Diagram for a typical electrolyte having predominant ionic conduction in the 'stoichiometric' region and electronic conduction in regions where the gas phase is either reducing or oxidizing the material outside the 'stoichiometric' range. Appropriate emf equations from the text are pictured along with the range over which they are applicable.
Figure 5 is a plot of ionic transference number vs oxygen activity for a classical electrolyte which is governed by Equations 60 through 64. In the oxygen concentration range where intrinsic or induced (by dopant addition) atomic defects predominate, electronic defects, the total conductivity will be that resulting from mobile ionic defects. The ionic transference number will be unity. In regions of extremely high or low oxygen activity, electronic defects will control total conductivity, and \( \langle t_{\text{ion}} \rangle \) will be zero. In the vicinity of \( P_\phi \) and \( P_{\psi} \), the electrolyte exhibits mixed conduction from both ionic and electronic conductivities, and the ionic transference number is in a transition zone between unity and zero.
FIGURE 5. Diagram showing the ionic transference number vs oxygen concentration for an electrolyte. Ion is significant only in the 'stoichiometric' region where predominant ionic conductivity is present. Outside this region, electronic shorting reduces $t_\text{ion}$ to zero.
IV. EXPERIMENTAL APPARATUS AND PROCEDURE

Total ac Conductivity Measurement

The measurement of total ac conductivity in oxides requires that samples be located in a high temperature environment such that the oxygen in the solid phase equilibrates with the oxygen activity in the controlled gas-phase. Additionally, it is good practice to estimate the oxygen concentration range which can reasonably be applied to the test oxides. Measurements conducted with a gas-phase activity which places the sample far outside its stoichiometric range can either over-oxidize or reduce the starting materials beyond the oxidation state of interest.

PZT was fabricated from three starting oxides: lead oxide, zirconia, and titania. The free energy of formation for zirconium oxide is 220 kcal/mole (600°C), while that for titanium oxide (rutile) is 186 kcal/mole (600°C). Lead oxide is considerably less stable, exhibiting a formation energy of 28 kcal/mole at the proposed operating temperature (600°C). The great difference between the free energy of formation results in a high oxygen dissociation pressure for the Pb/PbO system relative to that for TiO₂ and ZrO₂ and greatly limits the lower range of
applied gas-phase activity. The present work is conducted with a gas-phase oxygen activity which is always at least four orders of magnitude above the dissociation pressure of lead oxide at the operating temperature.

A schematic diagram of the ac conductivity apparatus is shown in Figure 5 and consists of three sub-assemblies: the high temperature furnace and controller, the electronic measuring circuitry, and the gas storage and purification system.

The high temperature portion of the apparatus consisted of a 24 inch long by 12 inch o.d. Marshall tube furnace (Model 1400) capable of maintaining a maximum temperature of 1400°C. Power is supplied through a 15 amp General Radio "Variac," which is used as a rough temperature control. Temperature regulation was accomplished by means of a Wheelco Model 404 off-on galvanometer controller, which maintained a temperature in the range 600°C to 800°C with an accuracy of ±2.0°C. During the course of the experiment, it was found that accurate conductivity measurements require better temperature control, and a time-proportioning circuit was added to the existing equipment. A solid state "Guoy" modulator54, 55 incorporated into the controller increased the stability of the system to ±50°C at the operating temperature (Appendix A).

Precise measurements of sample conductance were made using a Wayne Kerr universal bridge (Model B221A). This
instrument operates on the ratio-arm transformer principle and is accurate to ±10% from 0.01 microho to 11 millimho. Capacitive and inductive portions of a complex impedance can be measured to an accuracy of ±10% with this unit. Sample temperatures were monitored with a Leeds and Northrup (Model 8686) potentiometer. A (24 gauge) platinum, platinum-10% rhodium thermocouple was situated approximately ½ inch from the PZT samples.

The gas supply and purification system consists of several independent units discussed in detail in Appendix B. Commercial oxygen and argon gases are stored in 330 cubic foot "T" cylinders at 2500 lb/in\(^2\). Hoke "Phoenix" regulators (1 to 10 lbs/in\(^2\) output) are used to reduce the gas pressure to the 1½ to 2 lbs/in\(^2\) pressure used in the remainder of the experimental apparatus. The commercial argon is purified by removing oxygen, hydrogen, carbon dioxide and water in the gas purification train. Tank oxygen is passed through a similar purification train, with the exception of the oxygen removal catalyst stage, to remove carbon dioxide and water. Oxygen and argon are mixed by blending metered flows of each gas in a small chamber connected to both orifice flowmeters. The operation of the flowmeters is explained in Appendix C. The gas purification systems and the mixing equipment are made of Pyrex glass to minimize the introduction of foreign matter into the gas stream. Pyrex glass tubing is also used to connect the furnace to the purifying and mixing stages of the apparatus.
Copper/cuprous oxide powders located upstream from the samples were used to obtain low oxygen activities (10^{-6} atm and 10^{-8} atm). The dissociation oxygen pressure for the system can be calculated according to the free energy of formation which governs the reaction, \( \text{Cu}_2\text{O} + \frac{3}{2}\text{O}_2 \rightarrow 2\text{CuO} \).

**Procedure**

The following PZT compositions were studied in the measurement of ac conductivity, where subscripts within the parenthesis refer to the mole percent (m/o) of the respective constituents:

- \( \text{Pb}(\text{Zr}_{0.93}\text{Ti}_{0.07})_0.3 + 1.0\text{wt}\%\text{Nb}_2\text{O}_5 \) denoted as PZT 93/7
- \( \text{Pb}(\text{Zr}_{0.90}\text{Ti}_{0.10})_0.3 + 1.0\text{wt}\%\text{Nb}_2\text{O}_5 \) denoted as PZT 90/10
- \( \text{Pb}(\text{Zr}_{0.80}\text{Ti}_{0.20})_0.3 + 1.0\text{wt}\%\text{Nb}_2\text{O}_5 \) denoted as PZT 80/20
- \( \text{Pb}(\text{Zr}_{0.65}\text{Ti}_{0.35})_0.3 + 1.0\text{wt}\%\text{Nb}_2\text{O}_5 \) denoted as PZT 65/35

These compositions were obtained from the Clevite Corporation in the form of disks approximately 1.27 cm in diameter by .052 cm in thickness. Although the exact fabrication procedures are proprietary, it is known that the samples were prepared by core-drilling large cylinders of hot-press material and slicing wafers of the desired thickness (.052 cm).

Previous work has indicated that commercial samples of this type must be polished and cleaned carefully prior to application of porous Pt electrodes. All samples were

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* Cleveland, Ohio
polished with #600 alumina abrasive powder on a high quality plate glass surface to remove surface blemishes. Organic matter and other contaminants (from fingerprints and handling) were removed from the two flat surfaces using (in sequence) trichlorethylene, acetone, absolute alcohol, and distilled water rinses. The rinse baths were agitated in beakers using an ultrasonic cleaning tank to insure complete removal of contaminants.

After air-drying under an infrared heat lamp, Pt electrodes of approximately 0.2 cm² were applied (Englehard paste #6082). To insure a uniform electrode thickness and to facilitate control of electrode size, the samples were mounted in a brass holder and spun on the vertical shaft of a low speed (100 to 200 rpm) electric motor during paste application. The Pt paste contains very small platinum particles suspended in an organic binder, and the binder must be evaporated at high temperature to insure electrode continuity and uniform adhesion to the sample. All PZT samples were fired in air at 750°C for 10 to 15 minutes to remove the binder. Electrode sintering was assumed complete when the past color changed from black to light gray.

