A MEASUREMENT SYSTEM TO DETERMINE THE ELECTRICAL PROPERTIES
OF PIEZOELECTRIC CERAMICS AT HIGH TEMPERATURES

A Thesis
Presented to
The Graduate Faculty of The University of Akron

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

Zoltán Gubinyi
May, 2006
A MEASUREMENT SYSTEM TO DETERMINE THE ELECTRICAL PROPERTIES
OF PIEZOELECTRIC CERAMICS AT HIGH TEMPERATURES

Zoltán Gubinyi

Thesis

Approved: ___________________________________

Advisor
Dr. Celal Batur

Co-Advisor
Dr. Ali Sayir

Faculty Reader
Dr. Jiang Zhe

Accepted: ___________________________________

Dean of the College of Engineering
Dr. George K. Haritos

Dean of the Graduate School
Dr. George R. Newkome

Date

ii
ABSTRACT

Space exploration missions in the future will involve in-situ sampling and analysis under extreme environmental conditions, so these missions will require actuators and sensors that can operate reliably for a long period of time under these conditions. The commercially available sensors, actuators and motors cannot operate continuously at such a high ambient temperatures like +500°C, so this technical challenge requires new actuator and sensor designs. Piezoelectric materials with Curie temperature \( T_{\text{Curie}} \) that is higher than +1000°C would be ideal for this role, but the commercially available piezoceramics only able operate reliably at low temperatures and very little information is available about their electrical properties at elevated temperatures.

The original goal of this thesis was to develop a measurement system that is able to measure the properties of those high-temperature piezoelectric ceramics, \( \text{La}_3\text{Ga}_5\text{SiO}_{14} \) and \( \text{La}_2\text{Ti}_2\text{O}_7 \) that are currently being developed at the NASA Glenn Research Center (GRC). However up to date; our attempts to polarize these high-temperature piezoelectric ceramics were unsuccessful. To be able to demonstrate the capabilities of the developed measurement system, commercially available Lead Zirconate Titanate (PZT) samples were used to measure the changes in the different vibration mode frequencies and electrical properties as the temperature was increased up to and above their Curie temperature, around +450°C.
The developed measurement system was able to capture the changes as the operating temperature was increased to and above the Curie temperature of the materials. The description of the developed measurement system and the result of the measurements on a variety of piezoelectric materials are presented in this thesis.

The PZT samples showed changes in the frequency range of their vibration modes and electrical properties as the temperature was getting closer to the $T_{\text{Curie}}$, and in most cases these changes become very significant from around the $T_{\text{Curie}}-(50^\circ\text{C}~\text{to}~20^\circ\text{C})$ temperature. The focus in this thesis was on the radial and thickness-extensional vibration modes. Based upon the measurements, there was a definite trend that difference between the anti-resonant and resonant frequencies of a vibration mode never increases with the temperature. This observation helped to predict the behavior of the coupling factors and the permittivity components of the materials as the temperature increased. However, to predict changes of the rest of the electrical properties turned out to be very difficult, since their behaviors depend on several factors, like the actual values of the resonant and anti-resonant frequency pairs and their relative changes to each other.

This proves that to perform high temperature measurement is a reliable way to get information about the changes of the different vibration mode frequencies and electrical properties of the piezoelectric ceramics. This measurement system and the evaluation of measured data can be particularly useful to designers, because the collected information can help them to anticipate and incorporate the observed changes into their future actuator and sensor designs.
ACKNOWLEDGEMENTS

This work is part of the Multifunctional Structural Ceramics with Ferroelastic and Martensic Transformations DOD project financed by the AFOSR: F49620-01-1-0500.

The project has been hosted by NASA GRC as a part of the Actuator Ceramics for High Temperatures project, NASA GLENN: NNC04AA27A.

I am deeply indebted to many people who helped me pursuing and finishing this research. First of all, I would like to thank Prof. Dr. Celal Batur for serving as my advisor. His encouragement, questions and patience helped me to stay focused and better understand the nature of the piezoelectric ceramics.

I express my gratitude to Dr. Ali Sayir for the opportunity to work on this thesis in his laboratory at NASA GRC and for his everlasting optimism and great support during this project.

In addition, I would like to thank Dr. Frederic Dynys for his great help with the set-up and troubleshoot of measurement systems and programs. Dr. Serene Farmers, Tom Sabo and Greg Buchar are also highly acknowledged for their patience, flexibility and tremendous help during my time at NASA GRC.

I also would like to thank to my family and all my friends for their support and help during this work.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>ix</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>x</td>
</tr>
</tbody>
</table>

## CHAPTER

### I. INTRODUCTION

1.1 Background

1.1.1 Piezoelectric Effect

1.1.2 Piezoelectric Ceramics

1.1.3 Polarization

1.1.4 Depolarization

1.2 Objectives and Scope

### II. LINEAR THEORY OF PIEZOELECTRICITY

2.1 General

2.2 Linear Piezoelectricity

2.3 Radial Modes in Thin Plates

2.4 Radial Modes of Disks

2.5 Thickness Modes of Plates
III. MEASUREMENT APPARATUS

3.1 Measurement Equipments and Configurations

3.2 Measurement System Hardware, Configuration #5

3.2.1 PC Configuration

3.2.2 Agilent 4294A Precision Impedance Analyzer

3.2.3 Eurotherm 2404 Temperature Controller

3.2.4 Furnace

3.3 Measurement System Software, Configuration #5

3.3.1 User Interface

3.3.2 Block Diagram

IV. POLARIZATION, MEASUREMENT RESULTS AND ANALYSIS

4.1 Polarization Attempts of High Temperature Piezoelectric Ceramics

4.2 Measured and/or Calculated Parameters

4.3 Calculated Electrical Properties

4.4 Measurement Results and Analysis

4.4.1 PZT Sample #502–B

4.4.2 PZT Sample #502–A

4.4.3 PZT Sample #502–C

4.4.4 PZT Sample #850

4.4.5 PZT Sample #880

4.4.6 Capacitance at 1 kHz

4.4.7 Resonant and Anti-resonant Frequency Pairs

4.4.8 Electrical Properties
4.5 Conclusion ................................................................................................................. 98

V. SUMMARY, CONCLUSION AND FUTURE WORK ................................................... 99

5.1 Summary .................................................................................................................... 99

5.2 Conclusion ................................................................................................................ 99

5.3 Future Work and Recommendation ................................................................. 100

BIBLIOGRAPHY .............................................................................................................. 101
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Symbols and their units……………………………………………………………5</td>
</tr>
<tr>
<td>2.2</td>
<td>Matrix notation……………………………………………………………………9</td>
</tr>
<tr>
<td>2.3</td>
<td>Frequency constant of disk resonator and ratio of the first overtone frequency to the fundamental resonance frequency as a function of the planar Poisson’s ratio………………………………………………………………………………13</td>
</tr>
<tr>
<td>2.4</td>
<td>Motional capacitance constant $\Gamma$ for the thickness mode of a plate as a function of electromechanical coupling factor $k$……………………………………………………………………………………………………………15</td>
</tr>
<tr>
<td>4.1</td>
<td>Basic calculated or measured parameters………………………………………..34</td>
</tr>
<tr>
<td>4.2</td>
<td>Calculated electrical properties…………………………………………………..35</td>
</tr>
<tr>
<td>4.3</td>
<td>Vibration mode shapes for the 21 lowest symmetric modes of a circular PZT-5A disk with $d/t$ ratio of 10……………………………………………………………………………………………………………………………………41</td>
</tr>
<tr>
<td>4.4</td>
<td>PZT Sample #502–B, manufacturer provided vs. measured properties at 25°C…44</td>
</tr>
<tr>
<td>4.5</td>
<td>Comparison of vibration mode values of the PZT-5A and PZT-#502–B disks…44</td>
</tr>
<tr>
<td>4.6</td>
<td>PZT Sample #502–A, manufacturer provided vs. measured properties at 25°C…55</td>
</tr>
<tr>
<td>4.7</td>
<td>PZT Sample #502–C, manufacturer provided vs. measured properties at 25°C…65</td>
</tr>
<tr>
<td>4.8</td>
<td>PZT Sample #850, manufacturer provided vs. measured properties at 25°C…….75</td>
</tr>
<tr>
<td>4.9</td>
<td>PZT Sample #880, manufacturer provided vs. measured properties at 25°C…….85</td>
</tr>
<tr>
<td>4.10</td>
<td>Summarized trend of resonant and anti-resonant frequency pairs……………….96</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Radial mode excitation of a circular disk.</td>
<td>10</td>
</tr>
<tr>
<td>3.1</td>
<td>Configuration #1: Impedance measurement of low resistance ceramics.</td>
<td>18</td>
</tr>
<tr>
<td>3.2</td>
<td>Configuration #2: Impedance measurement of high resistance ceramics.</td>
<td>18</td>
</tr>
<tr>
<td>3.3</td>
<td>Configuration #3: Impedance measurements of ceramics, 20 Hz – 1 MHz.</td>
<td>19</td>
</tr>
<tr>
<td>3.4</td>
<td>Configuration #4: Impedance measurements of ceramics, 1 MHz – 1.8 GHz.</td>
<td>19</td>
</tr>
<tr>
<td>3.5</td>
<td>Configuration #5: Impedance measurements of ceramics, 40 Hz – 110 MHz.</td>
<td>20</td>
</tr>
<tr>
<td>3.6</td>
<td>Agilent 4294A Precision Impedance Analyzer front panel.</td>
<td>22</td>
</tr>
<tr>
<td>3.7</td>
<td>Furnace top view, furnace shown opened for clarity.</td>
<td>23</td>
</tr>
<tr>
<td>3.8</td>
<td>Furnace side view, half of the furnace shown removed for clarity.</td>
<td>24</td>
</tr>
<tr>
<td>3.9</td>
<td>Front panel of the measurement program, 4294A2.vi.</td>
<td>26</td>
</tr>
<tr>
<td>3.10</td>
<td>Part #1 of the block diagram of the measurement program, 4294A2.vi.</td>
<td>28</td>
</tr>
<tr>
<td>3.11</td>
<td>Part #2 of the block diagram of the measurement program, 4294A2.vi.</td>
<td>29</td>
</tr>
<tr>
<td>3.12</td>
<td>Part #3 of the block diagram of the measurement program, 4294A2.vi.</td>
<td>30</td>
</tr>
<tr>
<td>3.13</td>
<td>Part #4 of the block diagram of the measurement program, 4294A2.vi.</td>
<td>31</td>
</tr>
<tr>
<td>4.1</td>
<td>PZT Sample #502–B –</td>
<td>Z</td>
</tr>
<tr>
<td>4.2</td>
<td>PZT Sample #502–B – θ on the 100 kHz – 10 MHz frequency range.</td>
<td>46</td>
</tr>
<tr>
<td>4.3</td>
<td>PZT Sample #502–B –</td>
<td>Z</td>
</tr>
</tbody>
</table>
4.4 PZT Sample #502–B – θ – First radial mode

