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(Ph. D. thesis)

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Electrical Conductivity in Lithium Ferrite and Lead Zirconate-Titanate Ceramics

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ELECTRICAL CONDUCTIVITY IN LITHIUM FERRITE AND LEAD ZIRCONATE-TITANATE CERAMICS

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ABSTRACT

Electrical conduction in polycrystalline lead zirconate-titanate and lithium ferrite ceramics was investigated. The effects of temperature, impurities, defect structure, nonstoichiometry, and microstructure on the electrical conductivity were determined and compared with the existing theoretical models.

Polycrystalline compacts of lead zirconate-titanate and lithium ferrite were fabricated with various dopants and stoichiometry. A packing powder technique in 1 atm oxygen was used to control the stoichiometry of the samples. The dc resistivity was measured by using a guard-ring method. Thermoelectric power measurements were also conducted to characterize the type of charge carriers contributing to the conduction process.

It is shown that electrical conduction in lead zirconate-titanate follows typical semiconductor behavior. Holes contributed by lead vacancies are the major charge carriers. Impurity ions which serve as acceptors or donors significantly affect the conduction process. The activation energy is 3.6 eV for intrinsic conduction, 1.41 eV for extrinsic conduction due to Nb2O5 doping, and 1.01 eV due to Sc2O3 doping.

Data are presented to show the influence of stoichiometry which affects the concentration of charge carrier, and temperature which
affects the mobility of charge carrier, on the dc resistivity of lithium ferrite. The exponential temperature dependence of the mobility is in agreement with the proposed electron-hopping model. Charge transport occurs by thermally activated electron hopping between the octahedral Fe$^{+2}$ and Fe$^{+3}$ ions. The hopping activation energy is 0.06 eV. Experimental evidence indicates that there is no influence of microstructure on the electrical conduction behavior. The effect of controlled amounts of NiO and NiFe$_2$O$_4$ dopants on the dc resistivity of lithium ferrite is also presented.
I. GENERAL INTRODUCTION

The rapid growth of the electronics industry is requiring an ever greater number of materials beyond those presently developed semiconductors, piezoelectrics, insulators, and magnetics. Ceramic materials claim particular attention owing to their outstanding properties—especially their electrical resistivity. Ceramics have extensive applications in the electronic industry today, e.g., in their use in transistors, resistors, thermisters, resonators, etc.\(^1\)

Ceramics are also used as switching materials. A quantitative understanding of the basic mechanism of charge transport in ceramics is needed to predict electrical conductivity and for development of new materials.

One of the major problems in studying the electrical properties of ceramic materials is the difficulty to prepare a single crystal of high perfection and purity or a polycrystalline material with well-defined composition and microstructure. The presence of defects, mixed ionic-covalent bonding, and complex crystal structures make the analysis of transport of charge carriers in ceramic materials difficult.

The conductivity ($\sigma$) of any material is a product of the charge carrier concentration ($n$), their charge ($e$), and their mobility ($\mu$):

$$\sigma = ne\mu$$  

(1)

From the type of charge carrier contributing to the conduction process, electrical conduction in a ceramic solid can be characterized as ionic or electronic conduction.

Ionic conduction results from the movement of charged ions in the material.\(^2\) The mobility of ions can be related to the self-diffusion
coefficient (D) and thermal energy as follows:

\[ \mu = \frac{eD}{kT} = \frac{eD}{kT} \exp \left( -\frac{E}{kT} \right) \]  

(2)

where \( E \) is the activation energy for ion mobility. The ion movement also depends on the vacancy concentration. The number of intrinsic vacancies present at equilibrium is given by

\[ \frac{n}{n_0} = \exp \left( -\frac{W}{2kT} \right) \]  

(3)

where \( W \) is the energy required to form a lattice vacancy. Ionic conductivity can then be written as

\[ \sigma = \frac{Dn e^2}{kT} = \sigma_0 \exp \left( -\frac{W}{2kT} \right) \exp \left( -\frac{E}{kT} \right) \]  

(4)

Electronic conduction results from the movement of electrons or holes in solids. The existing models are described in the following sections:

A. Wide Band Semiconductors\textsuperscript{3,4}

Electrical conductivity in this model is based on the concentration of charge carrier being the significant term in Eq. (1). Thermal energy may free a fraction of the valence band electrons to the conduction band and leave holes in the valence band. Both electrons in the conduction band and holes in the valence band can serve as charge carriers. The valence band and conduction band are separated by an energy gap (\( E_g \)). The concentration of charge carriers is given by:

\[ n = n_0 \exp \left( -\frac{E_g}{kT} \right) \]  

(5)
If impurities are added to the lattice so as to introduce donor or acceptor states in the band gap, then the activation energy appearing in Eq. (5) becomes $\Delta E < E_g$, where

$$\Delta E = \begin{cases} E_c - E_d, & \text{donors} \\ E_a - E_v, & \text{acceptors} \end{cases}$$

The conductivity of the doped sample then becomes

$$\sigma = \begin{cases} \sigma_{\text{intrinsic}} + n_{d,o} e^u e^{(-\Delta E/kT)}, & \text{donors} \\ \sigma_{\text{intrinsic}} + n_{a,o} e^u e^{(-\Delta E/kT)}, & \text{acceptors} \end{cases}$$

If the concentration of either donor impurities, $n_{d,o}$, or acceptor impurities, $n_{a,o}$, is sufficiently high, then the intrinsic conduction process is masked by impurity conduction. The mobility of charge carriers is not strongly temperature dependent. It follows that the exponential increase in conductivity with temperature is due to the increase in charge carrier concentration.

B. Narrow Band Model (Hopping Mechanism)

The basic ideal of this model is that the electron-lattice interaction is so strong that the charge carrier cannot move freely even with the existence of a partially filled band. The charge carrier tends to be "localized" in a region. For transport to occur, an activation energy barrier must be overcome so that the charge carrier can hop to another favorable site. In this case, the charge carrier concentration is a constant. The mobility is then given by

$$\mu = \mu_0 T^n \exp\left(-\frac{E}{kT}\right)$$
where \( g \) is the activation energy for hopping and \( n = 1 \) or \( 3/2 \) has been proposed. It thus follows that the exponential growth in conductivity with temperature is due to the mobility dependence on temperature.

For economic reasons, polycrystalline ceramics rather than single crystals are used extensively in electronic devices. So the effect of microstructure on the electrical conductivity is of considerable importance. For heterogeneous materials, mixing rules based on a layered model have been derived to predict the upper and lower bound of the electrical conductivity. Porosity will decrease the conductivity due to the reduction of the conduction cross sectional area. Grain boundaries can serve as either an easy conduction path or a high resistivity path compared with bulk depending on the composition and structure of the grain boundary.
II. THE LEAD ZIRCONATE-TITANATE SYSTEM

A. Introduction

Lead zirconate-titanate (PZT) is an important ceramic material widely used for piezoelectric devices. It is ferroelectric and has a perovskite structure. The crystal structure may be described as a cubic close-packed ordered arrangement of lead and oxygen with the lead ions in the corner position and oxygen ions in the face position. The octahedral site at the center of the cell is bound by six oxygen ions and is occupied by either zirconium or titanium ions. The other six octahedra on the cube edges, bound by four oxygen anions and two lead ions, are unoccupied. The tetrahedral sites are bound by one lead ion and three oxygen anions. These are also empty. Lead zirconate-titanate ceramics are of interest because of their large piezoelectric effects, high curie temperature, and high dielectric permittivity. This material is also considered as a potential candidate in several electro-optical devices due to their superior electro-optical characteristics, and in memory storage elements due to their rapid and reversible ferroelectric domain reorientation.

Electrical conductivity is an important physical parameter in use of piezoelectric ceramics. Compositions which are too conductive are difficult to pole, tend to overheat in high power applications and generally have undesirably high dielectric losses which limits efficiency. The electrical conduction mechanism in PZT has not been clearly defined. The energy-band structure of PZT has not been determined.
Heckman et al. 12 studied the mechanism of conduction, i.e., whether electronic or ionic, for a number of compositions of polycrystalline lead zirconate-titanate Pb(ZrxTi1-x)O3 + 1 wt% Nb2O5 by using electrochemical concentration cells. The results indicated that the conduction is almost entirely electronic for x < 0.52 in the temperature range 250-500°C. Burt and Krokowski 13 reported that electronic conduction was dominant above x = 0.4 in Nb2O5 doped Pb(Zr1-xTi x)O3. Ideda and Tanada et al. 14 gave a brief report on niobia-doped PZT. The resistivity was greatly increased by the addition of Nb2O5. Gerson and Jaffe 15 found that lead zirconate-titanate ceramics prepared by sintering in air had p-type conduction. The resistivity of PZT decreased with increased oxygen pressure during sintering. They proposed that the electrical conduction in PZT resulted from an excess of lead vacancies. This proposed model has not been verified. Takahashi 16,17 measured the electrical resistivity and its temperature variation for lead zirconate-titanate ceramics containing various metal oxides as dopants in the temperature range of 25-400°C. It was found that some dopants had no effect, some increased the resistivity and others increased it in small concentrations, and they decreased it in larger concentrations. No complete explanation was given for these results.