After preparation and final inspection to insure that electrodes are uniformly attached to the sample pellets (no cracking or peeling), the four PZT compositions and a calcia stabilized zirconia standard were installed in the sample holder shown in Figure 6. Samples, (K), were
FIGURE 6. Schematic Illustration of Cell Holder for Two-Probe Conductivity Measurements Involving Numerous Specimens. LEGEND: (A) brass screw, (B) spring, (C) epoxy or glass-metal seal, (D) brass parts machined to standard taper (34/45 joint), (E) impervious alumina combustion tube, (F) alumina cell holder tube, (G) Pt lead wires, (H) hollow alumina pushrod, (I) alumina disks, (J) Pt foil electrodes, (K) specimens, (L) Pt/Pt-Rh thermocouple, (M) epoxy seal, (N) brass part machined to fit standard taper joint, (O) pyrex standard taper joint.
placed in a stacked arrangement separated by platinum foils, (J), which are connected to the external measuring circuit, (G). The brass screw, (A), was tightened to the point where spring pressure, (B), allows intimate contact between the samples and the platinum foils. The sample holder was then inserted into the furnace such that standard taper brass joints, (C,D), form a vacuum seal.

Six to eight hours are usually required for the furnace to reach operating temperature after power is applied. During this period, the gas mixing system was made operative and the desired argon/oxygen mixture flushed through the furnace. Exhaust gases from the sample chamber exit via the standard taper joint, (O,N), to an external bubble chamber where spent argon/oxygen mixture is vented to the atmosphere.

Electrical conductivity measurements were conducted at 500°C and 600°C over a wide range of oxygen activities (1 atm to 10⁻⁸ atm). After each change in oxygen activity or temperature, a number of readings were taken over a period of twelve to twenty-four hours to insure equilibrium with the gas-phase. Since calcia-stabilized zirconia exhibits total ionic conductivity over the entire experimental oxygen activity range of interest to this investigation, the conductance is a function of temperature along. Consequently, the zirconia sample pellet served as a sensitive indication of sample temperature during the
final equilibrium measurements. Four to five hours appeared to be a sufficient equilibration time at 600°C, however, twelve hours were allowed to pass before making final measurements. At 500°C, fluctuations were found in the initial readings, and twenty-four hour equilibration periods were needed to obtain consistent results.

Since accurate dilution of oxygen to concentrations below approximately $10^{-4}$ atm is very difficult, cuprous oxide-cupric oxide powders were placed in a ceramic boat immediately upstream from the samples and allowed to equilibrate with a low flow rate (10 cc/min) of pure argon. At 500°C the dissociation pressure above the CuO/Cu$_2$O system is $10^{-8}$ atm, while at 600°C it is $10^{-6}$ atm.

The experimental procedure adopted for conductivity measurements was to fix the temperature at either 500°C or 600°C and to vary the oxygen activity in the sample chamber over the entire range which could be mixed using the gas flow-meters. Using the metal oxide powders, low oxygen activity readings were then taken. No particular sequence of oxygen activities were studied and this procedure minimized systematic errors in the measurement.

Electromotive Force Measurement

To obtain meaningful emf measurements from ceramic oxides, the same limitation applies to the range of experimental oxygen activities as was outlined for the ac conductivity measurements. In addition, the application of
a voltmeter to the two electrodes on the sample must not perturb the equilibrium at the gas-solid interface. For this reason a very high impedance instrument is used to measure the potential developed by the gradient in defects. The impedance of the voltmeter must be several orders of magnitude above the electronic resistance of the sample to preclude electronic shorting between the two electrodes.

The electrode material must be carefully chosen for two reasons. First, the electrode must be highly conducting to electrons to insure an intimate electrical contact between the face of the sample and the external circuitry. Secondly, the electrodes must be porous to oxygen so that diffusion to the face of the ceramic does not limit the reaction taking place in the solid phase. For these reasons, platinum was chosen in a paint form that could be easily applied to the samples and later fired into the pores of the PZT materials.

In an earlier work on PZT by Ezis, the sample pellets were suspended between two highly polished alumina tubes, which served to segregate the two oxygen concentrations. Results of this work indicate the difficulty in obtaining good gas-phase isolation when scaling surfaces are on both sides of the sample. For the present work, the decision was made to construct a single-ended device, in which the sample is sealed only at one face.

The sample holder and furnace system employed in the EMF measurement are shown in Figure 7. Except for several
FIGURE 7. Sample Holder and Furnace System for emf Measurements. LEGEND: (A,B) standard taper brass joints, (C) furnace combustion tube, (D) calcia stabilized zirconia tube, (E) 'O'-ring seal to zirconia tube, (F) glass-to-metal feed-throughs, (G) standard taper seal to vacuum system, (H) porous Pt electrodes, (I) porous Pt electrodes on standard cell, (J) external lead wires, (K) thermocouple protection tubes.
modifications, the brass "header" is similar to the sample holder used in the ac conductivity measurement. The "header" is inserted in the furnace by means of standard taper joints, (A, B), which form a vacuum seal with the furnace combustion tube, (C). The brass "header" is connected to a calcia-stabilized zirconia tube, (D), which is 1.27 cm o.d. and 35 cm in length. A vacuum seal between the brass "header" and the zirconia tube is maintained by the set of threaded flanges having an "O"-ring seal, (E). Electrical connection between the samples and the external circuitry is via glass-to-metal fittings, (F). The sample is situated at the end of the calcia-stabilized zirconia rod as shown in the inset included in Figure 7. The end of the zirconia tube and one face of the samples are polished such that a good physical contact is maintained between the two when a partial vacuum is applied to the tube, (D), through the second standard taper joint, (G). Electrodes are applied to the samples, (H), and the zirconia standard, (I), to which are connected platinum wires, (J), leading to the external measuring equipment. Thermocouple protection tubes, (K), are used to isolate the various platinum lead wires.

Argon/oxygen gas mixtures from the purification and mixing equipment, (Appendix B and C), are introduced into the furnace combustion tube at the end opposite the brass "header." Spent gases exit the system via the "header", (A).
The gas mixture contained in the combustion tube represents the gas-phase in contact with the sample having the higher oxygen activity. A small quantity of the mixture will leak from the combustion tube into the zirconia tube, but, since the total pressure at the inside surface of the zirconia tube, (D), is lower than the total pressure in the combustion tube (resulting from the partial vacuum applied to the zirconia tube), the oxygen activity will be reduced. The ratio of oxygen activities on the two sides of the sample and zirconia standard can be regulated by the total pressure (partial vacuum) on the inside of the zirconia tube.

The vacuum system connected to the sample holder, (G), is shown schematically in Figure 8. The standard taper, (G), is connected to a mercury manometer, (A), which is used to indicate total pressure in the range between 0.5 atm and approximately $10^{-3}$ atm. Below pressures of $10^{-2}$ atm, the thermocouple vacuum gauge, (B), is used to obtain pressure readings on the low activity side of the PZT samples. The throttle valve, (C), can be set, and intermediate pressures can be obtained in the sample chamber. The Cenco 6.3 cu ft/min vacuum pump, (D), is connected to the system via cold trap, (E), and runs at maximum capacity at all times.