4.5 PZT Sample #502–B – \(|Z|\) – First radial overtone mode

4.6 PZT Sample #502–B – θ – First radial overtone mode

4.7 PZT Sample #502–B – \(|Z|\) – First thickness mode

4.8 PZT Sample #502–B – θ – First thickness mode

4.9 PZT Sample #502–B – \(f_r^{\text{r}(1)}\) and \(f_p^{\text{r}(1)}\) vs. Temperature

4.10 PZT Sample #502–B – \(f_s^{\text{r}(2)}\) and \(f_p^{\text{r}(2)}\) vs. Temperature

4.11 PZT Sample #502–B – \(f_s^{\text{t}(1)}\) and \(f_p^{\text{t}(1)}\) vs. Temperature

4.12 PZT Sample #502–B – \(\sigma^p\) vs. Temperature

4.13 PZT Sample #502–B – \(k_{33}^l, k_{31}, k_p\), and \(k_{\text{eff}}\) vs. Temperature

4.14 PZT Sample #502–B – \(d_{33}^l\) and \(d_{31}\) vs. Temperature

4.15 PZT Sample #502–B – \(s_{11}^{D, E}\) and \(s_{12}^{E}\) vs. Temperature

4.16 PZT Sample #502–B – \(c_{12}^p\) and \(c_{33}^{E, 33}\) vs. Temperature

4.17 PZT Sample #502–B – \(e_{31}^p\) and \(e_{33}\) vs. Temperature

4.18 PZT Sample #502–B – \(e_{33}^p\), \(e_{33}^T\), and \(e_{33}^S\) vs. Temperature

4.19 PZT Sample #502–B – Capacitance at 1 kHz vs. Temperature

4.20 PZT Sample #502–A – \(|Z|\) on the 100 kHz – 10 MHz frequency range

4.21 PZT Sample #502–A – θ on the 100 kHz – 10 MHz frequency range

4.22 PZT Sample #502–A – \(|Z|\) – First radial mode

4.23 PZT Sample #502–A – θ – First radial mode

4.24 PZT Sample #502–A – \(|Z|\) – First radial overtone mode

4.25 PZT Sample #502–A – θ – First radial overtone mode

4.26 PZT Sample #502–A – \(|Z|\) – First thickness mode
4.27 PZT Sample #502-A – $\theta$ – First thickness mode
4.28 PZT Sample #502-A – $f_s^{\tau(1)}$ and $f_p^{\tau(1)}$ vs. Temperature
4.29 PZT Sample #502-A – $f_s^{\tau(2)}$ and $f_p^{\tau(2)}$ vs. Temperature
4.30 PZT Sample #502-A – $f_s^{\tau(1)}$ and $f_p^{\tau(1)}$ vs. Temperature
4.31 PZT Sample #502-A – $\sigma^p$ vs. Temperature
4.32 PZT Sample #502-A – $k'_{33}$, $k_{31}$, $k_p$ and $k_{eff}$ vs. Temperature
4.33 PZT Sample #502-A – $d_{33}$ and $d_{31}$ vs. Temperature
4.34 PZT Sample #502-A – $s^{D}_{11}$, $s^{E}_{11}$ and $s^{E}_{12}$ vs. Temperature
4.35 PZT Sample #502-A – $e^{p}_{12}$ and $e^{E}_{33}$ vs. Temperature
4.36 PZT Sample #502-A – $e^{p}_{31}$ and $e_{33}$ vs. Temperature
4.37 PZT Sample #502-A – $\varepsilon^{p}_{33}$, $\varepsilon^{T}_{33}$ and $\varepsilon^{S}_{33}$ vs. Temperature
4.38 PZT Sample #502-A – Capacitance at 1 kHz vs. Temperature
4.39 PZT Sample #502-C – $|Z|$ on the 100 kHz – 10 MHz frequency range
4.40 PZT Sample #502-C – $\theta$ on the 100 kHz – 10 MHz frequency range
4.41 PZT Sample #502-C – $|Z|$ – First radial mode
4.42 PZT Sample #502-C – $\theta$ – First radial mode
4.43 PZT Sample #502-C – $|Z|$ – First radial overtone mode
4.44 PZT Sample #502-C – $\theta$ – First radial overtone mode
4.45 PZT Sample #502-C – $|Z|$ – First thickness mode
4.46 PZT Sample #502-C – $\theta$ – First thickness mode
4.47 PZT Sample #502-C – $f_s^{\tau(1)}$ and $f_p^{\tau(1)}$ vs. Temperature
4.48 PZT Sample #502-C – $f_s^{\tau(2)}$ and $f_p^{\tau(2)}$ vs. Temperature
4.49 PZT Sample #502-C – $f_s^{\tau(1)}$ and $f_p^{\tau(1)}$ vs. Temperature
4.50 PZT Sample #502-C – $f_s^{\tau(2)}$ and $f_p^{\tau(2)}$ vs. Temperature
4.50 PZT Sample #502-C – $\sigma^p$ vs. Temperature.................................71
4.51 PZT Sample #502-C – $k_{33}, k_{31}, k_p$ and $k_{eff}$ vs. Temperature......................71
4.52 PZT Sample #502-C – $d_{33}$ and $d_{31}$ vs. Temperature..............................72
4.53 PZT Sample #502-C – $s^{D}_{11}, s^{E}_{11}$ and $s^{E}_{12}$ vs. Temperature.....................72
4.54 PZT Sample #502-C – $c^p_{12}$ and $c^E_{33}$ vs. Temperature.........................73
4.55 PZT Sample #502-C – $e^p_{31}$ and $e_{33}$ vs. Temperature.............................73
4.56 PZT Sample #502-C – $e^p_{33}, e^T_{33}$ and $e^S_{33}$ vs. Temperature.....................74
4.57 PZT Sample #502-C – Capacitance at 1 kHz vs. Temperature........................74
4.58 PZT Sample #850 – $|Z|$ on the 100 kHz – 10 MHz frequency range..............75
4.59 PZT Sample #850 – $\theta$ on the 100 kHz – 10 MHz frequency range..............76
4.60 PZT Sample #850 – $|Z|$ – First radial mode........................................76
4.61 PZT Sample #850 – $\theta$ – First radial mode........................................77
4.62 PZT Sample #850 – $|Z|$ – First radial overtone mode..............................77
4.63 PZT Sample #850 – $\theta$ – First radial overtone mode..............................78
4.64 PZT Sample #850 – $|Z|$ – First thickness mode......................................78
4.65 PZT Sample #850 – $\theta$ – First thickness mode......................................79
4.66 PZT Sample #850 – $f_s^{r(1)}$ and $f_p^{r(1)}$ vs. Temperature..........................79
4.67 PZT Sample #850 – $f_s^{r(2)}$ and $f_p^{r(2)}$ vs. Temperature..........................80
4.68 PZT Sample #850 – $f_s^{t(1)}$ and $f_p^{t(1)}$ vs. Temperature..........................80
4.69 PZT Sample #850 – $\sigma^p$ vs. Temperature...........................................81
4.70 PZT Sample #850 – $k^l_{33}, k_{31}, k_p$ and $k_{eff}$ vs. Temperature...............81
4.71 PZT Sample #850 – $d^l_{33}$ and $d_{31}$ vs. Temperature.............................82
4.72 PZT Sample #850 – $s^{D}_{11}, s^{E}_{11}$ and $s^{E}_{12}$ vs. Temperature.................82
4.73 PZT Sample #850 – $c^{p, 12}$ and $c^{E, 33}$ vs. Temperature…………………………………….83
4.74 PZT Sample #850 – $c^{e, 31}$ and $e_{33}$ vs. Temperature…………………………………….83
4.75 PZT Sample #850 – $e^{p, 33}$, $e^{T, 33}$ and $e^{S, 33}$ vs. Temperature…………………………84
4.76 PZT Sample #850 – Capacitance at 1 kHz vs. Temperature……………………………………..84
4.77 PZT Sample #880 – $|Z|$ on the 100 kHz – 10 MHz frequency range…………………………85
4.78 PZT Sample #880 – $\theta$ on the 100 kHz – 10 MHz frequency range…………………………86
4.79 PZT Sample #880 – $|Z|$ – First radial mode…………………………………………………………86
4.80 PZT Sample #880 – $\theta$ – First radial mode…………………………………………………………87
4.81 PZT Sample #880 – $|Z|$ – First radial overtone mode………………………………………………87
4.82 PZT Sample #880 – $\theta$ – First radial overtone mode………………………………………………88
4.83 PZT Sample #880 – $|Z|$ – First thickness mode……………………………………………………88
4.84 PZT Sample #880 – $\theta$ – First thickness mode……………………………………………………89
4.85 PZT Sample #880 – $f^{s(1)}$ and $f^{p(1)}$ vs. Temperature……………………………………………89
4.86 PZT Sample #880 – $f^{s(2)}$ and $f^{p(2)}$ vs. Temperature………………………………………………90
4.87 PZT Sample #880 – $f^{s(t)}$ and $f^{p(t)}$ vs. Temperature………………………………………………90
4.88 PZT Sample #880 – $\sigma^p$ vs. Temperature…………………………………………………………91
4.89 PZT Sample #880 – $k^{33}$, $k_{31}$, $k_p$ and $k_{eff}$ vs. Temperature……………………………………91
4.90 PZT Sample #880 – $d_{33}$ and $d_{31}$ vs. Temperature………………………………………………92
4.91 PZT Sample #880 – $s^{D, 11}$, $s^{E, 11}$ and $s^{E, 12}$ vs. Temperature………………………………92
4.92 PZT Sample #880 – $e^{p, 12}$ and $e^{E, 33}$ vs. Temperature………………………………………………93
4.93 PZT Sample #880 – $e^{p, 31}$ and $e_{33}$ vs. Temperature………………………………………………93
4.94 PZT Sample #880 – $e^{p, 33}$, $e^{T, 33}$ and $e^{S, 33}$ vs. Temperature……………………………………94
4.95 PZT Sample #880 – Capacitance at 1 kHz vs. Temperature………………………………………94
CHAPTER I
INTRODUCTION

1.1 Background

The piezoelectric effect was discovered by Jacques and Pierre Curie in 1880. They found that if certain crystals were subjected to mechanical strain, they became electrically polarized and the degree of polarization was proportional to the applied strain. They also discovered that these same materials deformed when they were exposed to an electrical field. This has become known as the inverse piezoelectric effect [12].

In just over 125 years, piezoelectricity has moved from laboratories to common industrial applications. Today, piezoelectric materials are being extensively used in a wide variety of applications like electromechanical transducers, band-pass filters, ultrasonic generators, bubble chambers, monolithic filters, quartz-clocks, radio circuitries, telemetry systems, telephone ringers, vibration suppressors, sensors and actuators.

1.1.1 Piezoelectric Effect

The piezoelectric effect is exhibited by a number of naturally-occurring crystals, for instance quartz, tourmaline and sodium potassium tartrate, and these have been used for many years as electromechanical transducers. For a crystal to exhibit the piezoelectric
effect, its structure should have no centre of symmetry. A stress (tensile or compressive) applied to such a crystal will alter the separation between the positive and negative charge sites in each elementary cell leading to a net polarization at the crystal surface. The effect is practically linear, i.e. the polarization varies directly with the applied stress, and direction-dependent, so that compressive and tensile stresses will generate electric fields and hence voltages of opposite polarity. It's also reciprocal, so that if the crystal is exposed to an electric field, it will experience an elastic strain causing its length to increase or decrease according to the field polarity [12].

1.1.2 Piezoelectric Ceramics

An important group of piezoelectric materials are the piezoelectric ceramics. These are polycrystalline materials with the perovskite crystal structure - a tetragonal / rhombohedral structure very close to cubic. They have the general formula $\text{A}^{2+}\text{B}^{4+}\text{O}_3^{2-}$, in which $\text{A}$ denotes a large divalent metal ion such as; barium or lead, and $\text{B}$ denotes a tetravalent metal ion such as titanium or zirconium. These materials can be considered as a mass of minute crystallites. Above a temperature known as the Curie point, these crystallites exhibit simple cubic symmetry. This structure is centrosymmetric with positive and negative charge sites coinciding, so there are no dipoles present in the material. Below the Curie point, however the crystallites take on tetragonal symmetry in which the positive and negative charge sites no longer coincide, so each elementary cell then has a built-in electric dipole which may be reversed, and also switched to certain allowed directions by the application of an electric field. The dipoles are not randomly oriented throughout the material. Neighboring dipoles align with each other to form
regions of local alignment known as Weiss domains. Within a Weiss domain, therefore, all the dipoles are aligned, giving a net dipole moment to the domain, and hence a net polarization (dipole moment per unit volume). The direction of polarization between neighboring Weiss domains within a crystallite can differ by 90° or 180°, and owing to the random distribution of Weiss domains throughout the material, no overall polarization or piezoelectric effect is exhibited.

1.1.3 Polarization

The ceramic may be made piezoelectric in any chosen direction by a poling treatment which involves exposing it to a strong electric field at a temperature slightly below the Curie point. Under the action of this field, domains most nearly aligned with the field will grow at the expense of other domains. The material will also lengthen in the direction of the field. When the field is removed, the dipoles remain locked in approximate alignment, giving the ceramic material a remanent dielectric polarization and a permanent deformation (i.e. making it anisotropic) [12].

1.1.4 Depolarization

While the piezoelectric ceramic materials are very reliable and durable within the industry recommended operating parameters, certain changes in the environmental conditions like exposure to a strong electric field of polarity opposite that of the polarizing field or mechanical stress sufficient to disturb the orientations of the domains in a piezoelectric ceramic material can destroy the alignment of the dipoles and can result partial or complete depolarization of the piezoelectric ceramics. Within the recommended
operating temperature range, temperature-associated changes in the orientation of the domains are reversible, but these changes can create charge displacements and electric fields and sudden temperature fluctuations can generate relatively high voltages, capable of depolarizing the ceramic elements. In most application these are unwanted effects that can obstruct measuring accuracy, reduce the performance of the actuators by reducing the displacement and damage or destroy sensitive electronic components.

1.2 Objectives and Scope

The original goal of this thesis was to develop a measurement system that is able to measure the properties of high-temperature piezoelectric ceramics that are currently being developed in the Materials Laboratory of the NASA GRC, but despite all our efforts the available high temperature piezoelectric ceramics like La$_2$Ti$_2$O$_7$ and La$_3$Ga$_5$SiO$_{14}$ could not be polarized. To demonstrate the capabilities of the developed measurement system, the focus of this thesis is on measuring the changes in the resonant and anti-resonant frequencies and electrical properties of commercially available PZT samples as the operating temperature is increasing and getting close to the Curie temperature. The measurements data can help to better understand and if possible, to predict, how these properties of these piezoelectric ceramic materials are dependent on the temperature. The evaluation of these measurements can be particularly useful to control system designers, because the collected information can help them to anticipate and compensate for these changes in case of non-normal operation modes like accidental overheating of the piezoelectric ceramic materials.
CHAPTER II
LINEAR THEORY OF PIEZOELECTRICITY

2.1 General

In linear piezoelectricity the equations of linear elasticity are coupled to the charge equations of electrostatics i.e. the constitutive equations, by means of the piezoelectric constants. However, the electric variables are not purely static, but only quasistatic, because of the coupling to the dynamic mechanical equations [1].