All previous investigators measured the resistivity by using a two-point method. 11 The results obtained, therefore, did not represent the true bulk resistivity due to possible surface conduction present in high resistivity ceramic materials. In this investigation, a guardring method was used for measuring the true bulk resistivity. 2 Furthermore, thermoelectric effects which may introduce serious errors
in the measurement were also eliminated. The properties of polycrystalline ceramic materials cannot be directly correlated with the chemical composition without taking into account the effects of microstructure. No effort has ever been made to determine the influence of processing parameters and microstructure on electrical conduction of PZT in previous investigations. Another problem which has not been completely overcome by investigators is defining the electrical properties of PZT is the difficulty in controlling the sample composition during sintering. It is well known that PZT tends to decompose and lose PbO by evaporation at high temperature. Maintaining the correct stoichiometry during firing is necessary. It has been reported that even a small amount of PbO loss from the system can cause appreciable differences in electrical and physical properties. Consequently, the control of the compositional changes due to PbO evaporation is an important parameter during the fabrication of PZT samples. Several attempts have been made in sintering PZT samples in the presence of a PbO atmosphere. Stoichiometry variations were still observed due to the lack of information about the correct PbO activity. Recently, Holman and Fulrath established the PbO activity above the PbZrO$_3$-PbTiO$_3$ system and determined the single-phase width of the compounds in the system with temperatures. Thus, an improved packing-powder technique was established that allowed reproducible processing of PZT compositions to a known stoichiometry. In the present work, this fabrication procedure was employed to control the material loss from PZT during sintering. For the purpose of comparison, PZT samples were fabricated from chemically prepared solution as well as mixed oxide powder as raw materials. The purpose of this study
was to determine the mechanism of electrical conduction in lead zirconate-titanate ceramics with better defined compositions and using better measuring techniques. The affects of impurities, microstructure, and temperature on electrical conduction were determined.

B. Experimental (Chemically Prepared PZT)

1. Powder Preparation

In this research, a PZT composition of Pb(Zr_{0.5} Ti_{0.5})_3, which will be written as PZ_{0.5} Ti_{0.5}, was prepared from chemical compounds. A flow chart outlining the procedure of powder preparation is shown in Fig. 1. This chemical preparation method essentially followed the procedure outlined by Haertling and Land. The raw materials used for the principal constituents were lead oxide powder, zirconium tetra-butoxide liquid, and titanium tetra-butoxide liquid. Utilizing liquid solutions can substantially reduce chemical inhomogeneity. Scandium oxide and niobium oxide powder were used as dopant materials. Proper proportions of raw materials were mixed in a blender and then co-precipitated from solution by adding distilled water. The blended slurry was dried at 100°C for 24 hr. The dried product was calcined at 500°C for 24 hr. After calcining, the powder was milled for 4 hr in isopropyl alcohol using ZrO2 balls. The powder was calcined again at 500°C for 8 hr. After the second calcination, the powder was again

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* Baker, regent grade.
** Dynamite Nobel (TBT, TBZ).
† Ventrol Alfa product 99.9%
‡‡ Matheson, Coleman and Bell.
milled for 2 hr. The powder was then passed through a 325 mesh screen to complete the powder preparation process. Compositions were made containing no dopants, and 2 and 4 mole% ScO, 2 and 4 mole% NbO, and 2 and 4 mole% ScO, 2.

2. Sample Preparation

The powder was cold pressed at 10,000 psi in a 1 in. diameter steel die. The pressed pellets with a green density about 2.6 gm/cc were sintered in a platinum crucible. All sintering runs began by heating the furnace at a constant rate of 300°C/hr to the sintering temperature 1200°C, holding for 16 hr and then cooling at the natural rate of the furnace. The high vapor pressure of PbO necessitated the use of a packing powder to provide an exact known PbO vapor surrounding the pellets. Thus, the sample and the powder were in local atmospheric equilibrium and the material loss from the system could be controlled. Undoped and niobium-doped samples were always buried deeply in a packing powder of lead zirconate plus 5 wt% zirconia while sintering in 1 atm oxygen. For scandium-doped samples, lead zirconate-titanate plus 5 wt% PbO was used as a packing powder for sintering in 1 atm helium.

3. Sample Characterization

Density of the sintered samples were measured by water displacement and also by geometric measurements. Theoretical density for PZT was taken as 8 gm/cc. Density of the undoped and niobium-doped samples were above 98% theoretical density and the scandium-doped samples achieved 95%. X-ray diffraction was used to identify phases present. In all samples, X-ray peaks typical of the PZT phase were found. For the microstructure examination, samples were polished and then chemically
etched in a 35% HCl solution with three drops of HF per 100 ml of solution. Observations of etched surfaces were made using scanning electron microscopy and are shown in Fig. 2. From the grain-size measurements, the grain boundary mobility was found to be sensitive to the presence of dopants. The undoped composition showed discontinuous grain growth. Both niobium and scandium served as grain-growth inhibitors as observed by Atkins and Fulrath.\textsuperscript{19}

4. Electrical Conductivity Measurement

Direct current bulk resistivity was measured by using a guarding method as shown in Fig. 3. Sputtered gold electrodes were used to provide ohmic contacts. The surfaces of all the sintered samples were ground to a depth sufficient to eliminate inhomogeneity due to any surface effects before electrodes were applied. The contact resistance was found to be negligible. Direct current voltages provided by dry cells were used for all measurements. The fields used were 100 v/cm for a resistivity higher than $10^8$ $\Omega$-cm and 5 v/cm for resistivities lower than $10^8$ $\Omega$-cm. The voltages across the sample and known resistance were measured by a Keithly 610B electrometer. Bidirectional measurements were made and the results from each polarity were averaged to eliminate the thermoelectric contribution to the measured signal. Most of the measurements were conducted in the temperature range of 150-500°C.

5. Thermoelectric Power Measurements

Thermoelectric power measurements were made to determine the type of charge carrier contributing to the conduction process. The samples used were typically about 2 cm diameter and 3 mm thick. Both plane surfaces were sputtered with gold to improve electrical and thermal
contact. The gold-plated faces were placed between two stainless steel pistons, one of which was kept hotter than the other to establish a temperature gradient. The potential difference across the electrodes was measured by a potentiometer. The measurement system was calibrated by using p and n type Si wafers.

C. Results and Discussion (Chemically Prepared PZT)

The influence of dopants on the resistivity of PZT at various temperatures is shown in Fig. 4. The resistivity increases with increasing niobium and decreases with increasing scandium. In Fig. 5 the logarithm of the resistivity is plotted against reciprocal temperature. The resistivity for all samples decreases with increasing temperature. There is a straight-line relationship between log resistivity and inverse absolute temperature for a given composition. This is typical for a semiconductor with the simple expression.

\[
\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right)
\]

(9)

where \(\sigma\) = conductivity

\(\sigma_0\) = constant

\(\Delta E\) = activation energy

\(k\) = Boltzmann constant

and

\(T\) = absolute temperature.

The activation energy can be calculated from the slope of the resulting straightline segments in Fig. 5. Figure 5 shows that the addition of \(\text{Nb}_2\text{O}_5\) does not change the activation energy for electrical conduction, whereas 1 mole% \(\text{Sc}_2\text{O}_3\) is sufficient to decrease \(\Delta E\) from 1.41 eV to 1.01 eV.
Measurements of the thermoelectric voltage showed that hole conduction (p-type semiconductors) dominated in all samples.

In semiconducting materials, electrons can be excited from the valence band to the conduction band and contribute to the conduction process. For ceramic materials, the band gap is wide. Therefore, the probability of a conduction electronic state being occupied, that is, for intrinsic conduction, is rather small at low temperature. When a defect or impurity atom is added to the crystal, it destroys the periodicity and, as a result, introduces local electronic states which may lie within the band gap and serve as a donor or acceptor state as shown in Fig. 6. In considering electrical conduction in ceramics, we are mainly concerned with defects and impurities in the system.

For undoped PZT, high concentrations of interstitials are unlikely because the perovskite unit cell is already close-packed and the possible interstitial sites are bound by both positive and negative ions. Major defects are metal ion vacancies and oxygen ion vacancies. The p-type conduction suggests that electrical conduction in PZT is due to metal ion vacancies, that is, lead vacancies or zirconium/titanium vacancies.

In PZT ceramics, lead and oxygen are the two volatile components. The vapor pressure of zirconium, titanium, and their oxides are very low even at high temperature so these components are not readily lost by evaporation. The intrinsic nonstoichiometry of PZT across its single-phase region can be fixed by proper choice of multiphase packing powder composition. On this basis, an attempt was made to establish sample equilibrium with different multiphase packing powder compositions to determine the effect of the intrinsic nonstoichiometry on the
electrical conductivity of PZT. The packing-powder compositions chosen were lead zirconate plus 5 wt% zirconium oxide (PZ + Z) and lead zirconate-titanate plus 2.5 wt% zirconium oxide and 2.5 wt% titanium oxide (PZT + Z + T). The PbO activity of PZ + Z is higher than that of PZT + Z + T. The sintering of samples at 1200°C for 16 hr using different packing powder and 1 atm oxygen equilibrated the sample with the PbO activity set by the packing powder. Assuming that Schottky equilibrium is established such that

\[ [V_{Pb}] [V_{Zr/Ti}] [V_{O}]^3 = k_s \]  

where \( k_s \) = temperature-dependent constant

and brackets denote molar concentrations, is then predicted that lowering the lead activity at a fixed oxygen pressure will increase \([V_{Pb}]\), decrease \([V_{Ti/Zr}]\), and leave \([V_{O}]\) unchanged. It was found that the resistivity as shown in Fig. 7 of the samples equilibrated with the higher PbO activity by using PZ + Z packing powder is greater than that of the sample equilibrated with a PZT + Z + T packing powder during firing. Consequently, the electrical conduction in PZT is due to lead vacancies, not zirconium/titanium vacancies.