The high impedance electrometer (Keithley #610B) is connected to the PZT and zirconia electrodes as shown in Figures 7 and 8. A chromel-alumel thermocouple is located
FIGURE 8. Schematic Diagram of EMF Apparatus. LEGEND: (A) 780 mm manometer, (B) thermocouple vacuum gauge, (C) controlled leak throttle valve, (D) fore pump, (E) 610 B electrometer, (F) Varian 10" strip recorder, (G) Leeds & Northrup potentiometer connected to, (H) chromal-alumel thermocouple, (I) gas supply and purification system.
near the PZT sample and indicates the sample temperature during the experiment by means of a Leeds and Northrup potentiometer. The emf read from the electrometer was recorded as a function of time on a Varian G 2000 strip recorder.

The 7.5 w/o calcia-stabilized zirconia tube incorporated into the EMF apparatus serves as a reference electrolyte in the experiment. As discussed in an earlier section, doped zirconia is an ionic conductor over the entire experimental range of oxygen activities studied in this work. The emf developed across this standard represents a measurement of the true oxygen partial pressure ratio associated with the two sides of the standard and the PZT. Since the vacuum gauges are considerably remote from the sample chamber, it was decided that the emf developed across the standard electrodes represented the best value of oxygen activity in the two gas phases.

During the preliminary experiments conducted with this apparatus, erroneous values for emf were obtained which corresponded to oxygen partial pressure ratios greater than those present at the sample and standard cell. After rechecking all instrumentation and electrical connections, it was determined that grounding problems were the probable cause of difficulty. Subsequently, all external wires were shielded (using coaxial cable), the outside of the furnace combustion tube was coated with a conducting silver
paint, and all external electronic equipment was connected to this common ground point. No further ground loops were detected after these alterations.

Procedure

Virgin sample wafers having the compositions listed in the previous section on ac conductivity were studied in the EMT experiment to determine ionic transference number as a function of oxygen partial pressure and temperature. With one exception, sample preparation was essentially the same as reported previously on ac conductivity. The side of the PZT sample which is sealed against the calcia-stabilized zirconia standard tube requires a very flat polished surface to facilitate a reasonable vacuum fit. During the lapping stages of sample preparation, care was exercised to avoid scoring or scratching the PZT surface. This procedure improved the vacuum on the low pressure side of the samples. Each PZT wafer was placed in position against the zirconia tube and individually tested with the vacuum system prior to the experimental measurement. At room temperature, a vacuum of 200 to 300 microns as read by the thermocouple gauge was considered sufficiently leak-tight in this test.

After the leak check, the PZT composition to be studied was placed in position and full vacuum applied to the system. Platinum leads are placed in the proper positions on the PZT test electrodes and the calcia-stabilized zirconia electrodes. Contact between the Pt wires and the electrodes
was maintained under spring tension. Upon the completion of a simple electrical continuity check between external leads and the electrodes, the brass sample holder was inserted in the furnace and power applied. As in the ac conductivity measurement, sufficient time (at least four hours) was allowed to reach operating temperatures.

Upon reaching the desired temperature, as indicated by the furnace controller, the temperature at the samples was measured with the chromel-alumel thermocouple. Generally, the samples were found to be about 10 to 15°C below the indicated furnace temperature, and additional adjustment of the controller was required to fix the sample temperature at the desired value. Having determined the proper controller set point, and allowing the system to come to thermal equilibrium, the desired oxygen-argon gas mixture was introduced into the furnace combustion chamber.

The oxygen-argon gas from the mixer was introduced into the outer chamber, (C), at a pressure of 1 atm, and represented the gas-phase with the higher oxygen concentration. The total pressure at the inside surface of the calcia-stabilized zirconia tube was less than 1 atm and served as the gas-phase with the low oxygen activity. By adjusting the needle valve, (C) (controlled leak), the total pressure within the zirconia tube could be varied between .5 atm and $10^{-3}$ atm.
After obtaining the desired sample temperature (500°C or 600°C), the argon-oxygen mixture in the combustion tube and the partial vacuum within the calcia-stabilized zirconia tube were varied over all possible ranges. These ranges are indicated below.

1. The total pressure in the combustion tube maintained at 1 atm total pressure with argon dilution such that oxygen activity ranged from 1 atm to $10^{-4}$ atm.

2. The total pressure in the zirconia tube varied from $.5$ atm to $10^{-3}$ atm by adjustment of the needle valve.

The total pressure in the zirconia tube was monitored by the 780mm mercury manometer column and the thermocouple gauge, but the actual oxygen activity within this tube was calculated from the emf measured across the zirconia standard. Electrodes on the zirconia thus served as reference or standard electrodes and the emf corresponded to the maximum thermodynamic value. The comparison of PZT emf and zirconia standard emf was used in the calculation of transference numbers. Two PZT wafers of each composition were measured over partial pressure extremes of 1 atm and $10^{-6}$ atm to improve data correlation.
V. EXPERIMENTAL RESULTS

Ac Conductivity Measurement

Results of the total conductivity study for the four compositions of PZT are displayed in Figure 9 through Figure 12. Two samples of each composition are represented in these diagrams. At 500°C the range of oxygen activities studied is between 1.0 atm and $1.4 \times 10^{-8}$ atm, while at 600°C, the range is between 1.0 atm and $1.5 \times 10^{-6}$ atm. The lower limit of oxygen activity at each temperature results from the temperature dependence of oxygen dissociation pressure for the CuO/Cu$_2$O system.

As previously discussed, calcia-stabilized zirconia is an ionic electrolyte over the entire experimental range of oxygen pressure covered in this work. Consequently, the conductivity is independent of oxygen concentration at any fixed temperature. Hence, the stabilized zirconia pellet serves as a sensitive indication of PZT sample temperature, and was used in this capacity. The conductivity of the stabilized zirconia wafer is plotted in Figure 13, and the average value of 275 mho-cm is in good agreement (at 600°C) with reported results by Patterson et al.⁶
FIGURE 9. A. C. Conductivity vs oxygen concentration for PZT 93/7. ○—Sample temperature 500°C, oxygen concentration in atmospheres, data points normalized by factor $10^0$.
•—Sample temperature 600°C, oxygen concentration in atmospheres, data points normalized by factor $10^1$. 
FIGURE 10. A. C. Conductivity vs oxygen concentration for PZT 90/10. • - Sample temperature 500°C, oxygen concentration in atmospheres, data points normalized by factor x10. ○ - Sample temperature 600°C, oxygen concentration in atmospheres, data points normalized by factor x1.
FIGURE 11. A.C. Conductivity vs. oxygen concentration for PZT 80/20. •—Sample temperature 500°C, oxygen concentration in atmospheres, data points normalized by factor x10. ○—Sample temperature 600°C, oxygen concentration in atmospheres, data points normalized by factor x1.
FIGURE 12. A. C. Conductivity vs oxygen concentration for PZT 65/35. -Sample temperature 500°C, oxygen concentration in atmospheres, data points normalized by factor x10. -Sample temperature 600°C, oxygen concentration in atmospheres, data points normalized by factor x1.
FIGURE 13. A.C. Conductivity vs oxygen concentration for calcia-zirconia.
- Sample temperature 500°C, oxygen concentration in atmospheres, data points normalized by factor xi.
- Sample temperature 600°C, oxygen concentration in atmospheres, data points normalized by factor xi.
The following general observations were made concerning the ac conductivity measurements:

i. The conductivity of PZT compositions and calcia-stabilized zirconia samples alike is a very sensitive function of temperature, and meaningful measurements depend upon maintaining the sample temperature to better than ± 1.0°C.