The basis of the linear theory of piezoelectricity is lengthy and already well covered in the IEEE Std. 176-1987, IEEE Standard on Piezoelectricity, it will not be repeated here. This thesis focuses on those parts of the theory that are necessary to know in order to understand the meaning of the measured \( (T, f_p^{r(1)}, f_s^{r(1)}, f_p^{r(2)}, f_s^{r(2)}, f_p^{t(1)}, f_s^{t(1)}, a, w, \rho, t, C) \) and calculated \((\sigma^p, v^p, K^T, k^{33}, k_{31}, k_{p}, k_{eff}, s^{D}_{11}, s^{E}_{11}, s^{E}_{12}, d^{33}, d_{31}, c^{p}_{12}, c^{E}_{33}, e^{p}_{31}, e_{33}, e^{T}_{33}, e^{S}_{33})\) parameters. All of the following descriptions, symbols and equations mentioned in this chapter are based upon the IEEE Std. 176-1987, IEEE Standard on Piezoelectricity if not noted otherwise.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>SI Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>Area</td>
<td>meter(^2)</td>
</tr>
<tr>
<td>( a )</td>
<td>Radius of a disk</td>
<td>meter</td>
</tr>
<tr>
<td>( c_{ijkl}, c_{pq} )</td>
<td>Elastic stiffness constant</td>
<td>Newton/meter(^2)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Meaning</td>
<td>SI Unit</td>
</tr>
<tr>
<td>--------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>$C$</td>
<td>Capacitance</td>
<td>Farad</td>
</tr>
<tr>
<td>$C_o$</td>
<td>Shunt capacitance in resonator equivalent circuit</td>
<td>Farad</td>
</tr>
<tr>
<td>$d_{ijk}$, $d_{ip}$</td>
<td>Piezoelectric constant</td>
<td>meter/Volt</td>
</tr>
<tr>
<td>$D$ (superscript)</td>
<td>At constant electric displacement</td>
<td></td>
</tr>
<tr>
<td>$D_i$</td>
<td>Electric displacement component</td>
<td>Coulomb/meter$^2$</td>
</tr>
<tr>
<td>$e_{ijk}$, $e_{ip}$</td>
<td>Piezoelectric constant</td>
<td>Coulomb/meter$^2$</td>
</tr>
<tr>
<td>$E$ (superscript)</td>
<td>At constant electric field</td>
<td></td>
</tr>
<tr>
<td>$E_i$</td>
<td>Electric field component</td>
<td>Volt/meter</td>
</tr>
<tr>
<td>$f$</td>
<td>Frequency</td>
<td>Hertz</td>
</tr>
<tr>
<td>$f_p$</td>
<td>Frequency of maximum resistance</td>
<td>Hertz</td>
</tr>
<tr>
<td>$f_s$</td>
<td>Frequency of maximum conductance</td>
<td>Hertz</td>
</tr>
<tr>
<td>$\Delta f$</td>
<td>$f_p - f_s$</td>
<td>Hertz</td>
</tr>
<tr>
<td>$H$</td>
<td>Electromechanical enthalpy density</td>
<td>Joule/meter$^3$</td>
</tr>
<tr>
<td>$J_{ij}(z)$</td>
<td>Modified quotient of cylinder functions</td>
<td></td>
</tr>
<tr>
<td>$k'_{33}$</td>
<td>Thickness-extensional coupling factor</td>
<td></td>
</tr>
<tr>
<td>$k_p$</td>
<td>Planar coupling factor</td>
<td></td>
</tr>
<tr>
<td>$s_{ijk}$, $s_{pq}$</td>
<td>Elastic compliance constant</td>
<td>meter$^2$/Newton</td>
</tr>
<tr>
<td>$S$ (superscript)</td>
<td>At constant strain</td>
<td></td>
</tr>
<tr>
<td>$S_{ij}$, $S_{ip}$</td>
<td>Strain component</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K or °C</td>
</tr>
<tr>
<td>$T_C$</td>
<td>Curie point</td>
<td>K or °C</td>
</tr>
<tr>
<td>$T$ (superscript)</td>
<td>At constant stress</td>
<td></td>
</tr>
<tr>
<td>$t$</td>
<td>Thickness</td>
<td>meter</td>
</tr>
<tr>
<td>$T_{ij}$, $T_p$</td>
<td>Stress component</td>
<td>Newton/meter$^2$</td>
</tr>
</tbody>
</table>
Table 2.1 Symbols and their units continued

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>SI Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v$</td>
<td>Velocity</td>
<td>meters/second</td>
</tr>
<tr>
<td>$w$</td>
<td>Width</td>
<td>meter</td>
</tr>
<tr>
<td>$x_i$</td>
<td>Rectangular coordinate axis</td>
<td>meter</td>
</tr>
<tr>
<td>$Y$</td>
<td>Electric circuit admittance</td>
<td>Siemens</td>
</tr>
<tr>
<td>$Z$</td>
<td>Electric circuit impedance</td>
<td>Ohm</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Phase Angle of dielectric loss</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity of free space</td>
<td>Farad/meter</td>
</tr>
<tr>
<td>$\varepsilon_{ij}$</td>
<td>Permittivity component</td>
<td>Farad/meter</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Order parameter</td>
<td></td>
</tr>
<tr>
<td>$\theta$</td>
<td>Curie-Weiss temperature</td>
<td>K</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Mass density</td>
<td>kilogram/meter$^3$</td>
</tr>
<tr>
<td>$\sigma^p$</td>
<td>Planar Poisson’s ratio</td>
<td></td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency (2\pi f)</td>
<td>radians/sec</td>
</tr>
</tbody>
</table>

2.2 Linear Piezoelectricity

The conservation of energy for the linear piezoelectric continuum results in the first law of thermodynamics:

$$\dot{U} = T_i \dot{S}_i + E_i \dot{D}_i$$  \hspace{1cm} (2.1)

where $U$ is the stored energy density for the piezoelectric continuum and where $(\cdot)$ denotes $\partial(\cdot)/\partial t$. The electric enthalpy density $H$ is defined by

$$H = U - E_i D_i$$  \hspace{1cm} (2.2)

and from Equations (2.1) and (2.2) there results
\[
\dot{H} = T_{ij} \dot{S}_{ij} - D_i \dot{E}_i \tag{2.3}
\]

Equation (2.3) implies
\[
H = H(S_{kl}, E_k) \tag{2.4}
\]

and from Equations (2.3) and (2.4) there result
\[
T_{ij} = \frac{\partial H}{\partial S_{ij}} \tag{2.5}
\]
\[
D_i = -\frac{\partial H}{\partial E_i} \tag{2.6}
\]

where it should be noted that
\[
\frac{\partial S_{ij}}{\partial S_{ji}} = 0 \quad i \neq j \tag{2.7}
\]
in taking the derivatives called for in Equation (2.5).

In linear piezoelectric theory a quadratic form is assumed, so \( H \) is
\[
H = \frac{1}{2} c^{E}_{ijkl} S_{ij} S_{kl} - e_{kij} E_k S_{ij} - \frac{1}{2} e^S_{ij} E_i E_j \tag{2.8}
\]

where \( c^{E}_{ijkl}, e_{kij} \) and \( e^S_{ij} \) are the elastic, piezoelectric and dielectric constants, respectively.

In general there are 21 independent elastic constants, 18 independent piezoelectric constants and 6 independent dielectric constants. From Equations (2.5), (2.6) and (2.8) with Equation (2.7) there result the piezoelectric constitutive equations:
\[
T_{ij} = c^{E}_{ijkl} S_{ij} - e_{kij} E_k \tag{2.9}
\]
\[
D_i = e_{kij} S_{ij} + e^S_{ij} E_k \tag{2.10}
\]

In order to write the elastic and piezoelectric tensors in the form of a matrix array, a compressed matrix notation is introduced in place of the tensor notation, which has been used exclusively heretofore. This matrix notation consists of replacing \( ij \) or \( kl \) by \( p \).
or \( q \), where \( i, j, k, l \) take the values 1, 2, 3 and \( p, q \) take the values 1, 2, 3, 4, 5, 6 according to the Table 2.2.

The identifications

\[ c_{ijkl}^E \equiv c_{pq}^E, \quad e_{ijkl} \equiv e_{pq}, \quad T_{ij} \equiv T_p \]  \hspace{1cm} (2.11)

are made.

<table>
<thead>
<tr>
<th>( ij ) or ( kl )</th>
<th>( p ) or ( q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>1</td>
</tr>
<tr>
<td>22</td>
<td>3</td>
</tr>
<tr>
<td>33</td>
<td>3</td>
</tr>
<tr>
<td>23 or 32</td>
<td>4</td>
</tr>
<tr>
<td>31 or 13</td>
<td>5</td>
</tr>
<tr>
<td>12 or 21</td>
<td>6</td>
</tr>
</tbody>
</table>

Then the constitutive Equations (2.9) and (2.10) can be written:

\[ T_p = c_{pq}^E S_q - e_{qq} E_k \]  \hspace{1cm} (2.12)
\[ D_i = e_{ii} S_q + e_{ik} E_k \]  \hspace{1cm} (2.13)

where

\[ S_{ij} = S_p \]  \hspace{1cm} \text{when } i = j, \ p = 1, 2, 3
\[ 2S_{ij} = S_p \]  \hspace{1cm} \text{when } i \neq j, \ p = 4, 5, 6  \hspace{1cm} (2.14)
2.3 Radial Modes in Thin Plates

A schematic diagram of a thin circular polarized ceramic plate is shown in Figure 2.1. The major surfaces of the plate are fully covered by electrodes. The $x_3$ coordinate axis is directed normal to the circular surfaces in which $r$ and $\theta$ are measured. The plate is driven into radial vibration by the application of an alternate current voltage across the surface electrodes.

![Figure 2.1 Radial mode excitation of a circular disk](image)

The differential equation for radial motion of the disk is

$$c_{11}^p \left[ \frac{\partial^2 u_r}{\partial r^2} + \frac{1}{r^2} \frac{\partial u_r}{\partial r} - \frac{u_r}{r^2} \right] = \rho \frac{\partial^2 u_r}{\partial t^2}$$

(2.15)

where $u_r$ is the radial component of displacement and

$$c_{11}^p = \frac{s_{11}^E}{(s_{11}^E)^2 - (s_{12}^E)^2}$$

(2.16)

The pertinent constitutive equations are

$$T_{rr} = c_{11}^p \frac{\partial u_r}{\partial r} + c_{12}^p \frac{u_r}{r} - e_{31}^p E_3$$

(2.17)
\[ D_3 = e_3^p \frac{1}{r} \frac{\partial}{\partial r} (ru_r) + \varepsilon_{33}^p E_3 \] (2.18)

where

\[ c_{12}^E = \frac{-s_{12}^E}{(s_{11}^E)^2 - (s_{12}^E)^2} \] (2.19)

\[ e_{3i}^E = \frac{d_{31}}{s_{11}^E + s_{12}^E} \] (2.20)

\[ \varepsilon_{33}^p = \frac{-2d_{31}^2}{s_{11}^E + s_{12}^E} + \varepsilon_{33}^r \] (2.21)

and

\[ -E_3 = V / t \] (2.22)

where \( V \) is the driving voltage. The nontrivial boundary condition for the planar radial modes is

\[ T_r = 0 \quad \text{at} \quad r = a \] (2.23)

The steady-state forced vibrational solution of Equation (2.15), and satisfying Equation (2.23), may be written in the form

\[ u_r = AJ_1(\omega r / v^p) e^{i\omega r} \] (2.24)

where \( \omega \) is the driving frequency, \( J_1 \) is the Bessel function of the first kind and first order, and the speed of sound in the material is

\[ v^p = \sqrt{c_{11}^p / \rho} \] (2.25)

The electrical admittance is given by [13]

\[ Y = \frac{-i\omega \varepsilon_{33}^p \pi a^2}{t} \left[ \frac{2(k^p)^2}{1 - \sigma - J_1^2} \right] - 1 \] (2.26)
where $J'_1$ is the modified quotient of cylinder functions of the first order, defined by
\[ J'_1(z) = zJ_0(z)/J_1(z) \] (2.27)
and $J_0$ is the Bessel function of the first kind and zero order,
\[ \sigma^p = -s_{12}^E / s_{11}^E \] (2.28)
and may be interpreted as the planar Poisson’s ratio.

The coefficient $k_p^p$ is a planar radial piezoelectric coupling coefficient for the thin circular polarized ceramic disk is given by
\[ (k_p^p)^2 = \frac{(e_{31})^2}{e_{11}^p e_{33}^p} \] (2.29)
It is related to the usual planar coupling factor $k_p$ by the relation
\[ (k_p^p)^2 = \frac{1 + \sigma^p}{2} \left( \frac{k_p^2}{1 - k_p^2} \right) \] (2.30)
and, where $k_p$ is related to $k_{31}$, by the well-known relation
\[ k_p^2 = 2k_{31}^2/(1 - \sigma^p) \] (2.31)

2.4 Radial Modes of Disks

From the basic theory of the disk resonator presented in 2.3 one finds that the electrical impedance is given by
\[ Z(\omega) = \frac{t}{i\omega e_{33}^p \pi a^2} \left[ \frac{J'_1(\omega a / v^p) + \sigma^p - 1}{(1 - \sigma)J'_1(\omega a / v^p) + \sigma^p - 1 + 2k_p^2} \right] \] (2.32)
where $t$ is the thickness, $a$ is the radius and $J'_1$ is defined by Equation (2.27). If $\eta_1$ is defined as
\[ \eta_1 = 2\pi f_s a / v^p \] (2.33)
then $\eta_1$ is the lowest root of the Equation (2.34), that makes the impedance zero.

$$J'_1(\eta_1) = 1 - \sigma_p$$ \hspace{1cm} (2.34)

Table 2.3 gives the variations of $\eta_1$ with $\sigma_p$. Thus, from a measurement of the fundamental resonance frequency of a disk resonator, one obtains

$$s_{11}^E (1 - (\sigma_p^p)^2) = \eta_1^2 / \rho (2\pi f_s a)^2$$ \hspace{1cm} (2.35)

Equation (2.35) is clearly not sufficient to determine either $s_{11}^E$ or $\sigma_p$. One convenient method to obtain $\sigma_p$ is to measure also the resonance frequency $f_s^{(2)}$ of the first overtone radial mode, given by the second lowest root of Equation (2.34). The ratio $f_s^{(2)}/f_s$ then depends only on $\sigma_p$ and is given as a function of $\sigma_p$ in Table 2.3. Once $\sigma_p$ is found in this way, $s_{11}^E$ may be calculated from Equation (2.35).