Doping is another mechanism for introducing vacancies. It has been established that Nb\(^{+5}\) and Sc\(^{+3}\) substitute for (Ti,Zr)\(^{+4}\) to create lead and oxygen vacancies respectively, as shown in Fig. 8. The lead vacancy concentration increases with increasing Nb_2O_5 content in the system. However, the present experimental results show that the conductivity drops with increasing Nb\(^{+5}\) content. This can be explained as a compensation effect when Nb\(^{+5}\) substitutes for (Ti,Zr)\(^{+4}\) on the B site.
in the perovskite structure to contribute a donor state. This donor state contributes electrons to the conduction process.

The ionization of Pb vacancies and Nb substitutional impurities in Kröger-Vink notation is

\[ V_{pb} = V_{pb}'' + 2h' \quad (11) \]

\[ Nb_{Ti,Zr} = Nb_{Ti,Zr}^- + e' \quad (12) \]

Assuming that all impurity states are ionized at high temperature, the requirement of macroscopic charge neutrality yields the equality

\[ [e'] + 2 V_{pb}'' = [Nb_{Ti,Zr}^-] + [h'] \quad (13) \]

Then, since the product

\[ [e'][h'] = K \quad (14) \]

is small for a wide band gap semiconductor we have

\[ [h'] > [e'] \quad (15) \]

and consequently

\[ [h'] \approx 2 \left[ V_{pb}'' \right] - [Nb_{Ti,Zr}^-] \quad (16) \]

The p-type electrical conductivity is the

\[ \sigma = \left\{ 2 \left[ V_{pb}'' \right] - [Nb_{Ti,Zr}^-] \right\} e_\mu h \quad (17) \]

which can be expected to decrease with increasing Nb, O, doping.

For scandium-doped samples, the concentration of oxygen vacancies increases. The resistivity drops with increasing amount of scandium in PZT. In this case conduction still occurs by the migration of holes (p-type conduction). It is probable that Sc$^{+3}$ ions serve as
acceptors. The substitution of Sc$^{+3}$ ions for (Ti,Zr)$^{+4}$ ions creates an acceptor level on the B site in the perovskite structure. For Sc$_2$O$_3$ doping, the charge neutrality condition for fully ionized Sc$^{+3}_{\text{Ti,Zr}}$ substitutional impurities becomes

$$[\text{e}'] + [\text{Sc}^{+3}_{\text{Ti,Zr}}] + 2[V^{''}_{\text{pb}}] = [\text{h}']$$

Again, since $[\text{e}'] << [\text{h}']$, the conductivity expression becomes

$$\sigma = \left\{2[V^{''}_{\text{pb}}] + [\text{Sc}^{+3}_{\text{Ti,Zr}}]\right\} e \nu_h$$

and the addition of Sc$_2$O$_3$ should increase the electrical conductivity, as observed experimentally.

The mobility of charge carriers in a semiconductor is not strongly temperature dependent. The activation energy for either intrinsic or extrinsic conduction in a semiconductor can be correlated with the ionization energy. The activation energy was plotted against the amount of dopants as shown in Fig. 9. The activation energy, 1.41 eV, is the same for undoped and niobium-doped PZT. This indicates that the conduction mechanism is the same and is due to hole migration contributed by lead vacancies. The activation energy is low, 1.01 eV, for scandium-doped samples. Therefore, Sc$^{+3}$ in solid solution on the B site contributes an acceptor level and gives p-type conduction with a lower activation energy.

Impurities can be added to a material by intentional doping or unintentionally during processing. The effect of ball milling impurities on the electrical conductivity of PZT was investigated and the result is shown in Fig. 10. There is a clean difference in the activation
energy of the two samples where the difference in specimen preparation was only the milling media used. Both samples showed p-type conduction. The activation energy is 1.05 eV for the material ground by an Al₂O₃ grinding media and 1.41 eV for the material ground using ZrO₂ grinding media. Previous work has shown Al⁺³ ions go into solid solution in PZT.²⁸ Because Al⁺³ goes into solid solution on the B site, it has the same effect as Sc⁺³ and leads to a lower activation energy.

When Al⁺³ ions are substituted for (Ti,Zr)⁺⁴ ions in the B sites, each dopant atom has three valence electrons compared with four for (Ti,Zr). Therefore, Al⁺³ can serve as acceptors. Holes are generated from the acceptors as

\[ \text{Al}^{\text{Ti,Zr}} \rightarrow \text{Al}^{\text{Ti,Zr}}^\prime + h^+ \]  

(20)

The conduction expression becomes

\[ \sigma = 2\left[ V_{\text{pb}}'' \right] + \left[ \text{Al}^{\text{Ti,Zr}}' \right] e^\nu \]  

(21)

and the addition of Al₂O₃ should increase the electrical conductivity, as observed experimentally.

The exponential dependence of the resistivity on temperature observed by other investigators is shown in Fig. 11. The actual resistivity and activation energy from various investigators differ considerably. These differences are undoubtedly due to impurities present in the samples and the different preparation techniques.

There is no information concerning the impurity content of the PZT samples that previous investigators used for their measurements. Gerson and Jaffe's¹⁵ work was performed in the early 1960's. Their samples were sintered in air and no attempt has been made to control
the material loss. A very low activation energy (0.89 eV) was reported in their study. Takahashi's results\textsuperscript{17} were published in 1970. He tried to control the PbO loss by surrounding the sample with a packing powder of the same composition during firing. He also had his samples in contact with Pt. Experiments in this laboratory have shown that Pt is a sink for Pb. Therefore, exact PbO activity is unknown and the control of stoichiometry can be questioned. It is interesting to note that the resistivity and the activation energy reported by Takahashi is almost identical to that for a sample ground by an Al\textsubscript{2}O\textsubscript{3} grinding media in this study. This clearly shows how important the effect of impurity content in raw materials or introduced during sample processing and the material loss during firing is on the electrical conductivity.

In studying the electrical resistivity of PZT over the temperature range 150-800°C, a change in activation energy was observed above 650°C. Above 650°C the activation energy was 3.6 eV. It is suggested that this activation energy is that for intrinsic conduction.

D. Experimental (PZT Prepared from Oxides)

1. Powder Preparation

For the purpose of comparison, mixed oxide powder with composition PZ\textsubscript{0.5}T\textsubscript{0.5} was prepared from lead oxide powder*, zirconium oxide powder**, and titanium oxide powder.\textsuperscript{†} The powder preparation followed the flow chart shown in Fig. 12. Scandium oxide\textsuperscript{‡‡} and niobium

\textsuperscript{*} Reagent grade, Baker.
\textsuperscript{**} Electronic grade.
\textsuperscript{†} Reagent grade, B&A
\textsuperscript{‡‡} Ventron Alfa Product, 99.9%. 
oxide powder were used as dopant materials. Proper proportions of raw materials were mixed by using isopropyl alcohol and ZrO₂ balls as a grinding media in a Sweco mill for 4 hr. The mixed slurry was pan dried at 100°C for 24 hr. The dried product was calcined at 800°C for 2 hr in a zirconia crucible. After calcining, 5 wt% PbO was added to the powder. The excess PbO in the PZT system would form a lead oxide rich liquid phase on heating and enhance sintering. The PbO right powder was milled for 4 hr in isopropyl alcohol and ZrO₂ balls then dried in an oven at 100°C for 24 hr. The powder was passed through an 80 mesh screen to complete the powder preparation process. Compositions were made to contain no dopant, 2 and 4 mole% Nb₂O₅ and 2 and 4 mole% ScO₁.₅.

2. Sample Preparation

The powder was cold pressed at 5,000 psi in a 1 in diameter steel die. No binder was used. The pressed pellets with a green density about 4 gm/cc were sintered. The sintering conditions for mixed oxide PZT were the same as that for chemically prepared PZT, i.e., sintered at 1200°C for 16 hr with a packing powder to buffer the loss of PbO.

In order to fabricate a series samples with controlled porosity, organic material was incorporated into the PZT powder prior to cold pressing to create pores. Proper portions of organic material were

* Matheson Coleman & Bell.
** Koldmount Powder, Vernon-Benshoff Co., Inc.
mixed with 2 mole% NbO$_{2.5}$ doped PZT powder. The powder was cold pressed. The pressed pallets were sintered at 1200°C for 16 hr in 1 atm oxygen and using PZ + Z as the packing powder. All sintering runs began by heating the furnace very slowly to 400°C. The organic material was decomposed in this burn out process and did not affect the densification of the surrounding ceramic materials. Thus, a controlled amount of porosity was produced in the samples.