ii. Measurements were consistent for all flow rates between 10 cc/min and approximately 250 cc/min, indicating that the argon-oxygen mixtures are sufficiently heated prior to passage through the region where the samples are located.

iii. Metal oxide powder systems can be used to obtain reproducible oxygen activities if the gas flow rate over the powder system is sufficiently low (less than 10 cc/min) to allow equilibration with the system.

iv. The total conductivity vs oxygen activity plots for PZT compositions appear to have three definite regions as evidenced from the Figures 9 through 12.

v. Maintaining the oxygen activity in the gas phase several orders of magnitude above the dissociation pressure of lead oxide has resulted in little or no change in the PZT compositions used in this work.
vi. Equilibration times of 12 and 24 hours at operating temperatures of 600°C and 500°C, respectively are satisfactory for measurements of these materials. Consistent results have been obtained at both temperatures.

**EMF Measurement**

Results of the electromotive force study on the PZT compositions are displayed in Figure 14 through Figure 17. Two wafers of each composition were measured over an oxygen activity range of 1.0 atm to 10⁻⁸ atm at operating temperatures of 500°C and 600°C. The data reported in these Figures were recorded after the Varian strip recorder reached a fixed value, indicating the system is at equilibrium.

The emf measured across the calcia-stabilized zirconia tube was assumed to represent the true thermodynamic potential between the two gas phases and was used to calculate \( t_{\text{ion}} \).

The following observations were noted during the course of this study.

i. At modest partial vacua of the order .5 atm to .1 atm, agreement between the indicated vacuum on the downstream gauges and that calculated using the stabilized zirconia electrolyte was better than ± 5% for all cases.
\( \Delta, \Delta \) -Sample temperature 500°C, oxygen concentration in atmospheres. \( \circ, \circ \) -Sample temperature 600°C, oxygen concentration in atmospheres.
FIGURE 15. Ionic transference number vs oxygen concentration for PZT 90/10. △, Δ — Sample temperature 500°C, oxygen concentration in atmospheres. ○, ● — Sample temperature 600°C, oxygen concentration in atmospheres.
FIGURE 16. Ionic transference number vs oxygen concentration for PZT 80/20.

- $\Delta$, $\Delta$ - Sample temperature 500°C, oxygen concentration in atmospheres.
- $\circ$, $\circ$ - Sample temperature 600°C, oxygen concentration in atmospheres.
FIGURE 17. Ionic transference number vs oxygen concentration for PZT 65/35.
Δ, Δ - Sample temperature 500°C, oxygen concentration in atmospheres.
○, ○ - Sample temperature 600°C, oxygen concentration in atmospheres.
ii. PZT compositions having high zirconium content possess a larger transference number over a wide range of oxygen activity. This characteristic was noted at both 500°C and 600°C.

iii. All compositions display a dependence of transference number on oxygen activity that indicates a transition region between ionic and electronic conductivity in the range between $10^{-4}$ atm and $10^{-1}$ atm.

iv. As reported for the total conductivity experiment, the equilibration time for both PZT and the calcia-stabilized zirconia standard is a sensitive function of temperature. At 600°C the time required for equilibrium with the gas phases was on the order of minutes, while at 500°C, the time was of the order of an hour.

v. The stabilized zirconia tube serves as an excellent standard electrolyte. Reproducibility was good at both 500°C and 600°C over the entire experimental range of oxygen activities.

vi. The plot of emf as a function of time (Figures 18 and 19) show that the approach to equilibrium after a change in oxygen activity on one side of the sample is exponential in nature and independent of $P_{O_2}'/P_{O_2}''$ for any given temperature.
FIGURE 18. Emf approach to equilibrium for PZT 93/7 after a step change in oxygen activity at one face of the sample. Data obtained from strip chart driven by electrometer connected directly to electrodes. LEFT; temperature 600°C, RIGHT; temperature 500°C.
FIGURE 19. Emf approach to equilibrium for PZT 65/35 after a step change in oxygen activity at one face of the sample. Data obtained from strip chart driven by electrometer connected directly to electrodes. LEFT; temperature 600°C. RIGHT; temperature 500°C.
vii. For fixed temperature and oxygen activities, the dependence of (t<sub>ion</sub>) on titanium content is exhibited in Figures 20 and 21.
FIGURE 20. Plot of ionic transference number vs m/o titanium. LEFT; temperature 500°C, RIGHT; temperature 600°C.
FIGURE 21. Plot of ionic transference number vs m/o titanium. LEFT; temperature 500°C, RIGHT; temperature 600°C.
VI. DISCUSSION OF EXPERIMENTAL RESULTS

The discussion of results obtained from the ac conductivity and EMT experiments will be divided into two main sections:

i. The first section proposes an interpretation of total ac conductivity in PZT based on a combined lead vacancy and substitutional model. Although lead vacancies have been considered a predominant defect in PZT in earlier studies, the present work represents the first attempt to explain conductivity in terms of a more specific defect model.

ii. The second section interprets the ionic transference numbers in PZT as a function of oxygen activity and titanium content. A mechanism is proposed whereby the existence of associations or pairs limits the partial ionic conductivity.

Previous studies have already been discussed which indicate that undoped PZT compositions are normally nonstoichiometric and exhibit p-type conductivity in the oxygen activity range between 1.0 atm and 10^{-3} atm. The
predominant defect in these ceramics, based on preliminary conductivity data for pure and doped compositions, is reported to be a result of lead vacancies brought about by the excess oxygen incorporated into the solid.\(^3\text{4}, 3\text{7}\) The addition of niobia and other Group V oxides has been observed to increase resistivity, indicating a suppression of the holes by the donor addition.\(^3\text{4}, 3\text{7}\) Scandia additions have decreased resistivity, in accord with an increased hole concentration introduced by a foreign acceptor. In conjunction with these previous results, evaluation of the present studies allows the proposal of a lead vacancy model in PZT polycrystalline specimens. Undoped PZT ceramics will be considered in some detail prior to the formulation of a defect mechanism in niobia doped materials.

**Defects in Pure (Undoped) PZT**

In the study of binary or more complicated oxides at equilibrium with an oxygen gas phase, the number of cations in the solid is conserved for all times (e.g., no net gain or loss to/from the solid). Any weight gain or loss must result from a change in the total number of oxygen ions in the oxide. In a binary oxide, an increase in mass in the region where the composition is oxidized beyond its stoichiometric state can result in an increase in oxygen interstitials or an increase in cation vacancies. The actual result depends upon the free energy of formation.
for the respective defects. In a ternary or more complex metal oxide, the defect reaction that takes place between the gas phase and the solid must be balanced with respect to all cation sites as additional oxygen ions are incorporated into the solid. This "conservation of cations" approach to defects in a ternary oxide has been introduced by Tretyakov and Rapp\textsuperscript{31} to explain the defect equilibrium in LiFe\textsubscript{5}O\textsubscript{8}. The proposed oxidation reaction for PZT in an oxygen excess state is developed in the following paragraphs.