Table 2.3 Frequency constant of disk resonator and ratio of first overtone to fundamental resonance frequencies as a function of the planar Poisson’s ratio

<table>
<thead>
<tr>
<th>$\sigma_p$</th>
<th>$\eta_1$</th>
<th>$f_s^{(2)}/f_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1.87898</td>
<td>2.84258</td>
</tr>
<tr>
<td>0.10</td>
<td>1.91539</td>
<td>2.79360</td>
</tr>
<tr>
<td>0.15</td>
<td>1.95051</td>
<td>2.74826</td>
</tr>
<tr>
<td>0.20</td>
<td>1.98441</td>
<td>2.70617</td>
</tr>
<tr>
<td>0.25</td>
<td>2.01717</td>
<td>2.66699</td>
</tr>
<tr>
<td>0.30</td>
<td>2.04885</td>
<td>2.63043</td>
</tr>
<tr>
<td>0.35</td>
<td>2.07951</td>
<td>2.59625</td>
</tr>
<tr>
<td>0.40</td>
<td>2.10920</td>
<td>2.56423</td>
</tr>
<tr>
<td>0.45</td>
<td>2.13797</td>
<td>2.53416</td>
</tr>
<tr>
<td>0.50</td>
<td>2.16587</td>
<td>2.50589</td>
</tr>
<tr>
<td>0.55</td>
<td>2.19294</td>
<td>2.47926</td>
</tr>
<tr>
<td>0.60</td>
<td>2.21922</td>
<td>2.45414</td>
</tr>
</tbody>
</table>
If \( \xi_1 \) is defined as \( 2\pi f_p a / v^p \), that is,

\[
\xi_1 = \eta_1 \frac{f_p}{f_s} = \eta_1 \left(1 + \frac{\Delta f}{f_s}\right)
\]

then the planar coupling factor can be calculated as follows from measurements of the resonance and anti-resonance frequencies:

\[
k_p^2 = \frac{J_1'(\xi_1) + \sigma^p - 1}{J_1'(\xi_1) - 2}
\]

The dielectric constant \( \varepsilon_{33}^p \) introduced in 2.3 is related to the dielectric constant \( \varepsilon_{33}^T \) and \( \varepsilon_{33}^S \) by the following expressions:

\[
\varepsilon_{33}^p = \varepsilon_{33}^T (1 - k_p^2)
\]

\[
\varepsilon_{33}^p = \varepsilon_{33}^S \left[1 - (k_{33}^p)^2\right]
\]

In measuring radial-mode resonators one should normally have \( t<20a \) to approximate the assumed infinitely thin disk. However, when one is measuring the first overtone radial mode to determine \( \sigma^p \), this condition is not adequate, and one should have \( t<40a \) to ensure reliable results.

2.5 Thickness Modes of Plates

In general, the thickness modes of plates are quite complex. For both thickness extensional and thickness shear modes, there are three relevant material constants, an elastic constant \( c^E \), a piezoelectric constant \( e \) and a dielectric constant \( \varepsilon^S \).

The electromechanical coupling factor \( k \) is given in terms of these constants by

\[
k^2 / (1 - k^2) = e^2 / \varepsilon^S c^E
\]
The elastic constant is related to the frequency $f_p$:

$$c^e = 4(1 - k^2) \rho f_p^2 t^2$$  \hspace{1cm} (2.41)

where $t$ is the plate thickness, and the electrical impedance is of the form

$$Z(\omega) = \frac{t}{i\omega \varepsilon s A} \left[1 - k^2 \frac{\tan(\omega / 4 f_p)}{(\omega / 4 f_p)}\right]$$  \hspace{1cm} (2.42)

where $A$ is the electrode area.

Table 2.4 Motional capacitance constant $\Gamma$ for the thickness mode
of a plate as a function of electromechanical coupling factor $k$

<table>
<thead>
<tr>
<th>$k$</th>
<th>$\Gamma / \varepsilon S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>0.0187</td>
</tr>
<tr>
<td>0.20</td>
<td>0.0341</td>
</tr>
<tr>
<td>0.25</td>
<td>0.0548</td>
</tr>
<tr>
<td>0.30</td>
<td>0.0817</td>
</tr>
<tr>
<td>0.35</td>
<td>0.1162</td>
</tr>
<tr>
<td>0.40</td>
<td>0.1598</td>
</tr>
<tr>
<td>0.45</td>
<td>0.2150</td>
</tr>
<tr>
<td>0.50</td>
<td>0.2851</td>
</tr>
<tr>
<td>0.55</td>
<td>0.3752</td>
</tr>
<tr>
<td>0.60</td>
<td>0.4926</td>
</tr>
<tr>
<td>0.65</td>
<td>0.6492</td>
</tr>
<tr>
<td>0.70</td>
<td>0.8649</td>
</tr>
<tr>
<td>0.75</td>
<td>1.1752</td>
</tr>
<tr>
<td>0.80</td>
<td>1.6515</td>
</tr>
<tr>
<td>0.85</td>
<td>2.4606</td>
</tr>
<tr>
<td>0.90</td>
<td>4.1022</td>
</tr>
<tr>
<td>0.95</td>
<td>9.0765</td>
</tr>
</tbody>
</table>
From Equation (2.42) one finds that the $k$ coupling factor can be determined from the frequencies $f_s$ and $f_p$,

$$k^2 = \frac{\pi}{2} \frac{f_s}{f_p} \tan\left(\frac{\pi}{2} \frac{\Delta f}{f_p}\right)$$

or from the motional capacitance constant:

$$\Gamma = \left(8\varepsilon^S k^2 \sqrt{\pi}\right) \frac{(f_p / f_s)^2}{1 - 4k^2 (1 - k^2)(f_p / f_s)^2 / \pi^2}$$

When $k<0.1$, $\Gamma = 8\varepsilon^S k^2 / \pi$ is an adequate approximation to Equation (2.44), and for $k>0.1$, $\Gamma / \varepsilon^S$ versus $k$ are given in Table 2.4.

In pure thickness extensional mode the relevant constants are $c_{33}^E$, $e_{33}$, $\varepsilon_{33}^S$, and $k_{33}^l$, so the pertinent constitutive equations, based upon Equations (2.9) and (2.10) are

$$T_3 = c_{33}^E S_3 - e_{33} E_3$$

$$D_3 = e_{33} S_3 + \varepsilon_{33}^S E_3$$

In measuring the thickness mode resonances, the smallest $x_1$ or $x_2$ dimension should be 10 or more times larger than the plate thickness, $x_3$ dimension. Even if this is the case, coupling to high overtone contour modes is frequently a serious problem. Often the plate dimensions must be changed slightly to get a clear resonance for measuring $f_s$. 
CHAPTER III
MEASUREMENT APPARATUS

3.1 Measurement Equipments and Configurations

Five different control and measurement software were developed by the author of this thesis for five different measurement apparatus combinations, see Figures 3.1, 3.2, 3.3, 3.4, 3.5 to evaluate and quantify impedance measurements of piezoelectric ceramics at the NASA GRC. All of the instrument control programs were written using LabVIEW 7.1 software to integrate Solartron 1260 and Solartron 1296 Impedance/Gain Phase Analyzer, Solartron 1287 Electrochemical Interface, Agilent 4284A, Agilent 4294A and Agilent 4291B LCR meters, Eurotherm temperature controllers and Keithley 2182A temperature measurement hardware to determine electrochemical, dielectric, and conductance characteristics of the materials as function of temperature and frequency. By controlling the set point of the furnace, each of the developed control software was able to repeat the required measurements automatically at different temperatures.

The wide frequency range and superb accuracy of the Solartron 1260 Impedance/Gain Phase Analyzer enables to characterize material behavior, predict lifetime and failure rates, and for improving fabrication and curing processes. Since impedance measurement is repeatable and non-destructive, it can provide valuable insights into the behavior of a huge variety of substances, components and systems.
The Solartron 1287 Electrochemical Interface works equally well as a stand-alone instrument, or as part of a computer controlled system. Electrochemical measurements rely on the electrical aspect of chemical processes to provide readable data. This is based on Faraday’s law which relates the change in mass per unit area of a substance, to the magnitude of the current flowing through it. For these measurements the Solartron 1287 Electrochemical Interface can provide accurate direct current polarization to establish the rate of ionization in the sample and frequency response analysis to study the sample impedance characteristics.
The Solartron 1296 Impedance/Gain Phase Analyzer is a development of the Chelsea Dielectric Interface and it extends the capability of a Solartron 1260 Frequency Response Analyzer (FRA) and enables the FRA to be used for a wide range of materials testing.

The Agilent 4284A, Agilent 4294A and Agilent 4291B precision impedance analyzers provide highly accurate 4-terminal-pair impedance measurement in wide frequency ranges. Extremely small variation in component characteristics can be precisely evaluated with sweep measurements of 0.08% basic accuracy. These LCR meters are excellent for component evaluation like capacitors, inductors, resonators, semiconductors and for material evaluations like PC boards and toroidal cores.

Figure 3.3 Configuration #3: Impedance measurements of ceramics, 20 Hz – 1 MHz.

Figure 3.4 Configuration #4: Impedance measurements of ceramics, 1 MHz – 1.8 GHz.
Figure 3.5 Configuration #5: Impedance measurements of ceramics, 40 Hz – 110 MHz.

All of the above mentioned measurement systems developed at NASA GRC functioning well, but all of the piezoelectric ceramics measurements were performed only on Configuration #5, Figure 3.5, since the 40 Hz – 110 MHz frequency range of this measurement system setup covers all of the vibration modes necessary to evaluate the electrical properties of the measured piezoelectric ceramics.

3.2 Measurement System Hardware, Configuration #5

As it shows on Figure 3.5, the measurement system hardware, Configuration #5 consists of four main components. The Personal Computer (PC) that run the measurement software is connected to the Agilent 4294A Precision Impedance Analyzer via General Purpose Interface Bus (GPIB) and Local Area Network (LAN) connection and to the Eurotherm 2404 Temperature Controller via Universal Serial Bus (USB) to Recommended Standard-232C (RS-232) interface combination. The temperature of the furnace is monitored and controlled by the Eurotherm 2404 Temperature Controller. The electrical properties of the ceramic samples were measured via a 16089A fixture/electrodes setup by the Agilent 4294A Precision Impedance Analyzer.
3.2.1 PC Configuration

An IBM ThinkPad laptop with Pentium 4 processor and Windows XP Professional operation system, LabVIEW 7.1 and iTools Engineering Studio program packages were used during the measurements. The laptop was connected to the instruments using two built-in USB ports and the LAN connection.

3.2.2 Agilent 4294A Precision Impedance Analyzer

The Agilent 4294A Precision Impedance Analyzer provides highly accurate 4-terminal-pair impedance measurement in a wide frequency range of 40 Hz to 110 MHz and extremely small variation in component characteristics that can be precisely evaluated with sweep measurements of 0.08% basic accuracy. This instrument is very good for component evaluation like capacitors, inductors, resonators, semiconductors and for material evaluations like PC boards and toroidal cores and it also has a wide range of measurement parameters.

The front panel of the Agilent 4294A provides several blocks of hardkeys and an LCD display with a series of softkeys along its right-hand edge. Also, there are a number of test connectors and a power switch beneath the LCD display. Figure 3.6 shows the front panel of the Agilent 4294A [10].

The front panel keys were used only for calibration of the instrument since all the required measurement options were available via the GPIB using GPIB codes, so the instrument was controlled by the measurement software during the measurements. The electrical properties of the ceramic samples were measured via a 16089A fixture/shielded nickel electrodes setup by the Agilent 4294A Precision Impedance Analyzer.
The 16089A fixture is rated in the 5 Hz to 100 kHz frequency range. However, the 16089A fixture / shielded nickel electrodes combination were compared to the high frequency rated 16453A dielectric test fixture on the 40 Hz to 10 MHz frequency range and the difference in their measurement results were negligible. To compensate for this minor difference and to eliminate errors produced between the test fixture and the Agilent 4294A, fixture compensation calibration was performed on the 16089A fixture / shielded nickel electrodes combination before each measurement. The fixture compensation process was performed with a standard calibration kit [10].

The measured data was automatically saved on the internal flash memory of the instrument and at the end of the measurements it was manually downloaded to the PC via the LAN connection using the basic File Transfer Protocol (ftp).

Figure 3.6 Agilent 4294A Precision Impedance Analyzer front panel.
3.2.3 Eurotherm 2404 Temperature Controller

The temperature of the furnace was monitored and controlled by the Eurotherm Temperature Controller. The controller used a pre-set Proportional-Integral-Derivative (PID) control and received the temperature set-points from the PC via USB to RS-232 interface combination using the iTools program OPC (Object Linking and Embedding for Process Control) server option. The iTools is a complete configuration and monitoring program package for all Eurotherm Series 2000 controllers. It can edit, store and 'clone' complete controller configurations and in addition a set-point program editor and real time trend plots of the process values are provided [11].