3. Sample Characterization

Density of the undoped and niobium doped samples were above 99% theoretical density. The density of the 2 mole% ScO$_{1.5}$ doped sample achieved 95% theoretical density and that of 4 mole% ScO$_{1.5}$ doped sample was about 90%. X-ray analysis showed the typical PZT phase. No trace of a PbO phase appeared. The microstructures of the samples are shown in Fig. 13. The grain-growth behavior for doped and undoped material was found to be similar to that of chemically prepared samples. The line intercept method was used to measure the grain size. The measured grain size for mixed oxide and chemically prepared samples are shown in Fig. 14. The density of the NbO$_{2.5}$ doped controlled porosity samples were 85, 90, 95 and above 99% theoretical density.

4. Electrical Measurement

Guard-ring resistivity and thermoelectric power measurements were conducted. The techniques and the experimental conditions were the same as described in the previous sections.
The influence of temperature on the resistivity of the mixed oxide PZT with various dopants is shown in Fig. 15. They follow the same trend as the chemically prepared samples. This comparison is shown in Fig. 16. The activation energy for conduction in mixed oxide PZT was plotted against the amount of dopants shown in Fig. 17. All the samples showed p-type conduction. Niobium and scandium doped mixed-oxide PZT have the same activation energy as that of doped chemically prepared samples. This means that their conduction mechanism can be explained in the same way as that for chemically prepared samples. The activation energy of the undoped mixed oxide PZT is lower than that of undoped chemically prepared material. This is due to an impurity effect. Zirconium oxide and titanium oxide powder instead of tetrabutyl zirconate and tetrabutyl titanate chemical solutions were used as the principal constituents to prepare the sample. The impurity contents of elements such as Al are higher in the oxide powders than in the chemical solutions. Spectrographic analysis showed that the \( \text{Al}_2\text{O}_3 \) content is 0.05% in chemically prepared PZT and 0.3% in mixed oxide PZT.

Until now we have considered the resistivity problem only from the standpoint of defect structure. Because of differing fabrication techniques, complete densification is usually not achieved in ceramic materials. Consequently, most ceramic materials have residual porosity. For economic reasons, polycrystalline ceramics rather than single crystals are usually used for commercial application. A thorough understanding of the effects of porosity and grain size on the electrical properties of PZT is necessary for a complete characterization of these properties. Some work has been done to relate the ceramic microstructure of PZT to
its ferroelectric properties. Previous investigators always tried to control the grain size and porosity by varying the processing parameters, mainly the pressure, temperature, and time for hot-pressing or sintering. The PbO loss from the system is also affected by the processing parameters. Therefore, the previous studies, while obtaining data on the effect of grain size and porosity, have not clearly demonstrated that the defect structure has remained constant.

In this study, various amounts of an organic powder were introduced into the system to create pores. The sintering temperature and time were kept constant; therefore, the grain size and intrinsic defect structure remained the same for all samples with controlled porosity. The effect of porosity on the electrical resistivity is shown in Fig. 18. There is no evidence that porosity has a significant effect on the electrical conduction. Average grain size and bulk resistivity have been plotted against composition for both mixed oxide and chemically prepared samples in Fig. 14. It is observed that the smaller the grain size, the higher the electrical conductivity for both doped and undoped materials. It should be noted that the impurity content in the mixed oxide material was higher than in the chemically prepared material and, therefore, the grain-size effect is not the only factor in determining the electrical conduction.

In the NbO$_{2.5}$ and ScO$_{1.5}$ doped material, the electrical resistivity is greater in the larger grain-size material obtained from mixed oxide powders. Therefore, if the impurity content was reducing the resistivity as in the undoped material, this effect would not be observed. It is proposed that the grain boundaries can serve as lower
resistivity paths, but the effect is relatively insignificant when compared to the effect of the defect structure.

Tables summarizing the data from the measurements of bulk resistivity, thermoelectric powder, density, grain size, and the processing parameters of the chemically prepared and mixed oxide PZT are shown in Appendix Tables I and II, respectively.
III. THE LITHIUM FERRITE SYSTEM

A. Introduction

Because of its square loop magnetic properties coupled with superior temperature stability, lithium ferrite is a very promising magnetic material for use in core memories. It is ferrimagnetic and has an inverse spinel structure with the chemical formula

\[ \text{Fe}^{+3}_{1.0} \left[ \text{Li}^{+1}_{0.5} \text{Fe}^{+3}_{1.5} \right]_0^{-2} \text{O}_4. \]

The crystal structure of lithium ferrite may be thought of as a face centered cubic packing of oxygen ions with two different sites for the cations; i.e., the A site (tetrahedral site) and the B site (octahedral site). \( \text{Fe}^{+3}_{1.0} \) ions are on the A sites and \( \left[ \text{Li}^{+1}_{0.5} \text{Fe}^{+3}_{1.5} \right] \) occupy the B sites. Braun first discovered that a long-range ordering between \( \text{Li}^{+1} \) and \( \text{Fe}^{+3} \) on the B site can exist. The order-disorder transition temperature was reported as 735-755°C. Slow cooling causes the octahedral site ions to distribute uniformly in the space lattice with 3 \( \text{Fe}^{+3} \) ions followed by 1 \( \text{Li}^{+1} \) ion in the (110) direction.

Electrical conductivity which directly relates to the power loss of the system during use is an important physical parameter. The higher the conductivity, the larger the eddy current induced and thus the power loss. The electrical conduction in lithium ferrite has not been fully investigated. Reported resistivity data vary from a few ohm-cm to values many orders of magnitude higher.

For other inverse spinel ferrites (e.g., \( \text{CoFe}_2\text{O}_4 \)), it has been established that the electrical conduction can be satisfactorily described by a "hopping mechanism." Charge can transport among the octahedrally...
coordinated transition metal ions by electron or hole motion. The mobility of the charge carrier transported between like ion sites is given by a diffusion-type expression:

$$\mu = \frac{ed^2\nu}{kT} \exp\left(-\frac{g}{kT}\right)$$  \hspace{1cm} (22)

where $\mu$ = mobility of charge carrier
d = distance between octahedral sites
$\nu$ = effective lattice vibration frequency
and
$g$ = activation energy.

All previous investigators have adopted this hopping model for lithium ferrite.

West and Blankenship$^{35}$ studied the electrical properties for the series (Li$_{0.5}$Fe$_{0.5}$)$_{1-x}$Zn$_x$Fe$_2$O$_4$. Their results indicated that the measured resistivity of all compositions increased after heat treatment at 980°C for 4 hr due to oxygen pickup and reduction of the Fe$^{2+}$ content. Kato$^{36}$ observed that the dc resistivity of a B-site ordered polycrystalline lithium ferrite decreased by a factor of $\sim 10^4$ when a disordered structure was obtained by quenching into water from 1000°C. Wang, Gravel and Kestigian$^{37}$ studied the effect of heat treatment on the electrical resistivity of lithium ferrite. They also found that ordered lithium ferrite had a higher resistivity than the disordered material, and the most effective process in raising the resistivity was the oxidation of Fe$^{2+}$ to Fe$^{3+}$. Bandyopadhyay$^{38}$ investigated the influence of sintering temperature, time, and stoichiometry on the dc resistivity of lithium ferrite. His data was later found to be strongly
influenced by a thin surface layer. Rezlescu et al.\textsuperscript{39} measured the resistivity of Li-Zn ferrites as a function of composition. They found that the resistivity increased with Zn addition due to the decrease in Fe\textsuperscript{+2} concentration.

The primary problem in studying the electrical properties of lithium ferrite is due to the lack of information concerning the fabrication of the samples and their resulting composition. Most ferrites have a tendency to lose oxygen at high temperature. Lithium ferrite loses both oxygen and lithium during the heat treatment and thus adds to the problem of processing.\textsuperscript{40,41} Recently, Ridgeley et al. pointed out that the wide variation in the literature data, on the physical parameters of lithium ferrite, can probably be related to composition changes due to material loss in heat treatment. In this laboratory, Bandyopadhyay and Fulrath\textsuperscript{42} performed extensive studies to characterize the lithium and oxygen loss during heat treatment. A packing powder technique, as has been used successfully for the processing of lead zirconate-titanate ceramics, was developed to control the stoichiometry during sintering.\textsuperscript{24,26,38} The purpose of the present study was to investigate the dc conduction in polycrystalline lithium ferrite with better defined microstructure and composition. The charge carrier concentration and the mobility of charge carriers will be discussed separately.
B. Experimental

1. Sample Preparation

In order to make a series of samples with known deviation from the stoichiometric composition, LiFe$_5$O$_8$ powder was mixed with proper proportions of LiFeO$_2$ or Fe$_2$O$_3$ powder, ball milled, and dried. They were then pressed into disks and sintered at 1150°C for 2 hr in 1 atm O$_2$ while using LiFe$_5$O$_8$ as a stoichiometry packing powder. Specimens were always buried deeply into the packing powder.