Equation 66 represents a reaction between the solid and the gas phase for the oxidation of PZT. This reaction is balanced with respect to mass, sites, and charge — a necessary condition for defect equilibria.

\[ \text{Equation 66:} \quad 2O_2(g) \rightarrow 4O^{2-} + 2V_{\text{Pb}^+} + V_{\text{Ti}, Zr^4} + 8e^- \]

The common notation for defect reactions in ternary and more complex compounds which is used here is such that the actual charge associated with an ion is indicated instead of the relative charge.\textsuperscript{12, 13} The high relative valence state which would be associated with vacancies at the Ti\textsuperscript{+4} and Zr\textsuperscript{+4} sites probably precludes the existence of these defects. For this reason, as well as the known existence of Pb\textsuperscript{+4} ions at high oxygen activities, a re-arrangement (or substitution) reaction between any Ti or Zr vacancy and a lead ion seems likely. Hence the assumption is made,
Neither the formation of $\text{Pb}_{\text{Tl},\text{Zr}^{+4}}$ nor $V_{\text{Pb}^{+2}}$ is expected to require excessive formation energies. Combining Equation 66 and Equation 67, the following net defect reaction is obtained, which is also balanced with respect to charge, mass, and lattice sites,

$$
20_2(\text{g}) + \text{Pb}_{\text{Pb}^{+2}} \rightleftharpoons 4\text{O}^{2-} + 3V_{\text{Pb}^{+2}} + 6h^* + \text{Pb}_{\text{Tl},\text{Zr}^{+4}} \cdot 68
$$

Diffusion insures that an equilibrium concentration of $V_{\text{Pb}^{+2}}$ and $\text{Pb}_{\text{Tl},\text{Zr}^{+4}}$ defects are uniformly present throughout the ceramic. The equilibrium constant for Equation 68 is,

$$
K_{eq} = \frac{[V_{\text{Pb}^{+2}}]^3 [h^*]^6 [\text{Pb}_{\text{Tl},\text{Zr}^{+4}}]}{[\text{Pb}_{\text{Pb}^{+2}}]^2} \cdot 69
$$

Because the "conservation of cations" requires that the defects of Equation 69 be introduced in stoichiometric proportions, the increase in electronic and ionic defect concentrations obeys the expression,

$$
[h^*] = 6 [\text{Pb}_{\text{Tl},\text{Zr}^{+4}}] = 2 [V_{\text{Pb}^{+2}}] \cdot 70
$$

where the addition of 4 oxygen ions to the solid produces 6 holes, 3 lead vacancies, and 1 tetravalent lead ion.
substituted at a Ti (Zr) site. The following neutrality condition is proposed,

\[ [h^+] = 2 \left[ V_{\text{Pb}^{2+2}} \right] \]

Substitution of Equation 70 into Equation 69 results in a hole dependence upon oxygen activity,

\[ h^+ \propto P_{O_2}^{1/5} \]

This dependence is typically exhibited by many metal oxides in a region of excess oxidation. The assumption that a Pb atom substitutes at a Ti or Zr site is reasonable at least from the point of view of ionic radii (\( r_{\text{Ti}^{4+}} = 0.68 \text{Å}, r_{\text{Zr}^{4+}} = 0.80 \text{Å}, \) and \( r_{\text{Pb}^{2+}} = 0.84 \text{Å} \)).

**Defects in Nb_2O_5 - Doped PZT**

Based upon a number of previous studies, the addition of Nb_2O_5 in the amount of 1 to 3 w/o appears to produce lead vacancies in PZT. The large lead vacancy concentration is attributed to the substitution of Nb^{5+} at Ti or Zr positions. The divalent lead vacancies produced by dopant addition considerably outnumber the native vacancies, and the neutrality condition given by Equation 71 is no longer applicable. Considering all charged defects present in the crystal after doping, an appropriate neutrality condition is,
In the vicinity of stoichiometry, the neutrality condition can be modified to the form,

\[
\left[ \text{Nb}_{\text{Ti}}, \text{Zr}^{5+} \right] = 2 \left[ \text{V}_{\text{Pb}^{+2}} \right]
\]

Equation 74 is valid as long as the number of holes produced by the reaction between the solid and gas phases are insignificant in comparison to the number of foreign donors \( (\text{Nb}_{\text{Ti}}, \text{Zr}^{5+}) \) located at the Zr and Ti sites.

Equation 68 describes the reaction between the gas and the solid, but certain modifications must be introduced into the defect concentration balance before obtaining a defect dependence on \( P_{\text{O}_2} \). Obviously, the stoichiometric relation stated by Equation 70 is no longer valid because of the large concentration of divalent lead vacancies in the doped crystal. Consideration of equations 68 and 69 reveals that the large lead vacancy concentration will result in a reduction in holes and \( \text{Pb}^{+4} \) ions. Although the exact magnitude of these defects is not known in relation to the number of lead vacancies, Equations 68 and 70 indicate that the hole and \( \text{Pb}^{+4} \) concentrations will still be created in a ratio of 6 to 1. Inserting this information into the equation 69, along with the modified neutrality condition for the doped compositions, the hole dependence upon oxygen activity can be expressed by,

\[
h^\cdot \propto P_{\text{O}_2}^{1/3.5}
\]
The dependence of hole concentration on oxygen concentration is now considerably greater than for the undoped case, but the concentration of holes (and Pb⁺⁺ ions) has been suppressed by the large concentration of Nb⁺⁵ donor additions. In light of the large mobility of holes in comparison to that for ionic defects, the concentration of divalent lead vacancies must outnumber the hole concentration by five or more orders of magnitude before PZT will exhibit exclusive ionic conductivity. This behavior is apparently not the case, as evidenced by the non-zero slopes for ac conductivity displayed by all sample compositions (Figures 9, 10, 11 & 12).

Comparison of Figures 9 through 12 (ac conductivity vs oxygen concentration) with Figures 14 through 17 (ionic transference number vs oxygen concentration) indicates that between 10⁻⁸ atm and 10⁻⁴ atm, predominant, but not exclusive, ionic conductivity is present. The gradual increase in ac conductivity in this region apparently results from a significant hole conduction. The superposition of a constant \( \sigma_{\text{ion}} \) and a \( \sigma_{\text{PbO}^{1/n}} \) proposed here is consistent with experimental data, and will be designated as Region I in Figure 22.

At intermediate oxygen concentrations greater than approximately 10⁻⁴ atm, but less than 10⁻² atm, the ac conductivity plots for all PZT compositions (Figures 9 through 12) indicate a significant decrease in total
conductivity with increasing oxygen activities. This reduction in $\sigma_{tot}$ is not typical of most simple binary metal oxides, but is proposed here to be the result of a rapid decrease in ionic conductivity which results from an interaction between divalent lead defects and titanium ions incorporated into the PZT compositions. The mechanism for an interaction between lead defects and titanium ions is considered in greater detail in the following section dealing with associations. The concentrations of holes and Pb$^{+4}$ ions in this range of oxygen activity are determined, as before, by the reaction of the solid with the gas phase, and hence these defects possess a positive oxygen dependence of the form $P_{O_2}^{-1/n}$ similar to that obtained in Equations 72 and 75. The exact value for $n$ will depend upon the charged state of the defects and the appropriate neutrality condition, which is difficult to define in this intermediate range. The range of oxygen activities corresponding to this transition region between mixed conduction and predominantly electronic conduction is shown as Region II in Figure 22.