3.2.4 Furnace

The furnace is mounted on a frame that holds the ceramic tubes covered electrodes in place and allows the furnace to be opened without disturbing the sample in the center of the furnace.

Figure 3.7 Furnace top view, furnace shown opened for clarity.
The sample was held in place by spring loaded ceramic tubes. To ensure proper insulation, the silver/palladium coated surface of the samples was connected to the electrodes wires that run through the tubes to the top and to the bottom of the frame as shown on Figure 3.8. The furnace is rated for 1600°C, but only used up to 500°C to prevent the heat degradation of the electrode surfaces of the samples.

Figure 3.8 Furnace side view, half of the furnace shown removed for clarity.

3.3 Measurement System Software, Configuration #5

LabVIEW programs are called virtual instruments, or VIs, because their appearance and operation imitate physical instruments, such as oscilloscopes and multimeters. LabVIEW contains a comprehensive set of tools for acquiring, analyzing, displaying, and storing data, as well as tools to help you troubleshoot the graphical programming code. In LabVIEW, first the user interface, or front panel is built, with controls and indicators. Controls are knobs, push buttons, dials, and other input devices.
Indicators are graphs, LEDs, and other displays. After the user interface is ready, the programming code is added using VIs and structures to control the front panel objects. The block diagram contains this code. LabVIEW has some pre written, built in functions and sub-VIs to communicate with hardware such as data acquisition, control devices, GPIB and RS-232, instruments [9].

3.3.1 User Interface

Figure 3.9 show the whole user interface of the measurement program. The table on the left side shows the possible measurement pairs and their designation numbers. The program recognizes 24 different measurement pair combinations as listed with #1 to #24 and the #0 which means all 24 of them together.

The temperature chart which is shown in the bottom-left part of the interface allows the user to monitor the temperature of the furnace with 5 seconds sampling rate.

The bottom-right part of the interface where the user can input the set-points by loading the pre-written temperature file, in this case the temperature.txt. This text file is a simple list of the temperature set-point numbers the user wants to use and it can be edited or renamed very simply by a basic file editor like Notepad.

The set-points will be loaded to the ‘Temperature Set-points’ list indicator from the text file at the start of the program. The ‘Soak Time’ is optional, but i.e. if it set to 20 minutes, then it allows the sample to reach the temperature equilibrium at the current set-point required for reliable measurements. The ‘Elapsed Time’ indicator shows how many minutes passed already from the soak time. The ‘Current Temperature’ indicator shows
the actual temperature of the furnace while the ‘Current Temperature Setpoint’ indicator shows the required temperature of the furnace.

Figure 3.9 Front panel of the measurement program, 4294A2.vi.

The upper half of the interface is where the user can define the measurement parameters. The user has to set the first set of start and stop frequencies, the ‘Sample Designation’ characters and the ‘Measurement Setup’ numbers to be able to run the experiments. The second and third set of measurement parameters are optional, but in case it required then the ‘Sample Designation’ characters has to be different in each case, because the data files are DOS based and there are only 8 characters available for the name of the files. The names of the data files are determined by the following rule: 3 character from the ‘Sample Designation’ setting, 2 character from the number of the measurement like 01, 04 or 10…etc. and the last 3 characters denote the temperature when the measurement was taken like 25°C makes 025…etc. So, because of the actual
frequency range where the measurement was taken is in the data file and not in the file name, it is important, as it was mentioned before, that the ‘Sample Designation’ characters has to be different at each frequency range measurements. The ‘Cs, Cp Measurement @ 1 kHz’ is also optional, but if it is allowed, then the program runs the #5 and #24 measurements in the 500 Hz to 1.5 kHz frequency range at every temperature set-points saving the Cs, Rs, Cp and Rp values.

The most important option available for the user is the ‘Quick Scan’. If the ‘Quick Scan’ is allowed, then the program disregards the temperature set-points mentioned above and runs all of the required measurement once at the current temperature of the furnace. If the ‘Quick Scan’ is not allowed then the program runs all of the required measurement according to the loaded temperature set-point text file and soak-time.

In order to be able to send control signals to the temperature controller, the LabVIEW measurement program utilize the OPC server provided by the iTools program. The iTools program package employs an OPC server which uses MODBUS® protocol to communicate with the temperature controller. The server connects to the controller via serial communications allowing a third party programs, in this case the LabVIEW to communicate via this connection [11].

### 3.3.2 Block Diagram

The block diagram of a measurement system program shown on Figure 3.10, 3.11, 3.12 and 3.13 is for information only. To understand this program block diagram requires some basic knowledge of graphical programming used in LabVIEW. For more information about this programming code, visit the website listed in Reference [9].
Figure 3.10 Part #1 of the block diagram of the measurement program, 4294A2.vi.
Figure 3.11 Part #2 of the block diagram of the measurement program, 4294A2.vi.
Figure 3.12 Part #3 of the block diagram of the measurement program, 4294A2.vi.
Figure 3.13 Part #4 of the block diagram of the measurement program, 4294A2.vi.
CHAPTER IV

POLARIZATION, MEASUREMENT RESULTS AND ANALYSIS

4.1 Polarization Attempts of High Temperature Piezoelectric Ceramics

The poling procedure is usually the final, but very important step of piezoelectric ceramics manufacture. If an initially unpolarized piezoelectric sample is subjected to an increasing electrical field at temperature slightly below its Curie point, the dipoles in the sample become increasingly aligned with the field and if the field reduced to zero, the dipoles do not return to their original alignment. There are several preferred directions within the crystallites and the dipoles remain in the ones most closely aligned with the original electrical field [12]. The appropriate poling conditions have to be chosen carefully in order to obtain maximum piezoelectric response.

Piezoelectric materials, $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (Langasite) with $1100^\circ\text{C}$-$1200^\circ\text{C}$ and $\text{La}_2\text{Ti}_2\text{O}_7$ with $1500^\circ\text{C}$ Curie temperatures were developed at NASA GRC. Several poling experiments were performed on these materials using a Radiant Technologies’ Precision Pro Non-Linear Materials Analyzer. The impedance of the samples were measured in the $40\text{Hz} - 1.8\text{ GHz}$ frequency range before and after each poling experiment to detect the permanent polarization. The samples were heated up and cooled down at $4^\circ\text{C}$ per minute to minimize the thermal shock on the heating elements and the samples were held at the polarization temperatures for 15 minutes.
As soon as the samples reached the set poling temperature, dc electrical field was applied and held constant till the samples cooled down to room temperature. The samples were subjected to several different set of poling conditions from room temperature poling with 3000 VDC/mm electrical field strength to 1600°C temperature poling with 8000 VDC/mm electrical field strength. The polarization effect was not measured with the Radiant Technologies’ Materials Analyzer on any of the samples. Only minor shifts were observed in the impedance in the 40Hz – 1.8 GHz frequency range.

Based upon the performed poling experiments, it can be stated that the La$_2$Ti$_2$O$_7$ and La$_3$Ga$_5$SiO$_{14}$ piezoelectric polycrystalline ceramic materials could not be poled with the experimental conditions described above. There are a few possible explanations of this result. It is might be that there are not enough initial dipoles in the material that can change alignment or even if there are dipoles that can re-align perhaps separation distance of dipoles under the applied electrical field is not large enough, but it is also possible that the applied electrical field is simply not strong enough. Since the applicable electrical field has an upper limit due to breakdown voltage, it is not possible to increase the electrical field without damaging the samples during the poling treatment.

However, it might be possible to use these high temperature piezoelectric ceramics without any poling treatment, because signs of electrostrictive behavior were observed during the displacement measurements performed on the samples. The electrostriction is a form of elastic deformation of a dielectric induced by an electric field. When an electric field is applied to a dielectric it deforms, and the strain (ratio of deformation/original dimension) is proportional to the square of the voltage. Reversal of the electric field does not reverse the direction of the deformation.
But, regardless of this possible electrostrictive behavior, these piezoelectric ceramics did not show any resonance / anti-resonance characteristic. To demonstrate the capabilities of the developed measurement system, commercially available, poled Lead Zirconate Titanate (PZT) material samples were used for the measurements as the main experimental objective of this thesis.

4.2 Measured and/or Calculated Parameters

The basic parameters of the piezoelectric samples that were calculated or measured during the experiments are listed in Table 4.1.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>SI Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>°C</td>
</tr>
<tr>
<td>$f_p^{r(1)}$</td>
<td>Fundamental radial mode frequency of maximum resistance</td>
<td>Hz</td>
</tr>
<tr>
<td>$f_s^{r(1)}$</td>
<td>Fundamental radial mode frequency of maximum conductance</td>
<td>Hz</td>
</tr>
<tr>
<td>$f_p^{r(2)}$</td>
<td>First overtone radial mode frequency of maximum resistance</td>
<td>Hz</td>
</tr>
<tr>
<td>$f_s^{r(2)}$</td>
<td>First overtone radial mode frequency of maximum conductance</td>
<td>Hz</td>
</tr>
<tr>
<td>$f_p^{t(1)}$</td>
<td>Fundamental thickness mode frequency of maximum resistance</td>
<td>Hz</td>
</tr>
<tr>
<td>$f_s^{t(1)}$</td>
<td>Fundamental thickness mode frequency of maximum conductance</td>
<td>Hz</td>
</tr>
<tr>
<td>$a$</td>
<td>Radius of a disk</td>
<td>m</td>
</tr>
<tr>
<td>$A$</td>
<td>Area of an electrode (calculated from the radius of a disk)</td>
<td>m²</td>
</tr>
<tr>
<td>$w$</td>
<td>Thickness (without electrodes)</td>
<td>m</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>kg/m³</td>
</tr>
<tr>
<td>$t$</td>
<td>Distance between electrodes</td>
<td>m</td>
</tr>
<tr>
<td>$C$</td>
<td>Capacitance at 1kHz</td>
<td>F</td>
</tr>
</tbody>
</table>
4.3 Calculated Electrical Properties

All of the calculated electrical properties of the piezoelectric samples listed in Table 4.2 are based upon the parameters listed in Table 4.1.

Table 4.2 Calculated electrical properties

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>SI Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma^p$</td>
<td>Poisson's ratio</td>
<td></td>
</tr>
<tr>
<td>$\eta_1$</td>
<td>Order parameter</td>
<td></td>
</tr>
<tr>
<td>$\nu^p$</td>
<td>Speed of sound in the material</td>
<td>m/s</td>
</tr>
<tr>
<td>$K^T$</td>
<td>Free relative dielectric constant</td>
<td></td>
</tr>
<tr>
<td>$k_{33}^t$</td>
<td>Thickness–extensional mode coupling factor</td>
<td></td>
</tr>
<tr>
<td>$k_{31}$</td>
<td>Extensional mode coupling factor</td>
<td></td>
</tr>
<tr>
<td>$k_p$</td>
<td>Planar coupling factor</td>
<td></td>
</tr>
<tr>
<td>$k_{\text{eff}}$</td>
<td>Effective coupling factor</td>
<td></td>
</tr>
<tr>
<td>$s_{11}^D$</td>
<td>Elastic coefficient at constant electrical displacement</td>
<td>m²/N</td>
</tr>
<tr>
<td>$s_{11}^E$</td>
<td>Elastic coefficient at constant electrical field</td>
<td>m²/N</td>
</tr>
<tr>
<td>$-s_{12}^E$</td>
<td>Elastic coefficient at constant electrical field</td>
<td>m²/N</td>
</tr>
<tr>
<td>$d_{33}$</td>
<td>Thickness–extensional mode piezoelectric constant</td>
<td>C/N or m/V</td>
</tr>
<tr>
<td>$-d_{31}$</td>
<td>Extensional mode piezoelectric constant</td>
<td>C/N or m/V</td>
</tr>
<tr>
<td>$c_{12}^P$</td>
<td>Planar elastic stiffness constant</td>
<td>N/m²</td>
</tr>
<tr>
<td>$c_{33}^E$</td>
<td>Elastic stiffness constant at constant electrical field</td>
<td>N/m²</td>
</tr>
<tr>
<td>$-e_{31}^P$</td>
<td>Planar extensional mode piezoelectric constant</td>
<td>C/m²</td>
</tr>
<tr>
<td>$e_{33}$</td>
<td>Thickness–extensional mode piezoelectric constant</td>
<td>C/m²</td>
</tr>
<tr>
<td>$\varepsilon_{33}^P$</td>
<td>Planar thickness–extensional mode permittivity component</td>
<td>F/m</td>
</tr>
<tr>
<td>$\varepsilon_{33}^T$</td>
<td>Permittivity component at constant stress</td>
<td>F/m</td>
</tr>
<tr>
<td>$\varepsilon_{33}^S$</td>
<td>Permittivity component at constant strain</td>
<td>F/m</td>
</tr>
</tbody>
</table>
The electrical properties were calculated in the following order:

**σ**

In order to be able to automatically calculate the Poisson's ratio based upon the \( f_s^{r(2)}/f_p^{r(l)} \) ratio, the following 10th order polynomial approximation of the relations of Table 2.3 was used:

\[
\sigma = 100000000\times [0.00002795314806*(f_s^{r(2)}/f_p^{r(l)})^{10} - 0.0073437523227*(f_s^{r(2)}/f_p^{r(l)})^9 + 0.00867731854159*(f_s^{r(2)}/f_p^{r(l)})^8 - 0.06072621017601*(f_s^{r(2)}/f_p^{r(l)})^7 \\
+0.27874189616412*(f_s^{r(2)}/f_p^{r(l)})^6 - 0.87687338224803*(f_s^{r(2)}/f_p^{r(l)})^5 \\
+1.91458077662298*(f_s^{r(2)}/f_p^{r(l)})^4 - 2.86495439332219*(f_s^{r(2)}/f_p^{r(l)})^3 \\
+2.81186521683483*(f_s^{r(2)}/f_p^{r(l)})^2 - 1.63452106667819*(f_s^{r(2)}/f_p^{r(l)}) \\
+0.4273285043911] \quad (4.1)
\]

This approximation is a match to the relations of Table 2.3 up to the 4th decimal.