In order to study the influence of the processing parameters on the electrical resistivity, isothermal sintering runs in 1 atm O$_2$ and using the stoichiometry packing powder were carried out at two different temperatures (1150°C and 1250°C) for various times. The same amount of packing powder was used in all the sintering runs.

2. Sample Characterization

Density of the sintered samples was measured by water displacement and also by geometric measurements. Theoretical density for LiFe$_5$O$_8$ was taken as 4.752 gm/cc. Density of all samples with various compositions was above 98% theoretical density and those used in the isothermal sintering study were above 95%. X-ray diffraction was used to identify various phases. All samples showed typical peaks of a spinel phase after surface grinding. For the microstructure investigation, thermally etched surfaces were observed by using scanning electron microscopy. Dependence of the microstructure on the stoichiometry

*Samples used in this study were kindly provided by Dr. G. Bandyopadhyay.
and processing parameters are shown in Figs. 19 and 20.

3. Resistivity Measurement

Direct current bulk resistivity was measured by using a guard ring method as shown in Fig. 3. The surfaces of all the samples were ground to a sufficient depth to eliminate any inhomogeneity due to surface reactions. The ends of the sample were sputtered with gold to ensure intimate electrical contacts. The current, as a function of applied voltage for several ferrites at different temperatures, was plotted and is shown in Fig. 21. The slopes are unity, therefore sputtered gold provides ohmic contacts for lithium ferrite. Contact resistance or polarization is negligible over a wide range of voltage. Electrical resistivity was measured from room temperature to 300°C. A 1.5 volt dry cell was used as the voltage source.

4. Thermoelectric Power Measurements

Thermoelectric measurements were made on the same samples as used for resistivity measurements. Thermoelectric power data were obtained by placing the sample in a temperature gradient and then measuring the developed potential and the temperature difference developed between the thermocouple/potential leads. Gold-plated Cu electrodes were pressed directly against the gold-sputtered surface of lithium ferrite samples.

C. Results and Discussion

The influence of composition on the resistivity of lithium ferrite at various temperatures is shown in Fig. 22. The resistivity measured by Bandyopadhyay was much higher than that of the surface ground samples in this study. In Fig. 23, the resistivity was plotted
as a function of the thickness removed from an as-sintered sample. It clearly indicates that there is a thin surface layer with high resistivity. This is due to a reoxidation reaction of Fe$^{+2}$ on the surface of the sample upon cooling in the oxygen atmosphere. It has been reported that lithium ferrite has an oxygen partial pressure greater than 1 atm above 1000°C. Consequently, there is oxygen loss during firing. The ferric ions (Fe$^{3+}$) will reduce a ferrous (Fe$^{+2}$) ions to maintain charge neutrality. If electron hopping from Fe$^{+2}$ to Fe$^{+3}$ acts as the primary charge transfer process, the divalent iron formed in the body leads to high conductivity. Upon cooling such a material in an oxygen atmosphere, divalent irons that lie near the surface are reoxidized. The Fe$^{+2}$ concentration on the surface thus decreases substantially and a thin surface layer with high resistivity is formed.

Resistivity always drops while moving from the LiFeO$_2$ doped region into the Fe$_2$O$_3$ doped region as shown in Fig. 22. This is due to the increasing Fe$^{+2}$ ion content on the octahedral sites. As both Fe$^{+2}$ and Fe$^{+3}$ locate on the same lattice sites, electron hopping from Fe$^{+2}$ to Fe$^{+3}$ contributes to the conduction process. While moving away from the Fe-deficient region (LiFeO$_2$ doped) into the Fe-excess region (Fe$_2$O$_3$ doped), more and more Fe$^{+2}$ would be active in charge transport. So the resistivity decreases with increasing Fe$_2$O$_3$ in the near stoichiometric composition. Measurements of the thermoelectric voltage showed that electron conduction dominates in all the samples. This is consistent with the picture of n-type charge carriers due to the Fe$^{+2}$ ions.
For a single type of charge carrier, the conductivity $\sigma$ can be expressed as

$$\sigma = ne\mu$$  \hspace{1cm} (23)

where $n$ = concentration of charge carriers and can be related to the concentration of Fe$^{+2}$ ions in the octahedral site

e = electronic charge

and

$\mu$ = mobility of the electrons in this system.

In Fig. 24 all the resistivity data at the same temperature were normalized with that of the stoichiometry composition. The concentration of charge carrier (Fe$^{+2}$) for a particular composition should remain constant in the temperature range where the measurements were made. Therefore, the shift of the curve with temperature, as shown in the figure, is clearly an influence on the mobility term.

The temperature dependence of the resistivity for various compositions is shown in Fig. 25. The resistivity decreases with increasing temperature. Normalization of all the resistivity at a fixed composition with the resistivity at room temperature should indicate only the mobility effect as derived in Appendix II. As shown in Fig. 26, the temperature-compensated normalized resistivity follows an exponential relation with temperature. The activation energy of hopping for each composition as shown in Fig. 27 were calculated from the slopes of the straight lines in Fig. 26. It is found that the activation energy does not change significantly through the stoichiometric region. This clearly indicates that the conductivity change observed in the same region (Fig. 28) should be primarily due to the change in charge carrier
concentration. In fact, the conductivity increases linearly with the amount of dopant in that near stoichiometric region in Fig. 28. The resistivity increases when the composition changes away from the near stoichiometric region on the Fe$_2$O$_3$ rich side. Bandyopadhyay$^{42}$ suggested that this is probably due to a second phase effect or a disorder effect. With increasing Fe$_2$O$_3$ in the composition, more and more Fe$^{+2}$ would be active in charge transport. But, at the same time, Fe$^{+2}$ in the octahedral region would tend to introduce some disorder in the system. As suggested by Austin and Mott$^6$ this disorder may contribute to the activation energy term (g) in the mobility expression and thus decrease the mobility of the carriers. The data indicates that the activation energy still decreases while the resistivity goes up. Therefore, increasing resistivity is unlikely to be due to the disorder effect but probably due to a second phase. The decreasing activation energy is probably due to increasing Fe$_3$O$_4$ content in the system. Excess Fe$_2$O$_3$ in LiFe$_5$O$_8$ is mainly dissolved as Fe$_3$O$_4$ and only partly as Fe$_2$O$_3$. It was also found that the activation energy decreases with increasing Fe$_3$O$_4$ content in the NiFe$_2$O$_4$-Fe$_3$O$_4$ system.$^6$ This result is due to the shorter jump distance and increase in the number of overlapping electronic orbitals.

The influence of the processing parameters on the electrical conduction of polycrystalline lithium ferrites has been investigated using the samples from isothermal sintering runs. The density and the average grain size are shown in Fig. 29. Temperature dependence on the resistivity of each sample was plotted in Figs. 30 and 31. There is no evidence that the resistivity is grain size dependent. Thermoelectric
measurements showed that the major charge carriers were n-type for all the samples. In Figs. 32 and 33, the temperature-compensated normalized resistivity was plotted against inverse temperature and follows a straight line relationship. The activation energy of hopping is shown in Fig. 34 as a function of sintering time. There is a tendency for the activation energy to decrease with increasing sintering time. The resistivity and activation energy for 1250°C series are lower than that of 1150°C series. The lower activation energy and activation energy decrease with time can be explained as follows. The higher the sintering temperatures or the longer the sintering time, the more Fe$^{+2}$ is generated in the system owing to oxygen loss. As the concentration of charge carriers increases, the hopping activation energy decreases similar to the behavior observed when increasing the Fe$^{2+}$ by adding Fe$_3$O$_4$. 
IV. THE Ni-DOPED LITHIUM FERRITE SYSTEM

A. Introduction

In the preceding section, it has been established that nonstoichiometry of lithium ferrite markedly influences its electrical conduction. Previous studies on polycrystalline lithium ferrite have been primarily concerned with the improvement of its B-H hysteresis loop and loss factor for core memory application. It is well known that dopants may influence the properties of ceramics. In the case of lithium ferrite, the hysteresis loop squareness has been improved significantly by the addition of a small amount of nickel, zinc, nickel and zinc, and manganese. Electrical conductivity which directly relates to the loss factor in core memory applications is an important physical property. It is apparent that understanding the effect of dopants on the electrical conductivity in lithium ferrite is necessary. N. Rezlescu et al. investigated the resistivity of Li-Zn ferrites. His results indicated that the resistivity increased with increasing concentration of Zn ions in lithium ferrite. West and Blankenship also reported the same result. These results have been explained as a decrease in Fe concentration caused by the addition of Zn. In this laboratory, Bandyopadhyay and Fulrath performed a systematic study of the effect of varying amounts of NiO and NiFe₂O₄ dopants on the sintering, microstructure, and physical properties of lithium ferrite. Thermogravimetric analysis and X-ray diffraction were used to characterize the chemical changes during processing. The electrical conduction in Ni-doped lithium ferrite has not been fully investigated. In this work, a more detailed study of the charge transport phenomena in NiO and NiFe₂O₄.
doped lithium ferrite has been carried out. Not only the effect of varying amounts of dopants but also the temperature dependence on the electrical conductivity was studied.