Figures 9 through 12 indicate that at oxygen concentrations greater than approximately $10^{-2}$ atm, the ac conductivity vs oxygen activity again assumes a positive slope. According to results of the EMF experiment, the ionic transference numbers for the various compositions of PZT tend toward zero in this same range of oxygen
FIGURE 22. Plot of defect concentration vs oxygen activity for PZT compositions.
REGION I: partial or dominant ionic conduction resulting from mobile divalent lead
defects created by the addition of pentavalent niobium dopant. REGION II: mixed
conduction consisting of ionic and electronic (p-type) defects; total conductivity
exhibits a minima in this region according to the complexing of ionic defects. REGION
III: increased production of holes from the oxidation of PZT results in the p-type
conductivity typically displayed by materials in an over-oxidized state. Ionic
transference numbers tend to zero for all compositions in this region.
activities. It is reasonable to conclude that significant electronic conductivity is present in this range, and PZT is beginning to demonstrate a defect dependence characteristic of p-type conductors. The simplified neutrality condition given by Equation 74 must be replaced by the expression involving positive holes in addition to Nb$^{+5}$ ion. The appropriate neutrality condition has already been introduced in Equation 73. Substitution of Equation 73 into the equilibrium relation (Equation 69) results in an expression involving holes, divalent lead vacancies, and Pb$^{+4}$ ions which cannot be simplified to yield an elementary defect dependence upon oxygen activity. This difficulty results from the previously discussed limitations imposed upon the defect stoichiometry relation (Equation 70) in the doped PZT. Qualitatively, use of the modified neutrality condition in Equation 69 results in a hole dependence intermediate between 1/5 and 1/3.5. Since it is highly unlikely that the hole concentration can be increased by continued oxidation to the point where the concentration of Nb$^{+5}$ can be neglected in Equation 73, it is doubtful that the positive slope of 1/5 corresponding to pure PZT compositions will be observed in the Nb$^{+5}$-doped material. Rather, an intermediate value somewhere between 1/5 and 1/3.5 should be observed.
Partial Ionic Conductivity in PZT

Results of the EMF study indicate that at best, PZT compositions doped with 1 w/o Nb₂O₅ are mixed conductors. Even at the lowest oxygen activities in this work, \( P_{O_2} = 10^{-6} \) atm, the composition having the greatest transference number, \( (\frac{93}{7}) \), does not satisfy the criteria for an ionic electrolyte \( (t_{ion} >> .99) \). Figures 14 through 17 show ionic transference number vs oxygen activity for the various compositions \( (\frac{93}{7}, \frac{90}{10}, \frac{80}{20}, \text{and } \frac{65}{35}) \). These diagrams indicate the partial ionic conductivity over the range of the present measurement has generally reached its maximum value in the activity range between \( 10^{-1} \) atm and \( 10^{-5} \) atm. Further reduction in the oxygen activity would appear to produce little, if any, increase in the ionic transference number. Consideration of these results in the light of earlier studies on undoped PZT compositions by Gerson and Jaffe \(^{34}\) and others \(^{33, 35}\) point to a very low and perhaps insignificant ionic transference number in PZT compositions that have no donor additions. Figures 20 and 21 depict ionic transference number as a function of titanium content at several temperatures and oxygen activities. These diagrams clearly demonstrate that the centrally located (BCC) titanium atom has a great influence on the partial ionic conductivity in PZT. Based upon an earlier work by Kofstad, \(^{16}\) which considers trivalent as well as tetravalent titanium ions.
in rutile, Ezis\textsuperscript{41} has indicated the possibility of a trivalent titanium ion mechanism in PZT compositions. The formation of titanium +3 ions is based primarily upon a mass action equation between the gas phase, titanium +3, and titanium +4 ions. The greater the titanium content in the PZT composition, the greater the concentration of titanium +3 ions in the lattice. The existence of titanium +3 ions has been considered in rutile at temperatures between 900°C and 1300°C and oxygen activities ranging between $10^{-10}$ atm and $10^{-18}$ atm.\textsuperscript{16} In that work, Kofstad\textsuperscript{16} concludes that titanium in the +3 state occurs only at extremes of high temperature and low oxygen activities corresponding to a substoichiometric state in rutile.

Based upon results obtained by Kofstad\textsuperscript{16} and others\textsuperscript{15, 17}, it is proposed here that the change in ionic transference numbers resulting from titanium content in PZT compositions is not a result of titanium +3, but rather a low temperature effect such as associations or pairing.

The generalized reaction between two imperfections which combine to form an associated complex is given by,

$$nA + mB \rightarrow (A_n B_m)$$

where $n$ and $m$ represent the respective numbers of defects A and B required for the formation of the complex. If the assumption is made that both the single imperfections
and the associates are randomly distributed throughout the solid, the concentration of associates and independent defects are related by the law of mass action according to,

\[ K_{AB} = \frac{(A_n B_m)}{[A]^n [B]^m} \]

with the familiar result that the equilibrium constant is given by,

\[ K_{AB} = \exp \left( -\Delta G^0 / kT \right) \]

In the case where single imperfections combine to form a simple associate pair, both \( n \) and \( m \) are set equal to unity.

The possibility of association is not restricted to oppositely charged defects, and it is possible for neutral imperfections to combine and form a pair. One example of the pairing between uncharged imperfections is that between foreign atoms and vacancies in polar crystals. \(^1^2\)

The proposal is made that an association takes place between a lead vacancy and a titanium ion. The formation of an association between a lead vacancy and a titanium ion would be given by the equation,

\[ Ti_{Ti}^+ + V_{Pb}^+ \rightarrow (Ti_{Ti} V_{Pb}^+) \]

The equilibrium constant for this reaction is given by,

\[ K_{pair} = \frac{[(Ti_{Ti} V_{Pb}^+)]}{[Ti_{Ti}^+] [V_{Pb}^+]^2} \]
This assumption indicates that the formation of associated titanium ions and lead vacancies will be driven by the concentration of lead vacancies and the amount of titanium incorporated into the ceramic. Because the concentration of $V_{\text{Pb}^+2}$ increases as $P_{O_2}$ increases, complexing would increase as $P_{O_2}$ increases. This dependence is consistent with experimental results, shown in Figures 14 through 17.

A second possible association could conceivably take place between the titanium ions and lead vacancies, leading to pairing of lead vacancies in the vicinity of a titanium ion. The pertinent equations describing the reaction between vacancies and the resulting equilibrium constant are given by the following:

$$\text{Pair concentration} = \frac{(Ti_{\text{Ti}} V_{\text{Pb}^+2})^{+4} + V_{\text{Pb}^+2}^{+x} (V_{\text{Pb}^+2}^{+2} \cdot \frac{x}{2} Ti_{\text{Ti}})}{\left[(Ti_{\text{Ti}} V_{\text{Pb}^+2})^{+4}\right]}.$$  

$$K_{\text{triplet}} = \left[\frac{(Ti_{\text{Ti}} (V_{\text{Pb}^+2})^{+4})}{(Ti_{\text{Ti}}^{+4}) [V_{\text{Pb}^+2}]^2}\right].$$

The pair concentration will have the same titanium concentration dependence as that described for associations in Equation 31, but will now be related to the square of the concentration of unassociated lead vacancies.