**η**

In order to be able to automatically calculate the order parameter based upon the \( f_s^{r(2)}/f_p^{r(l)} \) ratio, the following 6th order polynomial approximation of the relations of Table 2.3 was used:

\[
\eta = 10000\times [-0.00084523658921*(f_s^{r(2)}/f_p^{r(l)})^{6} + 0.01359048512994*(f_s^{r(2)}/f_p^{r(l)})^5 - 0.09097672756895*(f_s^{r(2)}/f_p^{r(l)})^4 - 0.32452162108606*(f_s^{r(2)}/f_p^{r(l)})^3 \\
-0.65049087130736*(f_s^{r(2)}/f_p^{r(l)})^2 + 0.69448273629625*(f_s^{r(2)}/f_p^{r(l)}) - 0.30813284494365] \quad (4.2)
\]

This approximation is a match to the relations of Table 2.3 up to the 3rd decimal.

**ν**

The speed of sound in the material is calculated based upon Equation (2.33).

**K**

The free relative dielectric constant is defined as the ratio of the permittivity of the material to the permittivity of free space [2].
It is calculated from the following:

\[ K^T = \frac{tC}{\varepsilon_0 A} \]  \hspace{1cm} (4.3)

where \( \varepsilon_0 \) is the permittivity of free space (8.85 \times 10^{-12} \text{ F/m}).

**\( k'_{33} \)** The thickness–extensional mode coupling factor is calculated based upon Equation 2.41 using \( f_s^{t(1)} \) and \( f_p^{t(1)} \) values from Table 4.1.

**\( k_p \)** The planar coupling factor is calculated based upon a close approximation of the Equation (2.37) using the measured \( f_s^{r(1)} \) and \( f_p^{r(1)} \) values:

\[ k_p = \frac{(f_p - f_s)\left[(\sigma_p)^2 - 1 + \eta_1^2\right]}{(2f_s - f_p)(1 + \sigma_p) + (f_p - f_s)\left[(\sigma_p)^2 - 1 + \eta_1^2\right]} \] \hspace{1cm} (4.4)

**\( k_{31} \)** The extensional mode coupling factor is calculated based upon Equation (2.31).

**\( k_{\text{eff}} \)** The effective coupling factor is calculated based upon \( f_s^{r(1)} \) and \( f_p^{r(1)} \) using the following equation: [1]

\[ k_{\text{eff}} = \sqrt{\frac{f_p^2 - f_s^2}{f_p^2}} \] \hspace{1cm} (4.5)

**\( s_{11}^{E} \)** This elastic coefficient at constant electrical field is calculated based upon Equation (2.35) using \( f_s^{r(1)} \).

**\( s_{12}^{E} \)** This elastic coefficient at constant electrical field is calculated based upon Equation (2.28).

**\( d_{31} \)** The extensional mode piezoelectric constant is calculated based upon the following equation: [2]

\[ d_{31} = k_{31} \sqrt{\varepsilon_0 K^T_3 s_{11}^{E}} \] \hspace{1cm} (4.6)
\( \varepsilon_{33}^T \) The thickness–extensional mode permittivity component at constant stress is calculated based upon Equations (2.21) and (2.38).

\( s_{11}^{D} \) This elastic coefficient at constant electrical displacement is calculated based upon the following equation: [1]

\[
s_{11}^{D} = s_{11}^{E} - \frac{d_{31}^2}{\varepsilon_{33}^{E}} \quad (4.7)
\]

\( c_{12}^{p} \) This planar elastic stiffness constant is calculated based upon Equation (2.19).

\( c_{33}^{E} \) The thickness–extensional mode elastic stiffness constant at constant electrical field is calculated based upon Equation (2.41) using \( f_{p}^{n(t)} \).

\( e_{31}^{p} \) The planar extensional mode piezoelectric constant is calculated based upon Equation (2.20).

\( e_{33} \) The thickness–extensional mode piezoelectric constant is calculated based upon Equation (2.40).

\( \varepsilon_{33}^{p} \) The planar thickness–extensional mode permittivity component is calculated based upon Equation (2.38).

\( \varepsilon_{33}^{S} \) The thickness–extensional mode permittivity component at constant strain is calculated based upon Equations (2.38) and (2.39).

\( d_{33}^{t} \) The thickness–extensional mode piezoelectric constant is calculated based upon the following equation: [1]

\[
d_{33}^{t} = \frac{e_{33}}{\varepsilon_{33}^{E}} \quad (4.8)
\]
4.4 Measurement Results and Analysis

The following analysis presented here is only one of the possible interpretations of the measurement results on PZT. It only states the overall trends observed by the author based upon the analysis of the measurement results by the IEEE standard [1]. Because of the depolarization of the samples at high temperatures, the samples had history dependence and it is not expected that the experiments could be repeated exactly in the same way with the same samples. The samples could be re-polarized, but after the repeated polarization their characteristics will not be exactly the same as before due to the changes developed in the microstructure of the materials. To be able to identify and increase confidence for the change of the electrical parameters vs. temperature in a specific material system, it is recommended to collect more data with several different samples.

PZT samples from three different kinds of materials were measured during the test of the measurement system. The first two PZT samples, #850 and #880 are the products of APC International Ltd. and have different sizes and electrical properties, the last three samples #502-A, -B and -C are all the products of Piezo Kinetics Incorporated, represent the same material with different thicknesses. All samples were exposed to the following measurement process.

The impedance is an important parameter used to characterize piezoelectric materials. Impedance, \( Z \) is generally defined as the total opposition a material offers to the flow of an alternating current at a given frequency, and is represented as a complex quantity which is graphically shown on a vector plane. Impedance can be expressed using the polar form as a magnitude \( |Z| \) and phase angle, \( \theta \) [5]. As it was already mentioned in
Chapter II, if an alternate current (AC) voltage of varying frequency is applied to a piezoelectric ceramic of a certain shape, it can be seen that there are specific frequencies at which the ceramic produces strong vibrations. These frequencies are called resonant and anti-resonant frequencies, and depend on the ceramic's specific elastic vibration frequency, which is a function of the shape of the material. Piezoelectric ceramics have various vibration modes, which depend on their shape, the orientation of polarization, and the direction of the electric field. Each of these vibration modes has unique resonant frequencies and piezoelectric characteristics [6]. In order to determine these resonant and anti-resonant frequencies of the samples, first the magnitude and the phase angle of the samples were measured on the 40 Hz – 10 MHz frequency range.

The $f_p^{r(1)}, f_s^{r(1)}, f_p^{r(2)}, f_s^{r(2)}, f_p^{t(l)}$ and $f_s^{t(l)}$ resonant and anti-resonant frequency pairs of the samples were determined based upon the work of Jan Kocbach, Reference [7]. The symmetric vibration modes in circular piezoelectric ceramic disks have been classified by several authors, and seven different types of vibration modes have been identified, Radial (R), Lamb (L), Edge (E), Anharmonic (A), Terrace Structure (T), Thickness Shear (TS) and Thickness Extensional (TE) modes.

The lowest frequency modes in piezoelectric disks are the radial extensional modes (R modes); also called radial dilatational modes, lower frequency radial modes, harmonic radial modes, or only radial modes. Characteristic for the radial modes is that the disk contracts in the radial direction, and expands in the thickness direction, due to Poisson’s ratio effects [7].

The fundamental thickness extensional mode is the mode which is most often used in transducer applications of piezoelectric disks, and is also the mode for which the
vibration most closely resembles the plane piston vibration. There are overtones of the fundamental thickness extensional mode present in a piezoelectric plate/disk, and the fundamental thickness extensional mode is therefore often denoted the TE1 mode in the literature, especially when one-dimensional models are considered [7].

Table 4.3 Vibration mode shapes for the 21 lowest symmetric modes of a circular PZT-5A disk with $d/t$ ratio of 10.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (kHz)</th>
<th>Symbol/Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode 1</td>
<td>198 kHz (R1)</td>
<td></td>
</tr>
<tr>
<td>Mode 2</td>
<td>504 kHz (R2)</td>
<td></td>
</tr>
<tr>
<td>Mode 3</td>
<td>769 kHz (R3)</td>
<td></td>
</tr>
<tr>
<td>Mode 4</td>
<td>987 kHz (R4)</td>
<td></td>
</tr>
<tr>
<td>Mode 5</td>
<td>1156 kHz (R5)</td>
<td></td>
</tr>
<tr>
<td>Mode 6</td>
<td>1261 kHz (E+)</td>
<td></td>
</tr>
<tr>
<td>Mode 7</td>
<td>1324 kHz (R6+)</td>
<td></td>
</tr>
<tr>
<td>Mode 8</td>
<td>1457 kHz (R7)</td>
<td></td>
</tr>
<tr>
<td>Mode 9</td>
<td>1600 kHz (R8)</td>
<td></td>
</tr>
<tr>
<td>Mode 10</td>
<td>1623 kHz (TS1+/A1+)</td>
<td></td>
</tr>
<tr>
<td>Mode 11</td>
<td>1637 kHz (A2)</td>
<td></td>
</tr>
<tr>
<td>Mode 12</td>
<td>1707 kHz (A3+)</td>
<td></td>
</tr>
<tr>
<td>Mode 13</td>
<td>1750 kHz (R9)</td>
<td></td>
</tr>
<tr>
<td>Mode 14</td>
<td>1843 kHz (A4+)</td>
<td></td>
</tr>
<tr>
<td>Mode 15</td>
<td>1908 kHz (R10+)</td>
<td></td>
</tr>
<tr>
<td>Mode 16</td>
<td>1963 kHz (TE1+/L1+)</td>
<td></td>
</tr>
<tr>
<td>Mode 17</td>
<td>2007 kHz (R11+)</td>
<td></td>
</tr>
<tr>
<td>Mode 18</td>
<td>2093 kHz (L2+)</td>
<td></td>
</tr>
<tr>
<td>Mode 19</td>
<td>2103 kHz (R12+)</td>
<td></td>
</tr>
<tr>
<td>Mode 20</td>
<td>2181 kHz (A5+)</td>
<td></td>
</tr>
<tr>
<td>Mode 21</td>
<td>2269 kHz (L3+)</td>
<td></td>
</tr>
</tbody>
</table>

Note: A plus sign indicates strong coupling to other modes. In some cases this mode coupling is so strong that it may be difficult to identify the individual modes [7].
The edge mode (E mode) is a vibration mode for which nearly all of the vibration is conformed to the circular edges of the disk. For some materials and d/t ratios, there is strong coupling to radial modes, and the vibrations at the circular edges of the disk are of the same order as the vibration at the center of the disk [7].

The electromechanical coupling to the thickness shear mode (TS mode) resonance is very weak. This may be assigned to the fact that the shear plane wave is not piezoelectrically active, and therefore can not be driven directly by an $x_3$ directed electrical field. Due to the weak electromechanical coupling, this mode has not been clearly identified in the experimental works [7].

The T modes are only observed for PbTiO$_3$ disks [15], and no information about the mode shape of these modes is available. The modes which are denoted T modes are the modes which are observed as a terrace structure below the TE1 mode in the frequency spectra of piezoelectric disks (e.g. for BaTiO$_3$ and PbTiO$_3$), where the thickness extensional mode is below the thickness shear mode in frequency. This is similar to the terrace structure around the TS1 mode found in the frequency spectra of piezoelectric disks (e.g. for Pb(ZrTi)O$_3$), where the thickness extensional mode is above the thickness shear mode in frequency [7].

The last two groups of vibration modes observed in piezoelectric disks are the anharmonic modes (A modes), and the Lamb modes (L modes). The A modes are also called anharmonic radial modes, or high frequency radial modes. According to the theory on Lamb modes in an infinite isotropic plate, the plate mode is associated with a TS mode for materials with Poisson’s ratio larger than 1/3, and a TE mode for materials with Poisson’s ratio less than 1/3 [7].
Based upon the first measurement the location of the $f_{p(1)}$, $f_{s(1)}$, $f_{p(2)}$, $f_{s(2)}$ and $f_{t(1)}$ were determined, and the measurements were repeated on those frequency ranges at pre-defined temperatures from room temperature to up to 500°C. The temperature was increased at 4°C per minute to avoid thermal shock on the samples. To ensure thermal equilibrium, the samples were kept at each measuring temperature for at least 20 minutes. The measurement system recorded the $|Z|$ and $\theta$ values in all three frequency ranges mentioned above and the capacitance at 1 kHz. As the temperature was increased and was getting closer to the Curie point of the samples, the decrease in the measured impedance magnitudes and phase angles became clearly visible on the measured data.