B. Experimental

A control amount of NiO or NiFe$_2$O$_4$ was added to lithium ferrite powder and the mixture was milled for 24 hr in isopropyl alcohol. Specimen size and the powder preparation techniques employed were the same as described previously. Pressed samples were sintered at 1150°C for 2 hr in 1 atm oxygen while using a stoichiometric LiFe$_5$O$_8$ packing powder.

The techniques for the density determination, X-ray analysis, microstructural examination, and thermoelectric power and electrical conductivity measurements have been described in the previous sections.

In Fig. 35, the densities of the sintered specimens have been plotted against the amount of dopants. For both NiO and NiFe$_2$O$_4$ doped samples, a drop in density is observed. Dependence of the microstructure on the varying amounts of dopants is shown in Figs. 36 and 37. It was found that NiO favored discontinuous grain growth, whereas NiFe$_2$O$_4$ suppressed it.

C. Results and Discussion

The influence of the amount of dopants on the resistivity of lithium ferrite at room temperature is shown in Fig. 38. The resistivity drops with increasing amount of NiFe$_2$O$_4$. But in the NiO doped material, the resistivity drops sharply with the initial 1 mole% addition followed by an increase with increasing amounts of NiO. Measurements of the thermoelectric power showed that electron conduction (n-type) dominated
in all the samples. This is consistent with the picture of electron hopping from Fe$^{+2}$ to Fe$^{+3}$ as the primary charge transport process in these ferrites. The temperature dependence on the resistivity for doped samples is shown in Figs. 39 and 40. In Figs. 41 and 42, the temperature-compensated normalized resistivity on a logarithmic scale is plotted against inverse absolute temperature. It is believed that, in ferrites and most transition metal oxides, overlap of the partially filled d orbital is small due to the relatively large separation between the transition metal cations among which the charge transfer occurs. Therefore, the 3d electrons which contribute to the main current carriers in ferrites are "localized" in a region. For a transport process to occur, an activation energy $q$ must be provided so that the electron can hop to another favorable site. In the general case, the conductivity ($\sigma$) of a ferrite is described by the formula:

$$\sigma = n e \mu = n e \frac{A_0}{T} \exp\left(-\frac{q}{kT}\right)$$  \hspace{1cm} (24)

For a fixed composition, the charge carrier concentration ($n$) is a constant, and each Fe$^{+2}$ ion is presumed to contribute one conduction electron. The exponential growth in the electrical conductivity of ferrites with temperature is due to the increasing electron mobility by a thermally activated process according to the hopping model. So the slope of the straight line in Figs. 41 and 42 should indicate the hopping activation energy.

NiFe$_2$O$_4$ has the same inverse spinel structure as LiFe$_5$O$_8$, and complete solid solution is expected as lithium ferrite is doped with NiFe$_2$O$_4$. The slope shown in Fig. 41 indicates that NiFe$_2$O$_4$ doped samples
have the same hopping activation energy shown in Fig. 43 as that for stoichiometric lithium ferrite (i.e., 0.06 eV). Therefore, the decrease in resistivity with increasing NiFe$_2$O$_4$ content is mainly due to the increasing charge carrier concentration Fe$^{+2}$ in the sample. It is well known that NiFe$_2$O$_4$ will lose oxygen at high temperature and lithium ferrite loses both oxygen and lithium during the heat treatment. Oxygen loss from the system will reduce Fe$^{+3}$ ions to Fe$^{+2}$ ions to maintain charge neutrality and thus increase the charge carrier concentration. But the lithium loss has a tendency to retard this reaction. So adding NiFe$_2$O$_4$ in the lithium ferrite system consequently increases the charge carrier concentration.

In the case of the NiO-doped sample (~1 mole% NiO), its hopping activation energy shown in Fig. 43 is the same as that for undoped stoichiometric lithium ferrite as shown in Fig. 42. This also indicates that the initial drop of resistivity is mainly due to the increasing charge carrier concentration. Small amounts of NiO can go into solid solution in lithium ferrite. Ni$^{+2}$ ions replace some Li$^{+1}$ ions in the octahedral sites. The larger Ni$^{+2}$ ions would distort the spinel lattice and increase the degree of overlapping of the 3d electron orbits. This delocalization thus leads to the initial drops in the resistivity. The subsequent increase in resistivity with further addition of NiO is undoubtedly linked to the appearance of a second phase. It has been reported that only about 2 mole% of excess Ni$^{+2}$ is soluble in the inverse spinel structure. Bandyapadhyay has postulated that NiO reacts with lithium ferrite according to the reaction
\[\text{2NiO} + \text{LiFe}_5\text{O}_8 = \text{2NiFe}_2\text{O}_4 + \text{LiFeO}_2\]  

which suggests 2 moles of NiO reacts to form 1 mole of LiFeO₂.

Experimental results indicated that 10 mole% NiO in LiFe₅O₈ and 5 mole% LiFeO₂ in LiFe₅O₈ compositions which exhibit nearly identical weight loss behavior are in agreement with the proposed reaction. It is also interesting to note that both 10 mole% NiO doped and 5 mole% LiFeO₂ doped samples have nearly the identical activation energies for hopping as shown in Fig. 44.
V. SUMMARY

Lead zirconate-titanate is an important electronic ceramic material because of its excellent piezoelectric properties. Lithium ferrite is a promising magnetic ceramic material owing to its square-loop magnetic properties. Electrical conductivity which directly relates to the power loss of the system is a highly important physical parameter in the use of both materials in electronic devices. In this investigation, the electrical conductivity of polycrystalline lithium ferrite and lead zirconate-titanate ceramics was studied. The effect of temperature, dopants, defect structures and microstructure on the electrical conductivity were determined and compared with the existing theoretical models.

Processing of lead zirconate-titanate is difficult due to the loss of PbO during sintering. In this study, polycrystalline compacts were sintered using a packing-powder technique where the samples were contained in a known PbO atmosphere to control the PbO loss. This is important because the material loss has a strong influence on the defect structure. Lead zirconate-titanate samples were prepared from both chemical solutions and oxide powder. The intrinsic defect structures were established by equilibrating the samples with a controlled PbO atmosphere provided by the packing powder. The extrinsic defect structures were introduced into the samples by addition of Sc$^{+3}$ or Nb$^{+5}$ as dopants. A guard-ring method was employed to measure the bulk resistivity of the samples. Thermoelectric power measurements indicated p-type conduction dominated in all samples. The results showed that charge transport in lead zirconate-titanate followed
semiconductor type conduction. In intrinsic PZT samples, holes contributed by lead vacancies are the major charge carriers. The activation energy for conduction in undoped lead zirconate-titanate sample is 1.41 eV. Sc$^{+3}$ doped samples have a lower resistivity and an activation energy for conduction (1.01 eV) dominated by the Sc$^{+3}$ ions serving as acceptors. Nb$^{+5}$ as a dopant increased the resistivity due to the effect of Nb$^{+5}$ ions serving as donor contribute electrons which can compensate for the holes contributed by ionized lead vacancies and, therefore, reduce the number of charge carriers. It was also found that impurities introduced during processing can have a significant effect on the electrical conduction in lead zirconate-titanate. Intrinsic conduction with an activation energy 3.6 eV was observed in PZT above 650°C. Both chemically prepared and mixed oxide PZT showed the same results.

The electrical conductivity of Fe$_2$O$_3$ or LiFeO$_2$ doped and stoichiometric LiFe$_5$O$_8$ was determined as a function of temperature. Cold-pressed polycrystalline compacts of lithium ferrite with varying stoichiometry were sintered using a packing powder technique and 1 atm oxygen to control the lithium and oxygen loss. Data have been presented to show the influence of stoichiometry which affects the concentration of charge carriers and temperature which affects the mobility of charge carriers on the dc resistivity of lithium ferrite. The resistivity decreased with increasing Fe$^{+2}$ content. The thermoelectric power showed that n-type conduction predominated in all samples. The exponential dependence of the charge carrier mobility is in agreement with the hopping model. The hopping activation energy for stoichiometric lithium
ferrite is 0.06 eV. The influence of controlled amounts of NiO and NiFe$_2$O$_4$ dopants on the resistivity of lithium ferrite was also investigated. NiFe$_2$O$_4$ doped samples had a lower resistivity than undoped samples due to increased charge carrier concentration. The resistivity dropped sharply with a small addition of NiO due to the delocalization of charge carriers because Ni$^{+2}$ distorted the crystal lattice. The rapid increase of resistivity with increasing NiO is due to the presence of the second phase. There is no evidence that grain size or porosity will influence the conductivity of lithium ferrite significantly.
ACKNOWLEDGEMENTS

I am deeply indebted to Professor Richard M. Fulrath for his continuous guidance, support, and encouragement through the course of this work. I would like to express my special thanks to a good friend, Dr. Gautam Bandyopadhyay, for his invaluable suggestions and counsel, and for providing the lithium ferrite samples for this study. Discussions with Dr. John Sherohan at the early stage of this work were highly appreciated. I am also grateful to Dr. Joe Masaryk for his encouragement.

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Table I. Data from the measurements of bulk resistivity, thermoelectric power, density, grain size, and the processing parameters of chemically prepared PZT.