Although it is not clear which type of reaction is taking place in $\text{Nb}_2\text{O}_5$-doped PZT, there is ample evidence that the presence of the titanium ion in the BCC position
has a pronounced effect upon the concentration and/or mobility of lead vacancy imperfections. According to Figures 14 through 17, the 65/35 composition has a maximum ionic transference number of .50 at the low extremes of oxygen activity, while the 93/7 and 90/10 compositions possess a transference number greater than .90 in this region between $10^{-4}$ atm and $10^{-6}$ atm. The decreased ionic transference number in the high titanium compositions is noted over the entire experimental range of oxygen activities but is more pronounced at the higher activities corresponding to $10^{-2}$ atm to $10^{-1}$ atm. In this region the increased concentration of lead vacancies is possibly forcing the creation of many associations or pairs according to Equations 81 and 84. Qualitatively and experimentally the total fraction of associations or pairs in polar crystals have been found to be a sensitive function of unassociated defects, and an increase in independent defects over the range of one order of magnitude has resulted in an increase in the associated fraction from approximately 10% to greater than 90%, where the associated or paired fraction is represented by the quotient of associates and total independent imperfections according to,

$$\beta_{AB} = \frac{(AB)}{A + B}.$$
The rapid decrease in total conductivity and the decline in partial ionic conductivity in the oxygen activity range between $10^{-3}$ atm and $10^{-1}$ atm are very possibly the result of significant numbers of lead vacancies associating with the high concentration of titanium contained in 80/20 and 65/35 materials, although the same minima are noted in all PZT compositions. The creation of a large fraction of associates could lead to a concentration of lead vacancies which are immobilized in the lattice near the titanium ion, and are unable to participate in the net movement of ions under the influence of an externally applied electric field. The ability of the ceramic to form large numbers of pairs or triplets depends only upon the ability of one of the associated defects to move through the crystal. In this particular case, it would appear that the mobile lead vacancies, which have been assumed responsible for ionic conductivity, meet the requirement.

In this particular study, the approach to equilibrium emf was monitored by recording the electromotive force across specimens of the various compositions as a function of time after introducing step changes in the oxygen gas phase. Figures 18a and 18b show the result of these measurements at 500°C and 600°C for two compositions. It is apparent that the time constant is essentially fixed over the entire range of oxygen activities used in this
work. The invariant slopes are an indication that the same rate-limiting process is in effect at all oxygen activities and partial pressure ratios.
VII. SUMMARY AND CONCLUSIONS

The following conclusions can be deduced from experimental observations and data analysis concerning the system of lead zirconate titanate (PZT) polycrystallites.

i. A combined lead vacancy and substitutional model has been applied to the PZT ceramic system in the oxygen activity range between 1 atm and $10^{-6}$ atm ($600^\circ$C), and 1 atm and $10^{-8}$ atm ($500^\circ$C). The model has been used to predict the dependence of defect concentration on oxygen activity in the surrounding gas phase. Theoretical predictions for hole and lead vacancy concentrations are in accord with earlier studies by Gerson and Jaffe and others and are applicable to pure and doped PZT ceramics.

ii. Undoped PZT compositions have been considered theoretically, and in terms of data obtained using $\text{Nb}_2\text{O}_5$-doped compositions, and are concluded to be p-type semiconductors over the range of measurement covered in this work. PZT specimens having a 1 w/o addition of $\text{Nb}_2\text{O}_5$ have been studied in detail, and have been found to exhibit
mixed conduction in the oxygen activity range of $10^{-8}$ atm to $10^{-4}$ atm. At higher oxygen concentrations, all compositions tend to exhibit increased p-type semiconduction, with complete transition to p-conduction by approximately 1 atm (oxygen activity).

ii. It has been proposed that increased titanium content reduces the partial ionic conductivity by the formation of an immobile association or complex. This formation of defect complexes is favored at lower temperatures and high unassociated defect concentrations, corresponding to the more oxidizing regions of this work.

In summary, this effort appears to be the first complete study of conductivity and ionic transference numbers in PZT of several compositions covering a significant range of oxygen activities in the gas phase. Experimental results indicate that niobia-doped PZT compositions are mixed conductors at oxygen activities below $10^{-4}$ atm, while tending toward p-type semiconductors at increased oxygen concentrations. These results are in agreement with compositional studies by Gerson and Jaffe,\textsuperscript{3h} and EMF studies conducted by Ezis.\textsuperscript{41}
APPENDIX A

With most laboratory furnaces and their associated galvanometer on-off controllers, there are two effects which contribute to the variation above and below the set point temperature: thermal inertia of the furnace and galvanometer pivot friction. The first factor is the result of furnace winding and thermocouple proximity, while the second comes from the finite friction present in the galvanometer movement. The result of these two factors is a dead zone about the set point where the galvanometer movement is not affected by slight changes in the thermocouple signal, and an oscillation in furnace temperature having a period of 5-15 min. depending on the location of the thermocouple relative to the heating elements.

Reid has discussed a method for reducing the short- and long-term temperature fluctuation by modulating the thermocouple signal with a low-frequency a-c voltage. The superposition of the a-c signal on the d-c thermocouple output results in a voltage that drives the galvanometer above and below the dead zone that surrounds the set point. This effectively turns the controller on and off once.
during each modulated cycle, the ratio of "on" to "off"
time being determined by the average d-c signal. The power
delivered to the windings is proportioned in time such that
the furnace cannot oscillate with its natural frequency, and
the effect of the dead zone is minimized. In this particular
circuit, two n-channel FET's are used in a free running
multivibrator configuration to obtain a square wave
having a period of about 10 sec. Ten seconds was
chosen since the galvanometer movement is damped and
cannot follow any signal having a period of less than
5 sec/cycle.

The circuit shown in Figure 23 functions as follows.
When power is applied, both FET's are in the "on" mode
as the gates are at essentially the same potential as
the sources. As $S_1$ is closed, capacitor $C_1$ is charged
through $Q_2$ to the full supply voltage of the battery.
When this switch is released (a push button is used for $S_1$),
the source of $Q_1$ immediately returns to near ground and
$C_1$ drives the gate of $Q_2$ about 4V negative with respect
to ground. This negative pulse turns $Q_2$ off as the gate
is now negative compared to the source of $Q_2$. $C_1$
discharges through $R_2$ according to the $R_2C_1$ combination
allowing the gate of $Q_2$ to return to ground. At this
point, $Q_2$ will turn on driving the gate of $Q_1$ negative via
coupling capacitor $C_2$, turning $Q_1$ off. The RC decay at the
FIGURE 23. Solid State Thermocouple Modulator. LEGEND: (Q1 and Q2) n-channel FETs in a free-running multivibrator configuration, (Q3 and Q4) silicon pnp emitter-follower output transistors.
gate of $Q_1$ eventually turns $Q_1$ on and the sequence is repeated. The square wave obtained from the two FET's is integrated by the 1-meg resistors and the 4-$\mu$F capacitor to obtain a double ramp function which is more suitable for driving the galvanometer. $Q_3$ and $Q_4$ are pnp silicon transistors used in a common collector mode to drive the low impedance load which will be added to the galvanometer circuit. The 1-ohm resistor added to the galvanometer was chosen for two reasons; the addition of more than 1–2 ohms will alter the dampening of the galvanometer and require recalibration of the temperature scale, while any load of less than 1 ohm is difficult to drive with the output transistors. The two trimpots are incorporated into the circuit in order to adjust the magnitude of the modulating signal for optimum results. This adjustment also makes it possible to use the circuit to drive various types of thermocouples since the output voltage varies from one type to the next. When platinum-rhodium thermocouples are used, the modulating signal need only be about 1/10 mV, while for chromal-alumal it must be about 1 mV in order to sweep through the dead zone at 1000°C.
APPENDIX B

The gas storage and purification system is depicted in Figure 24, and is identical for both ac conductivity and emf measurements. The gas is stored in 330 cu. ft. "T" cylinders, (A), to which are connected Hoke "Phoenix" pressure regulators, (B). The regulator output pressure may be adjusted over a range from 1 to 10 lb/sq in. In an effort to minimize gas contamination prior to introduction into the sample chamber, all purification and mixing equipment are fabricated from Pyrex glass.