In the next step the measured data of the samples were collected as raw data and pre-processed with a simple Matlab program then transformed to Excel files and the resonance and anti-resonance frequencies were determined in the R1, R2 and TE1 modes. Because of the sometimes coupled vibration modes, the data analysis was not completely automatic, but if necessary, this problem can be easily corrected in the future.

4.4.1 PZT Sample #502–B

The PZT material denoted as Navy Type II, PKI–502, is designed for applications that require high electromechanical activity and high dielectric constant. It is used primarily as receivers e.g. hydrophones, phono pickups, sound detectors, accelerometers, delay lines, flow detectors and flow meters [3].

The measured resonant and anti-resonant frequency pairs must be sufficiently isolated from other modes to eliminate the effects of any adjacent modes. To assure isolation of these frequencies, the sample geometry must be chosen carefully, in case of a
thin, flat disk shape, it is recommended to keep $d/t > 10$ ratio of the samples. The measured #502–B PZT sample was a disk with 12.82 mm diameter and 1.02 mm thickness, so the $d/t$ ratio of the sample was ~12.57, just over the recommended $d/t > 10$ ratio [2].

Table 4.4 PZT Sample #502–B, manufacturer provided vs. measured properties at 25°C

<table>
<thead>
<tr>
<th></th>
<th>Manufacturer provided values</th>
<th>Measured values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_s^{(1)}$</td>
<td>155.2 kHz</td>
<td>155 kHz</td>
</tr>
<tr>
<td>$f_s^{(1)}$</td>
<td>1980 kHz</td>
<td>1985 kHz</td>
</tr>
<tr>
<td>$K_T$</td>
<td>1800</td>
<td>1904</td>
</tr>
<tr>
<td>$k_p$</td>
<td>0.60</td>
<td>0.61</td>
</tr>
<tr>
<td>$k_{31}$</td>
<td>0.34</td>
<td>0.33</td>
</tr>
<tr>
<td>$-d_{31}$</td>
<td>$175 \times 10^{-12}$ m/V</td>
<td>$181 \times 10^{-12}$ m/V</td>
</tr>
</tbody>
</table>

In this thesis, the focus is on the R1, R2 and TE1 vibration modes, because based upon those modes, all of the electrical properties listed in Table 4.2 could be calculated using the IEEE Standard [1]. The $d/t$ ratio of the measured #502–B PZT sample was ~12.57 that is very close to the $d/t$ ratio 10 of the PZT-5A disk that vibration mode shapes for the 21 lowest symmetric modes are listed in Table 4.3.

Table 4.5 Comparison of vibration mode values of the PZT-5A and PZT-#502–B disks

<table>
<thead>
<tr>
<th></th>
<th>PZT-5A</th>
<th>PZT-#502–B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode 1: R1</td>
<td>198 kHz</td>
<td>155 kHz</td>
</tr>
<tr>
<td>Mode 2: R2</td>
<td>504 kHz</td>
<td>396 kHz</td>
</tr>
<tr>
<td>Mode 16: TE1</td>
<td>~1963 kHz</td>
<td>1985 kHz</td>
</tr>
</tbody>
</table>
Because of the slight difference between the \( d/t \) ratio of the #502–B PZT and PZT-5A disks, the R1 and R2 vibration modes of the PZT-5A disk were at slightly higher frequencies than the R1 and R2 vibration modes of the #502–B PZT sample as shown on Table 4.5. However, the R1, R2 and TE1 vibration modes are still clearly recognizable as shown on Figure 4.1.

Figure 4.1 PZT Sample #502–B – \(|Z|\) on the 100 kHz – 10 MHz frequency range
Figure 4.2 PZT Sample #502–B – $\theta$ on the 100 kHz – 10 MHz frequency range

Figure 4.3 PZT Sample #502–B – $|Z|$ – First radial mode
Figure 4.4 PZT Sample #502–B – $\theta$ – First radial mode

Figure 4.5 PZT Sample #502–B – $|Z|$ – First radial overtone mode
Figure 4.6 PZT Sample #502–B – $\theta$ – First radial overtone mode

Figure 4.7 PZT Sample #502–B – $|Z|$ – First thickness mode
Figure 4.8 PZT Sample #502–B – $\theta$ – First thickness mode

Figure 4.9 PZT Sample #502–B – $f_s^{r(t)}$ and $f_p^{r(t)}$ vs. Temperature
Figure 4.10 PZT Sample #502–B – \( f_s^r(2) \) and \( f_p^r(2) \) vs. Temperature

Figure 4.11 PZT Sample #502–B – \( f_s^t(1) \) and \( f_p^t(1) \) vs. Temperature
Figure 4.12 PZT Sample #502–B – $\sigma$ vs. Temperature

Figure 4.13 PZT Sample #502–B – $k_{33}$, $k_{31}$, $k_p$ and $k_{eff}$ vs. Temperature
Figure 4.14 PZT Sample #502–B – $d_{33}$ and $d_{31}$ vs. Temperature

Figure 4.15 PZT Sample #502–B – $s_{D11}$, $s_{E11}$ and $s_{E12}$ vs. Temperature
Figure 4.16 PZT Sample #502–B – $c_{p12}$ and $c_{E33}$ vs. Temperature

Figure 4.17 PZT Sample #502–B – $e_{p31}$ and $e_{33}$ vs. Temperature
Figure 4.18 PZT Sample #502–B – $\varepsilon_p^{33}$, $\varepsilon_T^{33}$ and $\varepsilon_S^{33}$ vs. Temperature

Figure 4.19 PZT Sample #502–B – Capacitance at 1 kHz vs. Temperature
4.4.2 PZT Sample #502–A

The measured #502–A PZT sample was a disk with 12.77 mm diameter and 2.05 mm thickness, so the $d/t$ ratio was $\sim$6.23, less than the recommended $d/t > 10$ ratio for disks, but significantly larger than the recommended $d/t < 0.33$ ratio for rods, so it still could be considered and calculated as a disk [2].

Table 4.6 PZT Sample #502–A, manufacturer provided vs. measured properties at 25°C

<table>
<thead>
<tr>
<th>Manufacturer provided values</th>
<th>Measured values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_s^{(1)}$</td>
<td>152.5 kHz</td>
</tr>
<tr>
<td>$f_s^{(1)}$</td>
<td>1017 kHz</td>
</tr>
<tr>
<td>$K_T$</td>
<td>1800</td>
</tr>
<tr>
<td>$k_p$</td>
<td>0.60</td>
</tr>
<tr>
<td>$k_{31}$</td>
<td>0.34</td>
</tr>
<tr>
<td>$-d_{31}$</td>
<td>175 x 10^{-12} m/V</td>
</tr>
</tbody>
</table>

Figure 4.20 PZT Sample #502–A – $|Z|$ on the 100 kHz – 10 MHz frequency range
Figure 4.21 PZT Sample #502–A – $\theta$ on the 100 kHz – 10 MHz frequency range

Figure 4.22 PZT Sample #502–A – $|Z|$ – First radial mode
Figure 4.23 PZT Sample #502–A – $\theta$ – First radial mode

Figure 4.24 PZT Sample #502–A – $|Z|$ – First radial overtone mode
Figure 4.25 PZT Sample #502–A – $\theta$ – First radial overtone mode

Figure 4.26 PZT Sample #502–A – $|Z|$ – First thickness mode

58
Figure 4.27 PZT Sample #502–A – $\theta$ – First thickness mode

Figure 4.28 PZT Sample #502–A – $f_s^{r(l)}$ and $f_p^{r(l)}$ vs. Temperature
Figure 4.29 PZT Sample #502–A – $f_s^{r(2)}$ and $f_p^{r(2)}$ vs. Temperature

Figure 4.30 PZT Sample #502–A – $f_s^{t(1)}$ and $f_p^{t(1)}$ vs. Temperature
Figure 4.31 PZT Sample #502–A – σ vs. Temperature

Figure 4.32 PZT Sample #502–A – k_{33}, k_{31}, k_p and k_{eff} vs. Temperature
Figure 4.33 PZT Sample #502–A – $d_{33}$ and $d_{31}$ vs. Temperature

Figure 4.34 PZT Sample #502–A – $s_{11}^{D}$, $s_{11}^{E}$ and $s_{12}^{E}$ vs. Temperature
Figure 4.35 PZT Sample #502–A – $c_{12}$ and $c_{33}^E$ vs. Temperature

Figure 4.36 PZT Sample #502–A – $e_{31}$ and $e_{33}$ vs. Temperature
Figure 4.37 PZT Sample #502–A – $\varepsilon_{33}^p$, $\varepsilon_{33}^T$ and $\varepsilon_{33}^S$ vs. Temperature

Figure 4.38 PZT Sample #502–A – Capacitance at 1 kHz vs. Temperature
4.4.3 PZT Sample #502–C

The sample was a disk with 12.74 mm diameter and .60 mm thickness, the \( d/t \) ratio was 20.95, well over the recommended \( d/t > 10 \) dimensional requirement [2].

Table 4.7 PZT Sample #502–C, manufacturer provided vs. measured properties at 25°C

<table>
<thead>
<tr>
<th></th>
<th>Manufacturer provided values</th>
<th>Measured values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_s^{(l)} )</td>
<td>157 kHz</td>
<td>156.2 kHz</td>
</tr>
<tr>
<td>( f_s^{(l)} )</td>
<td>3295 kHz</td>
<td>3290 kHz</td>
</tr>
<tr>
<td>( K^T )</td>
<td>1800</td>
<td>1519</td>
</tr>
<tr>
<td>( k_p )</td>
<td>0.60</td>
<td>0.64</td>
</tr>
<tr>
<td>( k_{31} )</td>
<td>0.34</td>
<td>0.36</td>
</tr>
<tr>
<td>( -d_{31} )</td>
<td>( 175 \times 10^{-12} ) m/V</td>
<td>( 170 \times 10^{-12} ) m/V</td>
</tr>
</tbody>
</table>

Figure 4.39 PZT Sample #502–C – \(|Z|\) on the 100 kHz – 10 MHz frequency range
Figure 4.40 PZT Sample #502–C – $\theta$ on the 100 kHz – 10 MHz frequency range

Figure 4.41 PZT Sample #502–C – $|Z|$ – First radial mode
Figure 4.42 PZT Sample #502–C – θ – First radial mode

Figure 4.43 PZT Sample #502–C – |Z| – First radial overtone mode
Figure 4.44 PZT Sample #502–C – $\theta$ – First radial overtone mode

Figure 4.45 PZT Sample #502–C – $|Z|$ – First thickness mode
Figure 4.46 PZT Sample #502–C – $\theta$ – First thickness mode

Figure 4.47 PZT Sample #502–C – $f_s^{r(1)}$ and $f_p^{r(1)}$ vs. Temperature
Figure 4.48 PZT Sample #502–C – $f_s^{r(2)}$ and $f_p^{r(2)}$ vs. Temperature

Figure 4.49 PZT Sample #502–C – $f_s^{t(1)}$ and $f_p^{t(1)}$ vs. Temperature
Figure 4.50 PZT Sample #502–C – $\sigma^p$ vs. Temperature

Figure 4.51 PZT Sample #502–C – $k_{33}, k_{31}, k_p$ and $k_{eff}$ vs. Temperature
Figure 4.52 PZT Sample #502–C – $d_{33}$ and $d_{31}$ vs. Temperature

Figure 4.53 PZT Sample #502–C – $s_{D11}$, $s_{E11}$ and $s_{E12}$ vs. Temperature
Figure 4.54 PZT Sample #502–C – $c_{p12}$ and $c_{E33}$ vs. Temperature

Figure 4.55 PZT Sample #502–C – $e_{p31}$ and $e_{33}$ vs. Temperature
Figure 4.56 PZT Sample #502–C – $\varepsilon_{33}^{p}$, $\varepsilon_{33}^{T}$ and $\varepsilon_{33}^{S}$ vs. Temperature

Figure 4.57 PZT Sample #502–C – Capacitance at 1 kHz vs. Temperature
4.4.4 PZT Sample #850

The APC 850 PZT material is soft ceramic for sensors and ultrasonic applications with high dielectric constant and clean, noise–free frequency response [4].

The measured sample was a disk with 12.68 mm diameter and .25 mm thickness, the $d/t$ ratio was ~50.72, well over the recommended $d/t > 10$ ratio [2].