<table>
<thead>
<tr>
<th>Sample Compositions</th>
<th>Sintering Conditions</th>
<th>Temperature °C</th>
<th>Time hr</th>
<th>Packing Power Composition</th>
<th>Atmosphere 1 atm</th>
<th>Density gm/cc</th>
<th>Average Grain Size μm</th>
<th>Bulk Resistivity at 300°C (Ω-cm)</th>
<th>Activation Energy eV</th>
<th>Conduction Type</th>
</tr>
</thead>
</table>
Table II. Data from the measurements of bulk resistivity, thermoelectric power, density, grain size, and the processing parameters of mixed oxide PZT.

<table>
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<tr>
<th>Sample Compositions</th>
<th>Temperature °C</th>
<th>Time hr</th>
<th>Packing Powder Composition</th>
<th>Atmosphere 1 atm</th>
<th>Density gm/cc</th>
<th>Average Grain Size μm</th>
<th>Bulk Resistivity at 300°C (Ω-cm)</th>
<th>Activation Energy</th>
<th>Conduction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZ$_{0.5}$$^{+}$0.5 + 2 mole% Nb$_2$O$_5$</td>
<td>1200</td>
<td>16</td>
<td>PZ+Z</td>
<td>O$_2$</td>
<td>7.983</td>
<td>1.4</td>
<td>5.5×10⁹</td>
<td>1.41</td>
<td>P</td>
</tr>
<tr>
<td>PZ$_{0.5}$$^{+}$0.5 + 1 mole% Nb$_2$O$_5$</td>
<td>1200</td>
<td>16</td>
<td>PZ+Z</td>
<td>O$_2$</td>
<td>7.966</td>
<td>1.7</td>
<td>1.1×10⁹</td>
<td>1.41</td>
<td>P</td>
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<td>PZ$_{0.5}$$^{+}$0.5</td>
<td>1200</td>
<td>16</td>
<td>PZ+Z</td>
<td>O$_2$</td>
<td>7.970</td>
<td>2.5</td>
<td>1.8×10⁶</td>
<td>1.28</td>
<td>P</td>
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<tr>
<td>PZ$_{0.5}$$^{+}$0.5 + 1 mole% Sc$_2$O$_3$</td>
<td>1200</td>
<td>16</td>
<td>PZT+P</td>
<td>He</td>
<td>7.640</td>
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<td>1.0×10⁶</td>
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<td>P</td>
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APPENDIX II

The electrical conductivity, $\sigma$, or the inverse resistivity, $1/\rho$, and temperature $T$ is the product of the charge carrier concentration, $n$, their charge, $e$, and the charge carrier mobility $\mu$:

$$\frac{1}{\rho} = \sigma = n e \mu \text{ at } T_b$$

$$\frac{1}{\rho} = \sigma = n_o e \mu_o \text{ at room temperature } T_o$$

therefore,

$$\frac{\rho}{\rho_o} = \frac{n e \mu}{n_o e \mu_o}$$

For a fixed composition, $n_o = n_b$ in the extrinsic resistivity range; therefore,

$$\frac{\rho_b}{\rho_o} = \frac{\mu_o}{\mu_b}$$

such that normalization of all the high-temperature resistivity data at a fixed composition with the resistivity of that composition at room temperature should indicate only the mobility effect.

According to the hopping mechanism,

$$\frac{\rho_b}{\rho_o} = \frac{C}{T_o} \exp\left(-\frac{q}{RT_o}\right) = \frac{T_b}{T_o} \exp\left[-\frac{q}{R} \left(\frac{1}{T_o} - \frac{1}{T_b}\right)\right]$$
\[
\frac{\rho_b}{T_b} = \exp \left[ -\frac{q}{R} \left( \frac{1}{T_o} - \frac{1}{T_b} \right) \right]
\]

and

\[
\ln \left( \frac{\rho_b}{T_b} \right) = \frac{q}{R} \left( \frac{1}{T_o} - \frac{1}{T_b} \right) = -\frac{q}{R} 3.414 \times 10^{-3} + \frac{q}{R} \frac{1}{T_b}
\]

It is shown that the temperature-compensated normalized resistivity follows an exponential relationship with temperature. Thus, the hopping activation energy, \(q\), can be calculated.
REFERENCES

2. N. M. Tallan, ed., Electrical Conductivity in Ceramics and Glass (Dekker, 1974).
FIGURE CAPTIONS

Fig. 1. Flow chart for chemically prepared PZT.

Fig. 2. Scanning electron micrographs of chemically prepared PZT.
(a) 1 mole% Nb\textsubscript{2}O\textsubscript{5} doped, (b) 2 mole% Nb\textsubscript{2}O\textsubscript{5} doped, (c) undoped, 
(d) 1 mole% Sc\textsubscript{2}O\textsubscript{3} doped, (e) 2 mole% Sc\textsubscript{2}O\textsubscript{3} doped.

Fig. 3. Schematic of the method used for dc bulk resistivity measurements.

Fig. 4. Dependence of bulk resistivity on the compositions and 
temperature for doped and undoped PZT.

Fig. 5. Resistivity of chemically prepared PZT as a function of temperature.

Fig. 6. Schematic representation of energy levels in an oxide semiconductor.

Fig. 7. Variation of the resistivity of undoped PZT with the composition 
of the packing power used in sintering.

Fig. 8. Chemical formula for undoped, Sc\textsuperscript{3+} doped and Nb\textsuperscript{5+} doped PZT.

Fig. 9. Dependence of activation energy for conduction on type and 
content of dopants.

Fig. 10. Effect of ball milling impurities on the electrical resistivity 
of PZT.

Fig. 11. The temperature dependence of electrical resistivity in 
polycrystalline PZT as observed by Dih and Fulrath (in this 
study), Gerson and Jaffe,\textsuperscript{15} and Takahashi.\textsuperscript{17}

Fig. 12. Sample fabrication flow chart for the mixed oxide PZT.

Fig. 13. Microstructure of mixed oxide PZT. (a) 1 mole% Nb\textsubscript{2}O\textsubscript{5} doped, 
(b) 2 mole% Nb\textsubscript{2}O\textsubscript{5} doped, (c) undoped, (d) 1 mole% Sc\textsubscript{2}O\textsubscript{3} doped, 
(e) 2 mole% Sc\textsubscript{2}O\textsubscript{3} doped.
Fig. 14. Grain size and bulk resistivity vs amount of dopants for mixed oxide (MO) and chemically prepared (CP) PZT samples.

Fig. 15. The influence of temperature on the resistivity of mixed oxide PZT with various dopants.

Fig. 16. Resistivity vs temperature for both mixed oxide (MO) and chemically prepared (CP) PZT samples with various dopants.

Fig. 17. Influence of dopants on the activation energy for electrical conduction for mixed oxide PZT.

Fig. 18. Effect of temperature on the bulk resistivity of PZT samples with varying porosity.

Fig. 19. Microstructures of LiFe$_5$O$_8$ samples with varying amounts of LiFeO$_2$ or Fe$_2$O$_3$. (a) LiFe$_5$O$_8$, (b) LiFe$_5$O$_8$ + 3 mole% Fe$_2$O$_3$, (c) LiFe$_5$O$_8$ + 5 mole% Fe$_2$O$_3$, (d) LiFe$_5$O$_8$ + 3 mole% LiFeO$_2$, (e) LiFe$_5$O$_8$ + 5 mole% LiFeO$_2$.

Fig. 20-1. Microstructures of LiFe$_5$O$_8$ samples sintered at 1150°C for (a) 30 min, (b) 2 hr, (c) 3 hr, (d) 6 hr, (e) 8 hr.

Fig. 20-2. Microstructures of LiFe$_5$O$_8$ samples sintered at 1250°C for (a) 15 min, (b) 30 min, (c) 1 hr, (d) 1-1/2 hr, (e) 2 hr.

Fig. 21. Voltage vs current for various lithium ferrite samples at various temperatures.

Fig. 22. The influence of composition on the resistivity at various temperatures.

Fig. 23. The resistivity as a function of surface removed by grinding starting with as sintered samples.

Fig. 24. Normalized resistivity vs compositions.
Fig. 25. The effect of temperatures on the resistivity for various compositions.

Fig. 26. The temperature-compensated normalized resistivity for various compositions vs inverse temperature. $\rho_b$ is the resistivity at temperature $T_b$, $\rho_0$ is the resistivity at room temperature $T_0$.

Fig. 27. Activation energy for electron hopping vs composition of lithium ferrite.

Fig. 28. The influence of composition on the conductivity at various temperatures.

Fig. 29. Density, grain size and bulk resistivity data from isothermal sintering runs. ◎-LiFe$_5$O$_8$ sintered at 1150°C, □-LiFe$_5$O$_8$ sintered at 1250°C.

Fig. 30. Temperature dependence on resistivity for samples sintered at 1150°C.

Fig. 31. Temperature dependence on resistivity for samples sintered at 1250°C.

Fig. 32. The temperature-compensated normalized resistivity for samples sintered at 1150°C vs inverse temperature. $\rho_b$ is the bulk resistivity at temperature $T_b$, $\rho_0$ is the bulk resistivity at room temperature $T_0$.

Fig. 33. The temperature-compensated normalized resistivity for samples sintered at 1250°C vs inverse temperature. $\rho_b$ is the bulk resistivity at temperature $T_b$, $\rho_0$ is the bulk resistivity at room temperature $T_0$.