Water, carbon dioxide, and traces of hydrocarbons are removed in the first stage of purification which contains, in succession; Drierite(1), Ascarite(2), and magnesium perchlorate(3). After passage through this stage, the mixing gases are composed of either argon (with traces of oxygen and other inert gases) or oxygen (with traces of inert gases). Several argon/oxygen premixed gases were used upon occasion.

Commercially available argon contains oxygen on the order of 10 ppm, and for accurate mixing at low concentrations this oxygen must be removed. In the catalytic oven, (D), small pellets of activated copper
FIGURE 24. Gas Storage and Purification System. LEGEND: (A) 330 cu ft storage cylinder; (B) Hoke regulator; (C) first purification stage containing, (1) Drierite, (2) Ascarite, (3) magnesium perchlorate, (D) catalytic oven containing BASF catalyst, (E) last purification stage—identical to (c), (F) "Varia" for catalytic oven temperature control, (G) thermometer.
(BASF catalyst) are maintained at $250^\circ C$ which effectively reduces oxygen activity in the argon to the limits imposed by the equilibrium reaction $\frac{1}{2}O_2 + 2Cu = Cu_2O$. This reaction vessel is a 35 mm o.d. Pyrex manifold wrapped with asbestos tape and nichrome heating element. The temperature is controlled by the Variac, (F), and monitored by the thermometer, (G). This manifold is heated only when purifying argon gas, and is not used in the oxygen purification train.

The third stage of purification is identical to the first stage, and is included to remove any water vapor created in the catalytic oven section of the apparatus.
APPENDIX C

The precision gas mixing system is shown in Figure 25 and functions in the following manner. The purified oxygen and argon are independently admitted to the two flow meters via the 3-way stopcocks, (A). A portion of each gas passes through the back pressure vent tube, (C), and is bubbled up into the back pressure liquid column, (B). The height of the liquid column in this chamber establishes the gas pressure in the inlet portion of the flowmeter, since the regulator alone cannot be used accurately to maintain the low pressure in the mixing system. The second portion of the two mixing gases proceeds from stopcock, (A), into the orifice manifold, (D), where it passes through a very small glass capillary tube, (E). The pressure drop across the capillary tube is displayed by the manometer, (F), which is connected to both sides of the capillary orifice. The difference in manometer liquid levels is the direct indication of flow rate through the capillary. Using capillaries of three different sizes, calibrated mixing ratios for 1:1 to 250:1 can be obtained with good accuracy. The capillary manifold, (D), and ground glass joints, (J), have been incorporated into the system to facilitate quick
FIGURE 25. Precision Gas Mixing System. LEGEND: (A) 3-way stopcock, (B) back pressure liquid column, (C) back pressure vent tube, (D) orifice manifold, (E) capillary tube, (F) manometer, (G) mixing chamber, (H) bulk liquid column, (I) 5-way stopcock, (J) ground glass joints.
changes in the mixing ratio. The bulk liquid column, (H), and the two-way stopcock valve, (I), are used to maintain the desired liquid level in the back pressure column. Dibutylphthalate is used in both manometer columns and back pressure columns as it has essentially no vapor pressure which could contaminate the system. The output from both flowmeters is mixed in the mixing bulb, (C).
<table>
<thead>
<tr>
<th>Temperature</th>
<th>$P_02$(atm)</th>
<th>Conductivity (mho-cm)$\times 10^6$</th>
</tr>
</thead>
<tbody>
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<td>500</td>
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<td>32.5</td>
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<td>$1.4 \times 10^{-6}$</td>
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TABLE 1. Conductivity vs $P_02$ for Calcia (Figure 13) stabilized zirconia at 500°C and 600°C.
<table>
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<tr>
<th>Temperature (°C)</th>
<th>$P_{O_2}$ (atm)</th>
<th>Conductivity (mho-cm)$^{-1} \times 10^6$</th>
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</thead>
<tbody>
<tr>
<td>500</td>
<td>1.0</td>
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<tr>
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<tr>
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TABLE 3. Conductivity vs $P_0^2$ for PZT 90/10 at 500°C and 600°C.

<table>
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<th>Temperature ($^\circ$C)</th>
<th>$P_0^2$ (atm)</th>
<th>Conductivity (mho-cm)$^{-1} \times 10^6$</th>
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<tbody>
<tr>
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TABLE 4: Conductivity vs $P_{O_2}$ for PZT 80/20 at 500°C and 600°C.
(Figure 11)

<table>
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<th>Temperature (°C)</th>
<th>$P_{O_2}$ (atm)</th>
<th>Conductivity (mho-cm) x 10^6</th>
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TABLE 5. Conductivity vs $P_0^2$ for PZT 65/35 at 500°C and 600°C.

<table>
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<th>Temperature (°C)</th>
<th>$P_0^2 (\text{atm})$</th>
<th>Conductivity $(\text{mho-cm}) \times 10^6$</th>
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### TABLE 6: Ionic Transference Number vs Oxygen Concentration
(Figure 14) PZT 93/7 at 500°C and 600°C.

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<th>Temp.</th>
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<th>$t_{ion}$</th>
<th>Temp.</th>
<th>Conc. $P_{O_2}$ (atm)</th>
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<td>.88</td>
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<tr>
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<td>$2.0 \times 10^{-5}$</td>
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<td>$1.6 \times 10^{-3}$</td>
<td>.88</td>
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<td>$9.0 \times 10^{-3}$</td>
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<td>$4 \times 10^{-1}$</td>
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TABLE 7: Ionic Transference Number vs Oxygen Concentration. PZT 90/10 at 500°C and 600°C.

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<th>Temp.</th>
<th>Conc. P$_{O_2}$ (atm)</th>
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<th>Temp.</th>
<th>Conc.</th>
<th>t$_{ion}$</th>
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</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
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<td></td>
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<td>$10^{-8}$</td>
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<td>$10^{-8}$</td>
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<td>500</td>
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TABLE 9. Ionic Transference Number vs Oxygen Concentration. PZT 65/35 at 500°C and 600°C.

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<th>Temp.</th>
<th>Conc. (P_0^2) (atm)</th>
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Sample 2

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<th>Temp.</th>
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BIBLIOGRAPHY


52. Haertling, G. H., "Physical and Electrical Properties of Hot-Pressed Pb$_{90}$Hg$_{10}$(Zr$_{68}$Ti$_{10}$Sn$_{22}$)$_{96}$O$_{3}$," SCITM 199-62(51), 1962.