Table 4.8 PZT Sample #850, manufacturer provided vs. measured properties at 25°C

<table>
<thead>
<tr>
<th></th>
<th>Manufacturer provided values.</th>
<th>Measured values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_s^{(1)}$</td>
<td>156.2 kHz</td>
<td>163.2 kHz</td>
</tr>
<tr>
<td>$f_s^{(1)}$</td>
<td>8128 kHz</td>
<td>8132 kHz</td>
</tr>
<tr>
<td>$K_T$</td>
<td>1750</td>
<td>1936</td>
</tr>
<tr>
<td>$k_p$</td>
<td>0.63</td>
<td>0.58</td>
</tr>
<tr>
<td>$k_{31}$</td>
<td>0.36</td>
<td>0.33</td>
</tr>
<tr>
<td>$-d_{31}$</td>
<td>$175 \times 10^{-12}$ m/V</td>
<td>$167 \times 10^{-12}$ m/V</td>
</tr>
</tbody>
</table>

Figure 4.58 PZT Sample #850 – |Z| on the 100 kHz – 10 MHz frequency range
Figure 4.59 PZT Sample #850 – $\theta$ on the 100 kHz – 10 MHz frequency range

Figure 4.60 PZT Sample #850 – $|Z|$ – First radial mode
Figure 4.61 PZT Sample #850 – $\theta$ – First radial mode

Figure 4.62 PZT Sample #850 – $|Z|$ – First radial overtone mode
Figure 4.63 PZT Sample #850 – $\theta$ – First radial overtone mode

Figure 4.64 PZT Sample #850 – $|Z|$ – First thickness mode

78
Figure 4.65 PZT Sample #850 – $\theta$ – First thickness mode

Figure 4.66 PZT Sample #850 – $f_s(r^{(1)})$ and $f_p(r^{(1)})$ vs. Temperature
Figure 4.67 PZT Sample #850 – $f_s^{r(2)}$ and $f_p^{r(2)}$ vs. Temperature

Figure 4.68 PZT Sample #850 – $f_s^{r(1)}$ and $f_p^{r(1)}$ vs. Temperature
Figure 4.69 PZT Sample #850 – $\sigma^p$ vs. Temperature

Figure 4.70 PZT Sample #850 – $k_{33}$, $k_{31}$, $k_p$ and $k_{eff}$ vs. Temperature
Figure 4.71 PZT Sample #850 – $d_{33}$ and $d_{31}$ vs. Temperature

Figure 4.72 PZT Sample #850 – $s_{D11}^{E}$, $s_{E11}^{E}$ and $s_{E12}^{E}$ vs. Temperature
Figure 4.73 PZT Sample #850 – $c_{12}$ and $c_{33}^{E}$ vs. Temperature

Figure 4.74 PZT Sample #850 – $e_{31}$ and $e_{33}$ vs. Temperature

83
Figure 4.75 PZT Sample #850 – $\varepsilon^p_{33}$, $\varepsilon^T_{33}$ and $\varepsilon^S_{33}$ vs. Temperature

Figure 4.76 PZT Sample #850 – Capacitance at 1 kHz vs. Temperature
4.4.5 PZT Sample #880

The APC 880 PZT material is a hard ceramic with high dielectric stability and low mechanical loss [4].

The measured sample was a disk with 10 mm diameter and .43 mm thickness, the \( d/t \) ratio was \(~23.25\), well over the recommended \( d/t > 10 \) dimensional requirement [2].

Table 4.9 PZT Sample #880, manufacturer provided vs. measured properties at 25°C

<table>
<thead>
<tr>
<th></th>
<th>Manufacturer provided values</th>
<th>Measured values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_s^{(1)} )</td>
<td>212 kHz</td>
<td>234.4 kHz</td>
</tr>
<tr>
<td>( f_s^{(2)} )</td>
<td>4907 kHz</td>
<td>4918 kHz</td>
</tr>
<tr>
<td>( K^T )</td>
<td>1000</td>
<td>886</td>
</tr>
<tr>
<td>( k_p )</td>
<td>0.50</td>
<td>0.47</td>
</tr>
<tr>
<td>( k_{31} )</td>
<td>0.30</td>
<td>0.28</td>
</tr>
<tr>
<td>( -d_{31} )</td>
<td>(95 \times 10^{-12} ) m/V</td>
<td>(82.1 \times 10^{-12} ) m/V</td>
</tr>
</tbody>
</table>

Figure 4.77 PZT Sample #880 – \(|Z|\) on the 100 kHz – 10 MHz frequency range
Figure 4.78 PZT Sample #880 – $\theta$ on the 100 kHz – 10 MHz frequency range

Figure 4.79 PZT Sample #880 – $|Z|$ – First radial mode
Figure 4.80 PZT Sample #880 – $\theta$ – First radial mode

Figure 4.81 PZT Sample #880 – $|Z|$ – First radial overtone mode
Figure 4.82 PZT Sample #880 – $\theta$ – First radial overtone mode

Figure 4.83 PZT Sample #880 – $|Z|$ – First thickness mode
Figure 4.84 PZT Sample #880 – $\theta$ – First thickness mode

Figure 4.85 PZT Sample #880 – $f_s^{(r)}$ and $f_p^{(r)}$ vs. Temperature
Figure 4.86 PZT Sample #880 – $f_s^{r(2)}$ and $f_p^{r(2)}$ vs. Temperature

Figure 4.87 PZT Sample #880 – $f_s^{t(1)}$ and $f_p^{t(1)}$ vs. Temperature
Figure 4.88 PZT Sample #880 – $\sigma^p$ vs. Temperature

Figure 4.89 PZT Sample #880 – $k'_{33}$, $k_{31}$, $k_p$ and $k_{eff}$ vs. Temperature
Figure 4.90 PZT Sample #880 – $d_{33}$ and $d_{31}$ vs. Temperature

Figure 4.91 PZT Sample #880 – $s_{11}^D$, $s_{11}^E$ and $s_{12}^E$ vs. Temperature
Figure 4.92 PZT Sample #880 – $c_{12}$ and $c_{33}^E$ vs. Temperature

Figure 4.93 PZT Sample #880 – $e_{31}$ and $e_{33}$ vs. Temperature
Figure 4.94 PZT Sample #880 – $\varepsilon_{33}^p$, $\varepsilon_{33}^T$ and $\varepsilon_{33}^S$ vs. Temperature

Figure 4.95 PZT Sample #880 – Capacitance at 1 kHz vs. Temperature
4.4.6 Capacitance at 1 kHz

Near the Curie point the thermodynamic properties including dielectric, elastic, optical, and thermal constants of the piezoelectric ceramics show an anomalous behavior. This is due to a distortion in the crystal as the phase structure changes. The temperature dependence of the dielectric constant above the Curie point \((T > T_{\text{Curie}})\) in ferroelectric crystals is governed by the Curie-Weiss law:

\[
\varepsilon = \varepsilon_0 + \frac{C}{(T-T_0)} \tag{4.9}
\]

where \(\varepsilon\) is the permittivity of the material, \(\varepsilon_0\) is the permittivity of the free space, \(C\) is the material specific Curie constant, \(T\) is the absolute temperature, and \(T_0\) is the Curie temperature. The Curie temperature, \(T_0\) is different from the Curie point \(T_{\text{Curie}}\). \(T_0\) is a formula constant obtained by extrapolation, while \(T_{\text{Curie}}\) is the actual temperature where the crystal structure changes [14].

The 1 kHz and low excitation voltage capacitance measurements are used in determination of material properties like the permittivity of a material [2]. Based upon the measured capacitance at 1 kHz, the permittivity of the piezoelectric material is

\[
\varepsilon = \frac{t C}{A} \tag{4.10}
\]

where \(t\) is the distance between the electrodes, \(C\) is the capacitance and \(A\) is the area of an electrode. Based upon Equation (4.9) and (4.10), the capacitance of the piezoelectric ceramics, following the Curie-Weiss law, reaches its peak around \(T_0\), the Curie temperature.
4.4.7 Resonant and Anti-resonant Frequency Pairs

For each PZT sample, three figures were generated from the determined $f_{pr(1)}$, $f_{sr(1)}$, $f_{pr(2)}$, $f_{sr(2)}$, $f_{pt(1)}$ and $f_{st(1)}$ resonant and anti-resonant frequency pairs. There were some overall trends recognizable on the figures in the changes of these frequencies:

In case of the first radial vibration mode, the change of the $f_{pr(1)}$ were not significant till the temperature reached the $T_{Curie}-50^\circ C$ temperature where it dropped significantly, then around the $T_{Curie}-20^\circ C$ temperature started to increase again along with $f_{sr(1)}$ that showed more consistent and gradual increase till the $T_{Curie}-20^\circ C$ temperature.

<table>
<thead>
<tr>
<th>Table 4.10 Summarized trend of resonant and anti-resonant frequency pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_p$</td>
</tr>
<tr>
<td>Decrease $\downarrow$</td>
</tr>
<tr>
<td>Relatively Stable $\leftrightarrow$</td>
</tr>
<tr>
<td>Increase $\uparrow$</td>
</tr>
</tbody>
</table>

The trend of the change of the $f_{pr(2)}$, $f_{sr(2)}$ frequencies were completely different. There was also a steady increase of these frequencies as the temperature increased, but the $\Delta f^{(2)}$ was almost constant till the $T_{Curie}-20^\circ C$ temperature where the $\Delta f^{(2)}$ became smaller and the $f_{pr(2)}$, $f_{sr(2)}$ frequencies were increased drastically.
In case of the first thickness vibration mode, both the $f_p^{(1)}$ and $f_s^{(1)}$ were stable till around the $T_{Curie}$-50°C temperature where depending on the samples either both $f_p^{(1)}$ and $f_s^{(1)}$ or only the $f_p^{(1)}$ dropped significantly bringing these frequencies closer to each other.

The summarized observations of the behaviors of the resonant and anti-resonant frequency pairs are listed in Table 4.10. Based upon the measurements, there was a definite trend that $\Delta f$ always decreases with the temperature. It also means that as the temperature increases, based upon Equations (4.4) and (4.5), the values of coupling factors, $k_{33}^l, k_{31}, k_p$ and $k_{eff}$ should either remain stable or continually decrease and based upon Equations (2.38) and (2.39), the values of the related permittivity components, $\varepsilon_p^{33}, \varepsilon_T^{33}$ and $\varepsilon_S^{33}$ should either remain stable or continually increase that is exactly as predicted by the Curie-Weiss law. However, it is not so simple to predict the trends of the rest of the electrical properties, since the behaviors of those electrical properties do not only depend on the trend of $\Delta f$, but also on the actual values of the resonant and anti-resonant frequency pairs and their relative changes to each other.

4.4.8 Electrical Properties

The electrical properties listed in Chapter 4.2 were calculated based upon the equations mentioned there. The $\sigma^p$ of the samples showed some minor fluctuations as the temperature was increased, but in general it remained stable. The values of $k_{33}^l, k_{31}, k_p$ and $k_{eff}$ coupling factors behaved as it was predicted, gradually decreased till the temperature reached $T_{Curie}$-50°C then the values dropped significantly. The $d_{33}^l$ of the samples continuously increased with the temperature while absolute value of the $d_{31}$ remained stable till it reached $T_{Curie}$-50°C temperature then it dropped significantly. The
$s_{11}^D$, $s_{11}^E$, $s_{12}^E$, $c_{12}^P$ and $c_{33}^E$ values remained stable till the temperature reached $T_{Curie}$-20°C then they show a slight increase or decrease. The $c_{31}^P$ and $c_{33}^E$ values show the same trend as the $d_{33}$ and $d_{31}$ values. The values of the $c_{33}^P$, $c_{33}^T$ and $c_{33}^S$ permittivity components behaved as it was predicted, continually increased with the temperature.

4.5 Conclusion

The PZT samples show changes in the frequency range of their vibration modes and electrical properties as the temperature is getting closer to the Curie temperature, and in most cases these changes become very significant from around the $T_{Curie}$-(50°C~20°C) temperature. These trends have good correlations with the measurement results collected by researchers in the Jet propulsion Laboratory, Caltech Pasadena, CA on high temperature piezoelectric materials, Navy III, BS-PT, BMT-PT (TRS Technologies Inc.) and Bismuth Titanate samples PZ46 and B8613 (Ferroperm Piezoceramics A/S, Sinoceramics) in 2004 [8].

The changes in the piezoelectric properties of the PZT samples at the Curie temperature are determined by their crystal structure. The exact explanation of these mechanisms is beyond the scope of this thesis and should be addressed by the material scientists.
CHAPTER V
SUMMARY, CONCLUSION AND FUTURE WORK

This chapter will serve to summarize the results from all chapters shortly and discuss this thesis in general. The conclusion of this project is presented at the end of this chapter along with future research directions.

5.1 Summary

Chapter I is the introduction to the history and nature of piezoelectric ceramics then it states the objective and scope of this thesis. Chapter II start with a general discussion of the Linear Theory of Piezoelectricity, and then it focuses on the theory of the radial and thickness vibration modes of the piezoelectric disks. Chapter III describes the developed measurement system, its components and software. Chapter IV lists all of the measured and calculated electrical parameters and properties of the PZT samples used to demonstrate the effectiveness of the measurement system and present one of the possible interpretations of the measurement results. It also mentions the overall trends observed by the author during the experiments and their possible explanations.

5.2 Conclusion

This thesis investigated the feasibility and effectiveness of the developed measurement system to collect information about the electrical properties of piezoelectric
ceramics at high temperatures. The project was successful; the developed measurement system was able to capture the changes in the resonant and anti-resonant frequencies and related electrical properties of the measured PZT samples as the operating temperature was increased to and above the Curie temperature of the materials. The evaluation of these measurements can be particularly useful to designers, because the collected information can help them to anticipate and incorporate these changes into their control system design.

5.3 Future Work and Recommendation

As it was mentioned in the first chapter of this thesis, the original goal of this thesis was to develop a measurement system that is able to measure the electrical properties of those high-temperature piezoelectric ceramics that are currently being developed in the Materials Laboratory of the NASA Glenn Research Center. Based upon the results of this project, the author is confident, that the developed measurement system is able to accurately and automatically measure, collect and store any required data at any temperature range allowed by the heater and the measurement device.

There are several ways to improve the current configuration; for example, just to mention a few of it, it is possible to combine all five developed measurement systems under one master program or to replace the heater with an environmental chamber, so it can simulate rapidly changing environmental conditions or to develop direct memory access to the memory of the instruments via LAN, so it could perform virtually limitless number of measurements and also it can be monitored over the Internet.
BIBLIOGRAPHY