Fig. 34. The hopping activation energy vs processing parameters.
Fig. 35. Dependence of sintered density of LiFe$_5$O$_8$ on the amount of dopants (NiO or NiFe$_2$O$_4$).

Fig. 36. Microstructure of NiO doped LiFe$_5$O$_8$ samples (a) 1 mole% NiO doped, and (b) 3 mole% NiO doped.

Fig. 37. Microstructure of NiFe$_2$O$_4$ doped LiFe$_5$O$_8$ samples. (a) 1 mole% NiFe$_2$O$_4$ doped, (b) 3 mole% NiFe$_2$O$_4$ doped.

Fig. 38. Resistivity of LiFe$_5$O$_8$ at room temperature as a function of dopant concentration. All samples sintered at 1150°C for 2 hr.

Fig. 39. The effect of temperature on the bulk resistivity for NiFe$_2$O$_4$ doped lithium ferrite samples.

Fig. 40. The effect of temperature on the resistivity for NiO doped lithium ferrite samples.

Fig. 41. The temperature-compensated normalized resistivity for varying amount NiFe$_2$O$_4$ doped lithium ferrite vs inverse temperature. $\rho_b$ is the bulk resistivity at temperature $T_b$. $\rho_0$ is the bulk resistivity at room temperature $T_0$.

Fig. 42. The temperature-compensated normalized resistivity for varying amount NiO doped lithium ferrite vs inverse temperature. $\rho_b$ is the bulk resistivity at temperature $T_b$. $\rho_0$ is the bulk resistivity at room temperature $T_0$.

Fig. 43. Hopping activation energy vs amounts of dopants (NiO or NiFe$_2$O$_4$).

Fig. 44. The temperature-compensated normalized resistivity for 10 mole% NiO doped and 5 mole% LiFeO$_2$ doped lithium ferrites vs inverse temperature. $\rho_b$ is the bulk resistivity at temperature $T_b$. $\rho_0$ is the bulk resistivity at room temperature $T_0$. 
PbO
Zr(0Bu)₄
Ti(0Bu)₄
DOPENT OXIDE
DISTILLED H₂O

BLENDER
15 MINUTES

DRY
24 HOURS, 100°C

CALCINE
24 HOURS, 500°C

MILL
ISOPROPYL ALCOHOL
AND ZrO₂ BALLS

CALCINE
8 HOURS, 500°C

MILL
ISOPROPYL ALCOHOL
AND ZrO₂ BALLS

SCREEN

COLD PRESS
10,000 PSI

SINTER

XBL 759-7355

Fig. 1
Fig. 2
R, CONSTANT RESISTANCE
R₂ VARIABLE RESISTANCE
A NULL INDICATOR
B KEITHLEY ELECTROMETER

SAMPLE

Vₛ (1.5 V BATTERY)

Fig. 3
PZT Doped with:

- 2 mole % Nb_2O_5
- 1 mole % Nb_2O_5
- 2 mole % Sc_2O_3
- 1 mole % Sc_2O_3

Undoped

Fig. 5
PZ₅Ti₅ Equilibrium with

- PZ+Z Packing Powder
- PZT+Z+T Packing Powder

Fig. 7
Pb (Zr\textsubscript{0.5} Ti\textsubscript{0.5}) O\textsubscript{3}

Pb\textsubscript{1-\textfrac{X}{2}} \square\textsubscript{\textfrac{X}{2}} (Zr\textsubscript{0.5} Ti\textsubscript{0.5})\textsubscript{1-X} Nb\textsubscript{X} O\textsubscript{3}

Pb (Zr\textsubscript{0.5} Ti\textsubscript{0.5})\textsubscript{1-X} Sc\textsubscript{X} O\textsubscript{3-\textfrac{X}{2}} \square\textsubscript{\textfrac{X}{2}}

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Fig. 8
Fig. 9
PZT Powder Ground by:
- ZrO₂ Ball (ΔE = 1.41 ev.)
- Al₂O₃ Ball (ΔE = 1.05 ev.)

Fig. 10
\( PZ_{0.5}T_{0.5} \) (Dih-Fulrath) 
\( \Delta E = 1.41 \text{ ev} \)

\( PZ_{0.53}T_{0.47} \) (Gerson and Jaffe) 
\( \Delta E = 0.89 \text{ ev} \)

\( PZ_{0.52}T_{0.48} \) (Takahashi) 
\( \Delta E = 1.054 \text{ ev} \)

Fig. 11
PbO
TiO₂
ZrO₂
DOPENT

MIX 4 HOURS ISOPROPYL ALCOHOL and ZrO₂ BALLS

DRY 100°C, 24 HOURS

CALCINE 100°C, 2 HOURS

MILL ISOPROPYL ALCOHOL and ZrO₂ BALLS

DRY

SCREEN

COLD PRESS 5000 PSI

SINTER

XBL761-6125

Fig. 12
Fig. 14
Fig. 16
Fig. 17

Activation Energy (eV)

Mole % Dopent

Nb$_2$O$_5$ doped

Sc$_2$O$_3$ doped
Fig. 18

Nb Doped PZT
% Porosity

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<td>○</td>
<td>△</td>
<td>▼</td>
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Bulk Resistivity, Ω·cm

10^11

10^10

10^9

10^8

10^7

10^6

1000/T°K

XBL761-6124
\[ \text{LiFe}_5\text{O}_8 \]

\[ 20^\circ\text{C and } 200^\circ\text{C} \]

\[ I \quad \text{(amp)} \]

\[ V \quad \text{(volts)} \]

\[ \text{LiFe}_5\text{O}_8 + 3\% \text{LiFe}_2\text{O}_3 \]

\[ \text{and} \]

\[ \text{LiFe}_5\text{O}_8 + 3\% \text{Fe}_2\text{O}_3 \]

\[ 20^\circ\text{C} \]

\[ I \quad \text{(amp)} \]

\[ V \quad \text{(volts)} \]

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Fig. 21
Fig. 22

Bulk Resistivity (Ω·cm)

- T = 20°C
- 100°C
- 300°C

Mole % LiFeO₂ vs. Mole % Fe₂O₃

Stoich.
Fig. 23
Fig. 24
Li$_5$Fe$_3$O$_8$ doped with:

- $\Delta$ 5% Fe$_2$O$_3$
- $\bigcirc$ 3% Fe$_2$O$_3$
- $\triangleleft$ 1% Fe$_2$O$_3$
- $\times$ Undoped
- $\bullet$ 3% LiFeO$_2$
- $\blacktriangle$ 5% LiFeO$_2$

Fig. 25

[Graph showing the bulk resistivity as a function of temperature for various dopants]
LiFe$_5$O$_8$ doped with:

- 5% Fe$_2$O$_3$
- 3% Fe$_2$O$_3$
- 1% Fe$_2$O$_3$
- undoped
- 3% LiFeO$_2$
- 5% LiFeO$_2$

Fig. 26
Fig. 27
Fig. 28
**LiFe$_5$O$_8$**

Sintered at 1150 °C

**Bulk Resistivity (Ω-cm)**

**Figure 30**

XBL 762-6391
LiFe₅O₈
Sintered at 1250°C

Time, hrs

- 0.25
- 0.5
- 1.0
- 1.5
- 2.0

Fig. 31
LiFe$_5$O$_8$

Sintered at 1150 °C

Time, hrs

- 0.5
- 2
- 3
- 4
- 8

$\frac{\rho_b}{\rho_0} / T_b$

$1000 / T^\circ K$

Fig. 32
LiFe$_5$O$_8$
Sintered at 1250 °C

$\frac{\rho_b}{T_b} / \frac{\rho_0}{T_0}$

1000/T$_K$

Time, hrs
- 0.25
- 0.5
- 1.0
- 1.5
- 2.0
- 2.0 at 1150 °C

Fig. 33
Fig. 34
Fig. 35
Fig. 36
Fig. 37

(a) XBB 762-1991

(b)
Fig. 38
LiFe$_5$O$_8$ doped with NiFe$_2$O$_4$

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<th>% NiFe$_2$O$_4$</th>
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</table>

Bulk Resistivity (Ω-cm)

Fig. 39
LiFe$_5$O$_8$ doped with NiO

% NiO

- 1
- 3
- 5
- 10

Bulk Resistivity (Ω·cm)

1000 / $T$ °K

XBL 762-6401

Fig. 40
LiFe$_5$O$_8$ doped with NiFe$_2$O$_4$

$\%$ NiFe$_2$O$_4$

- 0  
- 1  
- 3  
- 5  
- 10

$\frac{\rho_b}{T_b} / T_0$

1000 / $T^\circ K$
LiFe$_5$O$_8$ doped with NiO

% NiO

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<tr>
<th>NiO %</th>
<th>Symbol</th>
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<tr>
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Fig. 42
Fig. 43
LiFe$_5$O$_8$

% Dopent:
- O 10% NiO
- □ 5% LiFeO$_2$

$\frac{\rho_b}{\rho_b^0}$ vs. $\frac{1000}{T}$ °K

Fig. 44

XBL 762-6404
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